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UNITED STATES GOVERNMENT

# Memorandum

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TO : The Commission *Edmund*

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THROUGH : James Hoebel, Program Manager  
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FROM : Ronald L. Medford, Project Manager  
Household Structural Products Program, OPMB *Ronald L. Medford*

SUBJECT : Information on LP-Gas (Propane) Odorant

Attached for your information are recent reports relating to LP-gas odorant. These are: a) a CPSC contract report entitled, "Characterization of LP-Gas Odorant Fade" prepared by Arthur D. Little, Inc. b) a report entitled, "Odorant Depletion in Portable Cylinders," and c) a paper published in Fire Technology (August 1987) titled, "Aging Impairs the Ability to Detect Gas Odor."

LP-gas, like natural gas, is odorless, and therefore must be odorized with a strong smelling compound so that users will be able to detect gas leaks. The predominant safety odorant currently used in LP-gas is ethyl mercaptan which has been used for many years. Questions have been raised concerning the adequacy of ethyl mercaptan as an odorant principally because of claims that it can chemically react with rust that sometimes forms on the inside of storage tanks. This chemical reaction (oxidation) may reduce the concentration of the odorant in the tank and has therefore been termed odorant "fade." Depending on the degree of fading, the odorant may not be detected during a gas leak.

In 1985, the Commission contracted with Frontier Technical Associates to review the overall safety of residential LP-gas systems, including the properties of the gas and the safety odorant. Included in the final report was information about the potential for ethyl mercaptan to "fade" in the storage tank and the possibility that masonry (concrete) surfaces, such as basement floors and walls, may absorb or adsorb the odorant, thereby decreasing its concentration in the air at the time of a gas leak.

In 1986, the Commission contracted with Arthur D. Little, Inc. to conduct tests to evaluate the effects of rust and masonry surfaces on odorant fade. The work by the contractor documents that in short-term tests (5 to 7 days), odorant reduction in storage tanks does occur (Tab A). The study also found that odorant concentration is reduced in the presence of masonry surfaces. This information raises concerns about the adequacy of ethyl mercaptan as a safety odorant for LP-gas. However, because the tests conducted were short-term, and because the contractor suggests that fading may diminish with repeated fillings, it is important to quantify the long-term effects.

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NOTE: This document has not been reviewed or accepted by the Commission.  
Initial *RM* Date 10/13/87

For this reason, the Commission contracted with Mining Safety Appliances Research Corporation in September 1987 to conduct long-term tests on odorant fade in LP-gas steel cylinders. In the meantime, we will be sharing the information provided by Arthur D. Little, Inc. with LP-gas industry representatives as well as with the National Fire Protection Association (NFPA), and the Department of Transportation (DOT). Currently, the National LP-Gas Association is conducting work of its own on odorants, including the evaluation of some possible replacements for ethyl mercaptan.

At Tab B is a report on a Canadian study that found similar information regarding odorant fade in small cylinders (1 lb. to 100 lbs.) as that reported by Arthur D. Little, Inc. However, the Canadian study also found a correlation between the steel cylinder manufacturing process (type of heat treatment) and odorant fade. The study indicated that odorized LP-gas stored in aluminum cylinders was less susceptible to odorant fade than gas stored in steel cylinders. Currently, the majority of LP-gas cylinders in the U.S. are reportedly made of steel.

An article titled, "Aging Impairs the Ability to Detect Gas Odor" was published in the August 1987 issue of Fire Technology (Tab C). The article provides results of two studies that compare the effects of weakened smelling ability associated with aging with the ability to detect ethyl mercaptan. The first study found that the older group (70-85 years) had a detection threshold (the level at which the odorant could be smelled) for ethyl mercaptan which on average was ten times higher than that of the younger group (18-25 years). Three of the 21 people in the older group failed to detect the odorant at a concentration where accompanying LP-gas would explode. In the second study, 50 of 110 persons over 60 years of age failed to reliably detect ethyl mercaptan in the LP-gas which was odorized at the level currently required by NFPA and DOT. The study concludes that the elderly would seem to be at a high risk of experiencing an LP-gas fire. Currently available data are not detailed enough to determine if the elderly experience more injuries than the population as a whole from the use of appliances fueled by LP-gas.

The staff will continue to keep the Commission informed of its work in the LP-gas area; which is a part of the ongoing work in the Gas Heating Systems project.

Attachments



UNITED STATES GOVERNMENT

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

MEMORANDUM

SEP 29 1987

TO : Ron Medford, OPMB  
Through: William W. Walton, AED, ES *W3*  
Through: William H. King Jr., Director, ESES *WHL*  
FROM : Donald W. Switzer, ESES *DS*  
SUBJECT: FY 86 LP-gas Report, "Characterization of LP-Gas Odorant  
Fade" CPSC contract CPSC-C-86-1281

Attached is the final report "Characterization of LP-Gas Odorant Fade" prepared under contract CPSC-C-86-1281. ES finds the report acceptable. ES is in the process of preparing a summary report to be delivered during November, 1987.

If you have any questions, or comments please contact me on 492-6508.

Attachment

**Final Report  
Characterization of LP Gas Odorant Fade**

**CPSC-C-86-1281**

**ADL Reference 56905**

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**June, 1987**

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#### ACKNOWLEDGEMENTS

The author appreciates the assistance afforded to him by Dr. Daniel Ehntholt, Mr. Raymond Cornish and Mr. Stephen Ellis of Arthur D. Little, Inc. My thanks to Mr. Donald Switzer, CPSC Project Officer, for the opportunity to assist in this meaningful endeavor and for his comments, guidance and support.

The author extends his gratitude to the members of the LPG industry who, through their input, have helped provide the information necessary for the completion of this report. My thanks to Mr. Hal Faulkner, Vice President of the National Liquified Petroleum Gas Association, Mr. Ron Cannon, Executive Director of the Gas Processors Association and Mr. Kevin Cyr, District Manager of Surburban Propane, Marlborough, MA.

## SUMMARY

Two potential routes of ethyl mercaptan (EM) fading in LPG were investigated by Arthur D. Little, Inc., for the CPSC:

1. Oxidation of EM by iron oxides in storage and
2. Reaction of EM with masonry surfaces.

The extent of oxidation of EM was determined by simulating conditions found in a typical LPG storage container. Using a Parr® mini-reactor with a formulation of 3.3 mg ethyl mercaptan in 100 grams of liquified propane (LP), conditions were simulated to produce the oxidation phenomenon. Initial tests showed that oxidation may occur even in the presence of clean stainless steel surfaces. Results show concentrations of the ethyl mercaptan in the LP well below what might be expected from the original odorization level (1.5 lbs./10,000 gals.) and well below the NFPA "recommended" levels. The rate of oxidation in the presence of iron oxides appears to slow with repeated fillings of the odorized LP into the container. Based upon results compiled in the liquid phase experiments, oxidation may take place in a matter of hours as in the case of a first time fill of a cylinder or a few days after repeated fills. Repeated fillings of the cylinder may therefore reduce the potential hazard from fading due to oxidation within the cylinder.

The introduction of odorized gas into an environment containing untreated masonry was shown to be another possible route for the selective loss of odorant compared to LPG, under steady-state exposure conditions.

In summary, a general trend is discernible as to the fate of the ethyl mercaptan odorant in LPG under the conditions studied. It is apparent that the ethyl mercaptan in an LPG mixture in steel cylinders is subject to oxidation. The surfaces of a cylinder in continuous use may become deactivated with respect to reduction of the ethyl mercaptan level (through oxidation mechanisms) or may at least have a lower rate of oxidation. In order to be fully characterized, this phenomenon would require experimental exposures longer than those examined in this study, e.g., weeks. In this study, the oxidation of EM was found to take place in both the liquid and vapor phases, but more rapidly and completely in the vapor phase. Diethyl disulfide was found to be the primary oxidation product of the ethyl mercaptan.

It has also been demonstrated that ethyl mercaptan is depleted much more quickly than the propane of an odorized LPG mixture in a steady state environment with masonry. In the presence of a concrete block, the ethyl mercaptan was shown to be undetectable within six hours.

Several recommendations became apparent as a result of this study:

- (1) The appropriate odorization level of ethyl mercaptan in LPG vapor and practices to achieve it require better definition in order to assure uniform, safe practices. Acceptable levels of odorization in the pure vapor phase and at subsequent dilutions in air should be determined. The

NFPA recommendation of 1.0 lb./10,000 gals. cannot readily be correlated with a delivered vapor phase concentration except by using liquid/vapor equilibrium data. A study correlating the odorization level with final delivery concentrations using both chemical and human sensory analysis may be appropriate. In addition, a study of the odorization level vs. delivery concentration incorporating some of the phenomena noted in this work would assist in developing a more thorough understanding of the potential hazards involved.

- (2) While a trend of odorant oxidation in storage of LPG in steel cylinders appeared to occur during our short term study (5 - 7 days/test), a longer term study should be initiated. The oxidation taking place in the environment of the steel cylinder should be studied over weeks or months to gain a fuller understanding of the phenomenon. In addition, a more comprehensive range of exposure conditions (surfaces, temperatures, etc.) should be evaluated. It might also be of interest to determine whether or not there are practices or techniques available to mitigate the oxidation produced by the storage container, e.g., whether or not a polymer coating might be effective. Similarly, polymer coatings (paints) on masonry might be important inhibitors of odorant loss. In this latter case, it should also be recognized that in actual practice, a dynamic situation exists, and relative rates of loss and replenishment become important.
- (3) During the course of this program, the potential for odorant loss at cold temperatures (near freezing) in the vapor phase concentration of the LPG was suggested. A study to determine whether or not this effect is real and might occur under normal (or even unusual, but plausible) conditions would be appropriate.

## I. INTRODUCTION

On behalf of the Consumer Product Safety Commission (CPSC), Arthur D. Little, Inc. (ADL), investigated the occurrence and possible mechanisms for the fading of odorant, specifically ethyl mercaptan (EM) in Liquefied Petroleum Gas (LPG). A previous report<sup>1</sup> cited two possible areas for investigation:

1. Odorant fading due to oxidation of EM upon contact with the iron oxide in cylinder storage, and
2. Odorant fading due to absorption into, adsorption onto, or other loss due to masonry surfaces.

The approach taken to this program was to separately examine the two mechanisms for potential odorant fading. A major focus of the technical effort was on the examination of the occurrence of fading due to reaction of ethyl mercaptan (EM) with the oxides found in typical 100 lb. storage containers. The second focus of the effort was to investigate the possible occurrence of fading due to the potential for ethyl mercaptan to interact with masonry more readily than the LP-gas, resulting in a lower odorant to gas ratio.

The objectives of the experiments performed in this program were to obtain the following information:

- (1) With respect to the fading of ethyl mercaptan due to reaction with container material oxidation products,
  - a. Attempt to confirm or refute the possible occurrence of odorant reaction (oxidation) by characterization and duplication of container corrosion in newly manufactured as well as used 100 lb. capacity LPG containers, followed by a study of the reaction.
  - b. Measure the concentration of odorant and reaction products (to include primarily ethyl mercaptan and diethyl disulfide) as a function of time and the number of fillings with LPG, and analyze the results to answer the following questions:
    - (i) Does EM, while mixed with LPG in the liquid phase, react with the corrosion typically found in residential LPG containers?
    - (ii) Does EM, while mixed with LPG in the vapor phase, react with the corrosion typically found in residential LPG containers?

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<sup>1</sup>Bullardiek, W.A., "Engineering Hazard Analysis of Residential LP-Gas Fuel Usage," Report No. T-162-1, Frontier Technical Associates, Buffalo, NY (1986).

- (iii) What are the reaction products formed?
  - (iv) Are the reactions reversible?
  - (v) Once reacted, are the oxides unavailable (inhibited) for further reaction with EM?
  - (vi) Could the equilibrium vapor phase concentration of EM fall below concentrations predicted by Hankison and Wilson from the NFPA specified levels (1.0 lbs./10,000 gals.), i.e., 11 ng/mL, given the liquid phase concentration of 1.5 lbs. EM/10,000 gals. LPG,
    - a) if a rusted new container is used for storage?
    - b) if a rusted previously used container is used for storage?
  - (vii) What are the effects on EM vapor phase concentration with repeated fillings?
- (2) With respect to fading of EM due to selective interactions with masonry,
- a. Confirm or refute the occurrence of odorant fading by "preferential" loss of EM vs. LPG in masonry.
  - b. Measure odorant concentration vs. LPG component concentration under controlled conditions as a function of time to answer the following questions:
    - (i) Is EM, in the vapor phase, selectively removed by masonry materials commonly found in the residential environment at a faster rate than the LPG?
    - (ii) Could the equilibrium vapor phase concentration of EM fall below the predicted value of 11 ng/mL as determined by the NFPA specified level (1.0 lb./10,000 gals LPG), given the liquid phase concentration of 1.5 lbs. EM/10,000 gals. LPG, if the EM/LPG vapor is released into a residential LPG installation with typical masonry surface/living space volume ratio?
    - (iii) What is the concentration profile of EM as a function of time?

## II. EXPERIMENTAL APPROACH

The two major areas investigated in this work are described separately below.

### A. Odorant Fading in LPG Cylinders

#### 1. Oxide Recovery/Characterization

The extent of oxidation of the ethyl mercaptan odorant was determined by simulating conditions found in a typical LPG storage cylinder. To determine what constituted a typical cylinder, ten empty 100 lb. capacity LPG cylinders were obtained from a local major LPG supplier. As requested by the CPSC, five new

and five used cylinders were purchased for characterization. The five unused (new) cylinders were purchased from available stock and of the earliest manufacture date possible. The used cylinders were chosen to represent the range of available manufacturers and ages available at the site. The oxidation in each cylinder was then characterized according to mass and type. Once characterized, the typical oxide was duplicated for use in a 300 mL Parr® Pressure Reaction Vessel (PRV) as a simulator for the 100 lb. cylinder.

The used cylinders were chosen by members of the project team. In late October, 1986, five cylinders were tagged for the study from the supplier's inventory of several hundred. The ADL project team at that same time purchased a new 20 lb. cylinder (Flushed and filled with LPG at the time of purchase) to be used in the LPG experiments. Any residual LPG in the 100 lb. cylinders was vented by the supplier, the valves were removed and replaced by caps to preclude exposure of the cylinder to air.

The LPG supplier also located and obtained five unused cylinders from a regional distributor, Tarryton Tank and Equipment Co., (Freeholt, NJ). All five cylinders were manufactured by Manchester in March, 1986, with serial numbers ranging from R013808 to R013958 (Table 1). The cylinders were received by the supplier in late November, 1986.

All cylinders were received at ADL in early December, 1986, and were found to be intact upon inspection. They were then placed in a secure remote building for complete inspection and characterization. The new cylinders were noted as having light vertically striated oxidation on the interior surface. Upon removal of the protective caps from the used cylinders, a pressure buildup from within the cylinder was noted as being released with a strong sulfide/mercaptan odor. The pressure buildup was probably created by vaporization of residual organics left in the cylinders from their numerous fillings over the years. This was noted as being a typical occurrence by the LPG suppliers. The oxidation in the used cylinders varied from light (<10g) to heavy (>400g). Additionally, the quantities of residual organics, an oily material, found in the cylinder ranged from 104 to 0 milliliters (mL) in an apparent inverse relationship to the mass of oxide. The oily residues recovered from each cylinder were retained for possible later use.

In order to facilitate the collection of the iron oxides, the cylinders were cut in half. Before the cutting operation was started, however, the cylinders were completely cleaned of combustible materials, i.e., residual propane and other hydrocarbons. To accomplish the cleaning, the residual free liquid was first collected. The cylinders were then rinsed with methylene chloride (a reasonably fire retardant organic solvent) several times, the rinses recovered and the cylinder then purged with nitrogen throughout the cutting procedure.

Once opened, the oxides were collected and X-ray diffraction patterns determined for each sample. The surface oxide was removed using a combination of a steel brush, steel wool, and polymer abrasive pads. Any contamination of the oxides by the removal process, i.e., the steel wool and wire and polymer fibers, was removed by a combination of magnetic separation and sieving the material. Each sample was milled with a nitrocellulose acetate solution to present a homogeneous mixture and reduce orientation effects of the material. Table 2 shows the mass of oxides collected from each cylinder as well as the types and approximate

TABLE 1

Cylinder Characterization

<u>Cylinder Number</u>	<u>Manufacturer</u>	<u>Serial #</u>	<u>Vol Free Liquid (mL)</u>	<u>Mass Oxide (g)</u>	<u>Mfr. Date</u>
1	[REDACTED]	[REDACTED]	N/A	3.5	3-86
2	[REDACTED]	[REDACTED]	N/A	.25	3-86
3	[REDACTED]	[REDACTED]	N/A	.25	3-86
4	[REDACTED]	[REDACTED]	N/A	.34	3-86
5	[REDACTED]	[REDACTED]	N/A	.30	3-86
6	[REDACTED]	[REDACTED]	104	7	10-50
7	[REDACTED]	[REDACTED]	10	57	5-36
8	[REDACTED]	[REDACTED]	13	16	9-50
9	[REDACTED]	[REDACTED]	20	35	9-64
10	[REDACTED]	[REDACTED]	0	414	8-39

TABLE 2

Oxide Recovery/Characterization

<u>Iron Type</u>	<u>Formula</u>	<u>Cylinder Number (Manufacture Date)</u>									
		<u>1</u> 3-86	<u>2</u> 3-86	<u>3</u> 3-86	<u>4</u> 3-86	<u>5</u> 3-86	<u>6</u> 10-50	<u>7</u> 5-36	<u>8</u> 9-50	<u>9</u> 9-64	<u>10</u> 8-39
Elemental Iron	Fe	-	-	-	□	□	□	-	-	-	-
Wustite	FeO	-	0	□	-	□	✓	-	✓	□	-
Hematite	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	✓	-	□	✓	✓	0	-	-	✓	-
Maghemite	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	0	✓	0	□	✓	0	✓	0	✓	-
Goethite	$\alpha$ -FeO(OH)	-	-	-	-	-	-	-	-	-	0
Lepidocrocite	$\gamma$ -FeO(OH)	-	-	-	-	-	-	□	-	-	-
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	-	-	-	□	□	-	-	□	-	-
Total Mass (g)		3.5	.25	.25	.34	.30	7	57	16	35	414
‡ Represented as $\alpha$ & $\gamma$ Fe <sub>2</sub> O <sub>3</sub>		100	100	50	100	100	50	100	25	100	0

- - Indicates material not present (0%).

□ - Indicates material present in small quantities (0-25) or of poorly formed crystallinity.

0 - Indicates material present in moderate quantities (25-50%) or of poorly formed crystallinity.

✓ - Indicates material clearly present (40 - 100%).



fraction of oxides indicated by X-ray diffraction. Review of the X-ray diffraction data indicated two types of iron (III) oxide to be predominant;  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Hematite) and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Maghemite). Based upon this finding, an estimate of the material recovered, which could be attributed to the two oxides of interest, was indicated as a percentage of the total mass. (The total mass attributed to Fe<sub>2</sub>O<sub>3</sub> in nine of the ten cylinders, (cylinder #10 was deemed an outliner) was approximately 104g or approximately (ca.) 11.6g/100 lb. cylinder.)

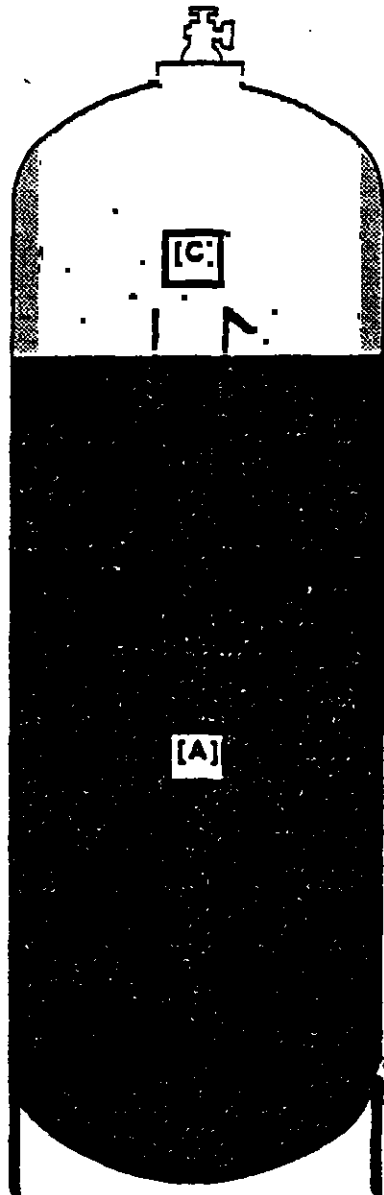
It was determined that the material recovered from cylinder #9 best represented the typical oxide, and was therefore chosen to be used in the simulation experiments. To prepare the material for use in the experiments, a portion was thoroughly rinsed with combinations of methanol and methylene chloride to remove any residual oils. An X-ray diffraction pattern produced after cleaning showed no change except for increasing the definition in the original pattern. To maintain the proper ratio of iron oxide to LPG for use with 100 g of LP for the experiments, 25.5 mg of tank number 9 oxide was required.

## 2. Experimental Procedure and Results

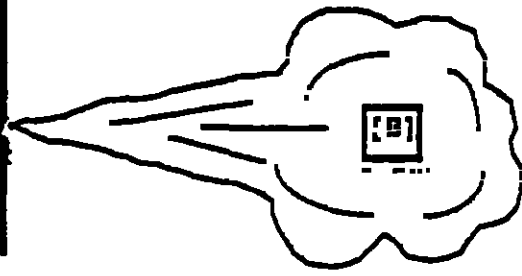
As indicated earlier, a set of experiments were designed which attempted to simulate a 100 lb. cylinder. Using a Parr® Pressure Reaction Vessel (PRV), a series of laboratory scale experiments were conducted (100 g instead of 100 lbs., the 300 mL PRV used having a total capacity of approximately 150 g LPG). The experiments were designed using the following data:

- LPG is essentially propane with less than 12% other hydrocarbons (average density = .54 g/mL).
- LPG is odorized by industry practice at 1.2 - 1.5 lbs. EM/10,000 gals. LPG (EM density = .84 g/mL).
- The NFPA recommended odorization level is at least 1.0 lbs. EM/10,000 gals. LPG.
- The expansion ratio of LPG (vapor):LPG (liquid) is approximately 270:1 (based on ideal gas volume of 22.4 liters/g mole).

For the purpose of this report, a clear distinction must be made in the data for samples taken from the vapor phase (cylinder headspace) versus those taken from the liquid phase (Figure 1). Samples taken from the vapor phase are shown with concentrations in terms of nanograms of ethyl mercaptan per milliliter of propane vapor (ng EM/mL C<sub>3</sub>, vapor), and represents the ethyl mercaptan concentration in the vapor phase which is in equilibrium with the ethyl mercaptan in the liquid phase. Samples originating from the liquid phase similarly are analyzed as vapors but directly indicate the EM concentration present in the liquid phase. In sampling, as liquefied propane and ethyl mercaptan are expelled from the PRV into a gas bag, the mixture vaporizes at the ratio of approximately 270 mL vapor/mL liquid. The vapor from the liquid phase is then analyzed to determine its ethyl mercaptan concentration (ng/mL, gas). The concentration of this vapor, therefore, is essentially a 1/270 dilution of the liquid and factored as such to determine the liquid phase concentration ( $\mu$ g/mL, liquid) indicated. The relationships between the various odorization levels and propane phases are shown in Table 3.



- [A] represents the liquid phase concentration of ethyl mercaptan in  $\mu\text{g/mL}$  (liq) propane which is in equilibrium with the vapor phase (may also be given as lbs EM/ 10,000 gals.LPG).
- [B] represents the ethyl mercaptan concentration in the propane vaporized directly from the liquid phase ( $\text{ng/mL}$  (vap)); related to the liquid phase concentration [A] by the expansion ratio of approximately 270 mL gas/ mL liquid.
- [C] represents the ethyl mercaptan concentration in the head space of the LPG storage cylinder which is in equilibrium with the ethyl mercaptan in the liquid phase; related to the liquid phase concentration [A] by values predicted by Hankinson and Wilson.



**FIGURE 1 ETHYL MERCAPTAN CONCENTRATION DETERMINATIONS**

TABLE 3

Ethyl Mercaptan Concentration Determination

<u>EM ODORIZATION LEVEL</u>			<u>PREDICTED LIQUID-VAPOR PHASE EQUILIBRIUM CONC.</u>		
<u>Liquid Phase</u>		<u>Vapor Phase</u>	<u>Liquid Phase</u>		<u>Vapor Phase</u>
<u>lb./10,000</u>	<u>µg/ml</u>	<u>ng/ml</u>	<u>µg/ml (Liquid)</u>	<u>ng/ml (Vap)</u>	<u>ng/ml (Gas)</u>
<u>gals.</u>			<u>[A]</u>	<u>[B]</u>	<u>[C]</u>
1.0	12	44	9.0	33	11
1.5	18	66	13.5	50	16

For the 100 gram vessel, it was determined that 3.33 mg of ethyl mercaptan (ca. 4.0  $\mu$ L) would yield the appropriate ratio for the 1.5 lbs/10,000 gal. industry practice. Based on the indicated expansion ratio, an aliquot of the liquid phase brought to ambient temperature and pressure would yield approximately 66 ng EM/mL gas as indicated in Table 3. Based upon work by Hankinson and Wilson on the vapor-liquid equilibrium for EM in propane<sup>2</sup> which indicates an equilibrium ratio of .27 at 0°F and .37 at 100°F, a ratio of ca. .33 at 20°C is expected. The NFPA guidelines would result in a liquid phase concentration of 33 ng EM/mL gas (9  $\mu$ g/mL liquid) and a vapor phase concentration of 11 ng/mL. For the industry practice of 1.5 lbs/10,000 gals., this yields a liquid phase concentration of approximately 50 ng EM/mL gas (13.5  $\mu$ g/mL liquid) vs. a vapor phase concentration of 16 ng/mL.

#### a. Baseline Tests

Before determining whether or not oxidation of ethyl mercaptan occurred in contact with the iron oxides, baseline experiments without oxides were conducted for the liquid and vapor phases. To closely mimic the conditions found in the 100 lb. LPG storage cylinder, the stainless steel pressure reaction vessel was the best standard use equipment available. Although it was the original intent on this program to monitor commercially odorized LPG using laboratory scale apparatus, the mixture previously purchased already showed significant levels of other sulfur-containing compounds. A chromatogram showing the major sulfur compounds found in the commercially odorized LPG, after several months of storage, is presented in Appendix A (Figure A). Additionally, the analytical methods used in this program to measure concentrations of EM and other sulfur compounds are also detailed in Appendix A. Mass spectral data confirmed the presence of diethyl disulfide, the primary oxidation product of EM, as well as dimethyl disulfide and methyl ethyl disulfide, in addition to the ethyl mercaptan. The presence of the latter two disulfides clearly indicated the presence of methyl mercaptan in the starting mixture. To more easily monitor the concentration of ethyl mercaptan and its oxidation product(s) in LPG without interference from the methyl mercaptan, an analytical grade mixture of liquefied propane with ethyl mercaptan was formulated (4.0  $\mu$ L EM/100 g propane) by Arthur D. Little, Inc. The commercial grade LPG was used only periodically as a reference.

The preparation of the propane/EM mixture proved to be a non-trivial task. As both components vaporize at ambient conditions (propane - B.P., -42°C; ethyl mercaptan - B.P., 35°C), the ethyl mercaptan could not simply be added to the propane due to the elevated pressure in the PRV. Conversely, the ethyl mercaptan would be swept from the vessel on filling with propane. We therefore encapsulated the ethyl mercaptan (pre-measured for the 100 g mixture) in a 2-in glass capillary tube which was then wedged in the PRV mechanical stirrer. After taring and filling the PRV with liquefied propane to 100 grams, the capillary tube was broken, and the ethyl mercaptan mechanically mixed. The PRV was then

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<sup>2</sup>Hankinson, R.W. and G.M. Wilson, "Vapor-Liquid Equilibrium Data for Ethyl Mercaptan in Propane Vapors," Proceedings of Fifty-third Annual Convention of the Gas Processors Association, 98-100 (1974).

warmed to 20°C. A more detailed description of the PRV and the sampling procedure is presented in Appendix B.

The initial tests to determine the reactivity of the ethyl mercaptan in the storage container showed that oxidation occurs even in the presence of clean stainless steel surfaces. The first trial run using the ADL formulated liquid propane, without oxides in the vessel, showed the ethyl mercaptan concentration to be 4.9 µg/mL, well below the expected 13.5 µg/mL, as indicated in Table 4. The data presented in Figure 2 shows the ethyl mercaptan concentration versus time as well as the diethyl disulfide concentration. The general trend in this set appears to show a slow decrease in the ethyl mercaptan concentration with a concurrent increase of the diethyl disulfide concentration. (This was shown much more dramatically in the baseline vapor phase experiment described below when only vapor phase LPG was present.) Additionally, in the liquid phase experiment there was a dramatic increase in the ethyl mercaptan concentration as the last of the liquid phase was expended. In cases where only vapor phase LPG is removed, as in normal cylinder use, this type of increase in concentration would be expected as indicated using a computer simulated depletion of LPG indicated in Table 5. Figure 3 depicts the expected EM concentration rise as a function of use of the LPG vapor. In the case of removal of only liquid phase LPG, ideally a homogeneous mixture, there should be no change in concentration. There is no clear explanation for this apparent EM concentration increase in the liquid phase, since every attempt was made to properly mix the vessel contents before any samples were taken for analysis. However, incomplete mixing caused by ethyl mercaptan being trapped in the capillary tube cannot be ruled out. The observation of an increase in EM concentration near the end of the test corresponds to observations in the field, where consumers frequently notice an odor when tanks are near empty.

In order to examine the baseline concentrations for the vapor phase study, the PRV was thoroughly rinsed with methanol and methylene chloride, then purged with nitrogen. For this phase of experimentation, we looked at only the headspace vapor from the commercially odorized LPG. Since there was no liquid reservoir to replenish the vapor phase for bag sampling, a septum port was fitted to the PRV to allow direct syringe sampling. The PRV was subsequently flushed with the headspace of the commercially odorized LPG. The first two fills with the vapor phase LPG showed anomalous behavior of the EM odorant. While not in use, the 20 lb. LPG cylinder had been stored outside of the building in a secure area. As the work for this study was conducted between January and March 1987, the ambient storage temperature for the cylinder was typically near 32°F (b.p. of LPG = -43.6°F, b.p. EM = 95°F). On the attempt of the first filling of the PRV for the vapor phase experiment, the ambient temperature was approximately 40°F. The equilibrium cylinder pressure at the time of filling was noted to be under 50 psig indicating the interior temperature of the cylinder to be approximately 20°F. No ethyl mercaptan was detected in the gas sampled, while the DEDS concentration was noted to be approximately 8 ng/mL. On a second attempt, the LPG was warmed slightly by bringing the cylinder indoors. The PRV was again filled to equilibrium pressure (ca. 70 psig) with the 20 lb. cylinder. On analysis of this filling the ethyl mercaptan concentration was observed to be 3 ng/mL and the DEDS to be 5 ng/mL. This finding may have occurred as a result of the cold storage temperature of the cylinder or may be due to an activation of the metal surface of the PRV due to the solvent rinsing process.

## LIQUID PHASE ODORANT OXIDATION

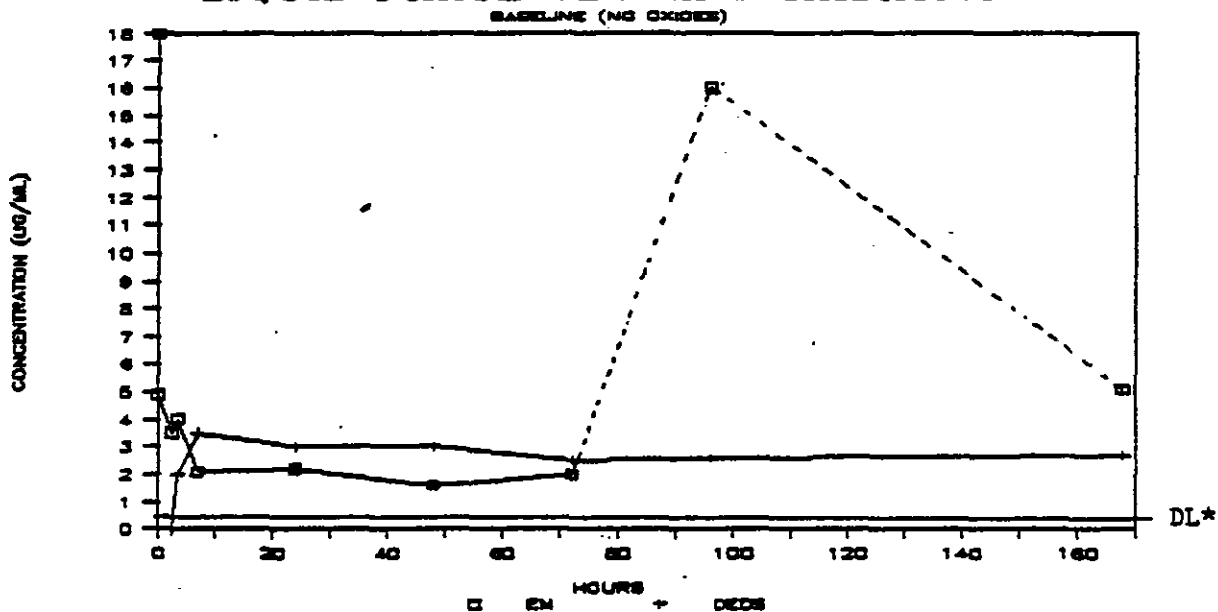


FIGURE 2

TABLE 4

### Baseline Liquid Phase LPG Odorant Oxidation (No Oxides: Analytical Grade EM/LP)

Elapsed Time (hrs)	Ethyl Mercaptan		Diethyl Disulfide	
	Vapor Conc. [B] (ng/mL)	Calculated Liquid Phase [A] (ug/mL)	Vapor Conc. [B] (ng/mL)	Calculated Liquid Phase [A] (ug/mL)
0	18	4.9	ND	-
2.5	13	3.5	ND	-
3.5	15	4	7.0	2
7	7.6	2.1	13	3.5
24	8.2	2.2	11	3
48	5.9	1.6	11	3
72	7.4	2	9.3	2.5
96	60	16	9.6	2.6
168	19	5.1	10	2.7

\*DL = Detection Limit of ethyl mercaptan (.42 ug/mL by Hubaux and Vos\*\* with 95% confidence based upon column limit of 1.56 ng and analysis of 1.0 mL vapor with an expansion rate of 270 mL vapor/mL liquid. (See page 31 for calibration data.)

\*\*A. Hubaux and G. Vos, "Decision and Detection Limits for Linear Calibration Curves," Anal. Chem., 42 (8), 849-855 (1970).

## ETHYL MERCAPTAN CONCENTRATION PROFILE

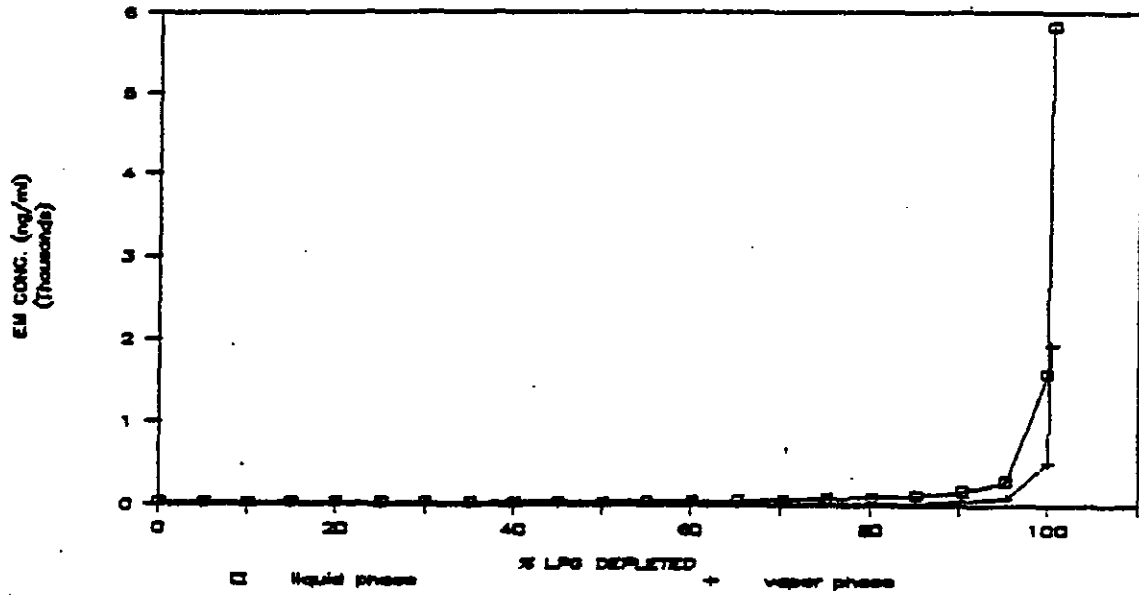


FIGURE 3

TABLE 5

Theoretical Equilibrium EM Profile  
(Concentration vs. % LPG Depleted)

% LPG Depleted	Liquid Phase Concentration (ng/mL) [B]	Vapor Phase Concentration (ng/mL) [C]
0	33	11
10	36	12
20	39	13
30	43	14
40	48	16
50	55	18
60	65	22
70	81	27
80	109	36
90	183	61
95	302	101
99.9	1610	537
100	5830	1943

## VAPOR PHASE ODORANT OXIDATION

BASELINE (NO OXIDES; NO LIQUID PHASE)

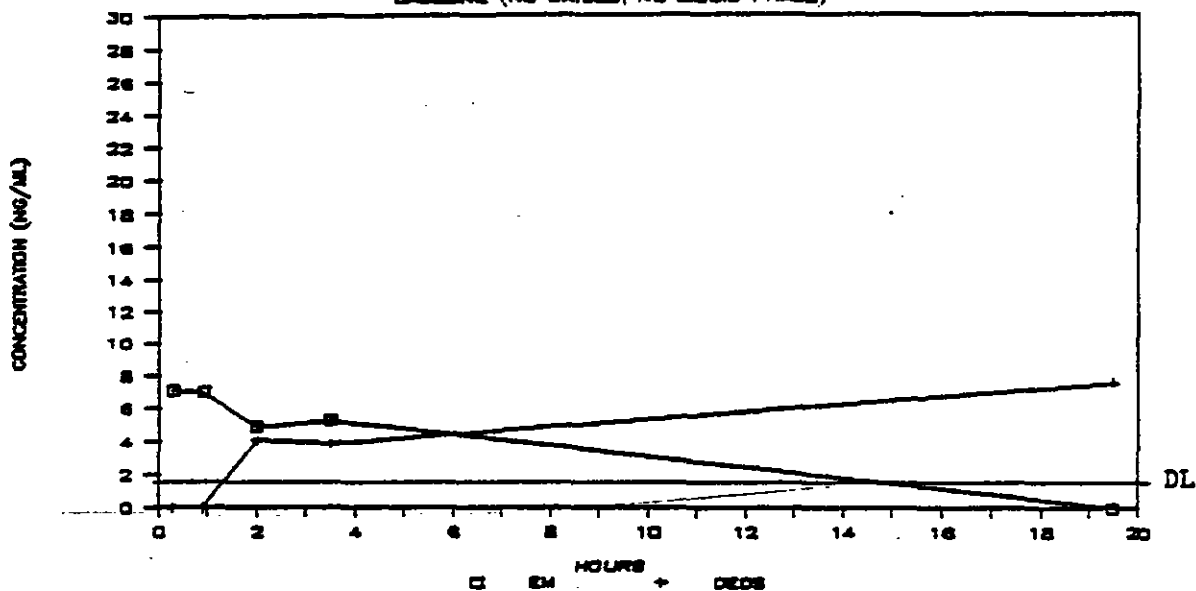


FIGURE 4

TABLE 6

Baseline Vapor Phase LPG Odorant Oxidation  
(No Oxides: Commercial Grade LPG)

<u>Experiment</u>	<u>Elapsed Time</u> (hrs)	<u>Ethyl Mercaptan</u> <u>Concentration</u> (ng/mL) [C]	<u>Diethyl Disulfide</u> <u>Concentration</u> (ng/mL) [C]
1st Attempt	0	ND	7.6
2nd Attempt	0	3.1	4.6
3rd Attempt	.3	7.1	ND
	.9	7.0	ND
	2	4.9	4.1
	3.5	5.3	3.9
	19.5	ND	7.6

\*DL = Detection Limit of ethyl mercaptan (1.56 ng on column) by Hubaux and Vos with 95% confidence.



# LIQUID PHASE ODORANT OXIDATION

1st FILL W/ OXIDES

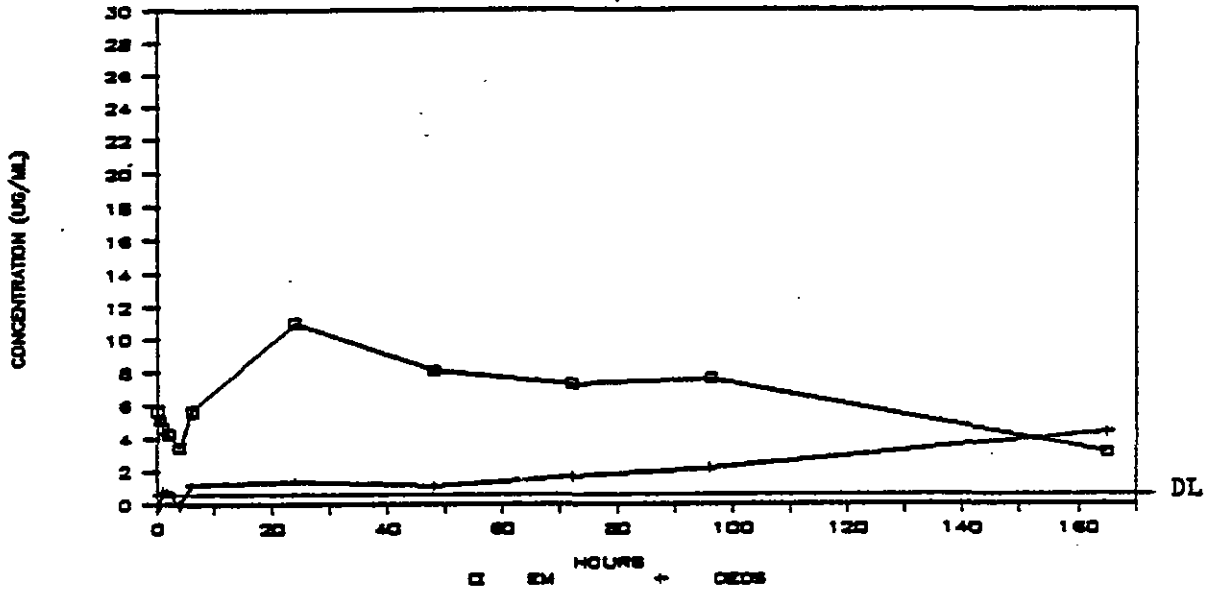


FIGURE 5

TABLE 7

## Liquid Phase LPG Odorant Oxidation (.025 g Oxides)

1st Fill

<u>Elapsed Time</u> (hrs)	<u>Ethyl Mercaptan</u>		<u>Diethyl Disulfide</u>	
	<u>Vapor Conc. [B]</u> (ng/mL)	<u>Calculated Liquid Phase [A]</u> (µg/mL)	<u>Vapor Conc. [B]</u> (ng/mL)	<u>Calculated Liquid Phase [A]</u> (µg/mL)
0 <sup>-</sup>	ND	-	ND	-
0 <sup>+</sup>	21	5.7	ND	-
.5	19	5.1	ND	-
1	17	4.6	2.8	.76
2	16	4.3	2.7	.72
4	13	3.5	ND	-
6	21	5.7	4.5	1.2
24	39	11	5.2	1.4
48	30	8.1	4.0	1.1
72	27	7.3	6.4	1.7
96	28	7.6	8.2	2.2
165	12	3.2	16	4.4

\*DL = Detection Limit of ethyl mercaptan (.51 ug/mL) by Hubaux and Vos with 95% confidence based upon on column limit of 1.88 ng and analysis of 1.0 mL vapor.

## LIQUID PHASE ODORANT OXIDATION

4th FILL W/ OXIDES

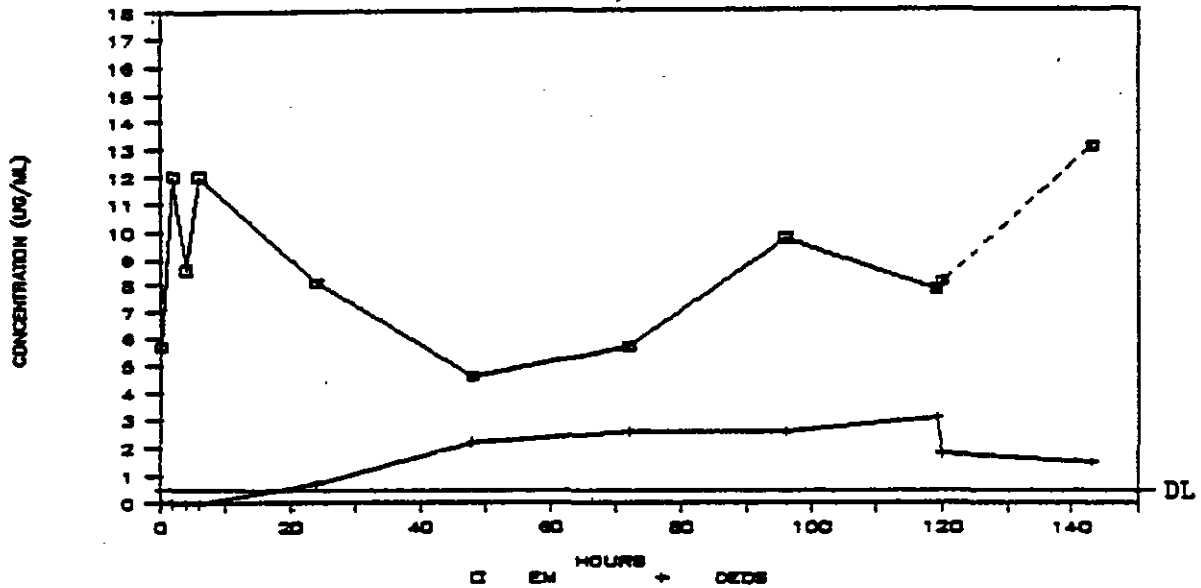


FIGURE 6

TABLE 8

### Liquid Phase LPG Odorant Oxidation (4th Fill with Oxide)

<u>Elapsed Time</u> (hrs)	<u>Ethyl Mercaptan</u>		<u>Diethyl Disulfide</u>	
	<u>Vapor Conc. [B]</u> (ng/mL)	<u>Calculated Liquid Phase [A]</u> ( $\mu$ g/mL)	<u>Vapor Conc. [B]</u> (ng/mL)	<u>Calculated Liquid Phase [A]</u> ( $\mu$ g/mL)
.25	21	5.7	ND	-
2	43	12	ND	-
4	32	8.6	ND	-
6	46	12	ND	-
24	30	8.1	2.6	.69
48	17	4.6	8.1	2.2
72	21	5.7	9.6	2.6
96	36	9.7	9.5	2.6
119	29	7.8	11	3.1
120	30	8.1	6.8	1.8
143	47	13	5.5	1.5

\*DL = Detection Limit of ethyl mercaptan (.46 ug/mL) by Hubaux and Vos with 95% confidence based upon column limit at or below 1.7 ng and an analysis of 1.0 mL vapor.

diethyl disulfide concentration again remained near 2  $\mu\text{g/mL}$ , but appears to have taken slightly longer to begin forming (i.e., twenty-four hours in the fourth filling vs. one hour in the first). Using Figure 7/Table 9 as a comparison to the liquid phase, the ethyl mercaptan concentration behavior in the vapor phase closely mimics that in the liquid phase. The converted liquid LP concentration (Column B) shows that the vapor phase concentration (Column C) is approximately one-third that found in the liquid phase (-10 ng/mL [gas] vs. -30 ng/mL). However, there was no diethyl disulfide detectable in the vapor phase, possibly due to the splashing from the mixer which would wash the DEDS from the container walls into the liquid phase.

With the fifth filling, the diethyl disulfide formation continues to slow. Figure 8/Table 10 shows that the ethyl mercaptan concentration in the liquid phase remains near 11  $\mu\text{g/mL}$  (allowing for scatter in the analytical results), as expected. The diethyl disulfide does not appear significantly until after three days. As in the previous tests, and as predicted by Hankinson, the vapor phase concentration of ethyl mercaptan is approximately one-third that in the liquid phase as converted to vapor (Figure 9/Table 11). Again no diethyl disulfide appears in the vapor phase, presumably due to the removal of any DEDS by the washing action of the LPG.

#### B. Odorant Fading in the Presence of Masonry

The introduction of odorized propane gas into an environment containing untreated masonry had been suggested as a second possible route for odorant loss. Using the LP odorized with ethyl mercaptan in the PRV at ca. 60 ng/mL gas (vapor phase), we performed a set of three experiments. The first of the three tests as a background blank was simply to determine the rate of loss of ethyl mercaptan vs. the propane in the chamber without masonry present. The other tests would therefore determine the difference produced by the presence of concrete block (cinder block) and poured concrete. Previous experience with this type of reaction suggested that any absorption, binding, or catalytic conversion would occur relatively quickly compared to the previously described oxidation reaction studied in the cylinder.

The experimental plan therefore called for spiking a standard EM/LP mixture to the lower explosive limit (LEL - 1.9% LP in air) into a rigid chamber of known volume. For this experiment we used a .1 m<sup>3</sup> chamber constructed of 1/4" Lexan acrylic with interior dimensions 40 cm x 50 cm x 50 cm as shown in Figure 10. The hinged loading door on the front of the chamber sealed the chamber on closing by means of silicone rubber gasketing and twist plates. Ports located on the sides near the top allowed for addition of the odorized propane and removal of aliquots of the air for analysis. A small fan at the top of the chamber (resembling a miniature ceiling fan) provided the air circulation and mixing to ensure representative sampling.

Given the detection limits for the compounds of interest, a 5.0 mL aliquot of the chamber contents at the lower explosive limit allowed for adequate monitoring from the acceptable odorization level of .319 ng/mL to near 1/5 the lower explosive limit (.064 ng/mL). Samples for EM analysis were taken from the chamber via 5.0 mL gas-tight syringes, with mixing of the chamber air by the small fan, and directly analyzed by the GC/FPD system described in Appendix A. The propane concentration was similarly determined by removal and analysis of a

## VAPOR PHASE ODORANT OXIDATION

4th FILL W/ OXIDES

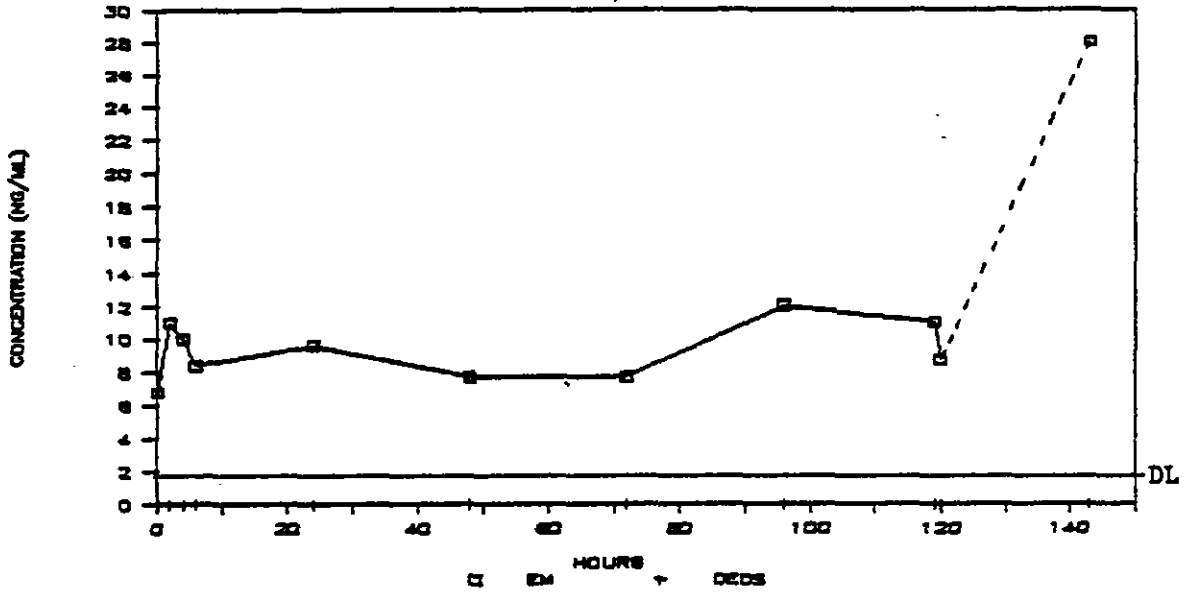


FIGURE 7

TABLE 9

### Vapor Phase LPG Odorant Oxidation (4th Fill with Oxides)

<u>Elapsed Time</u> (hrs)	<u>Ethyl Mercaptan</u> (ng/mL) [C]	<u>Diethyl Disulfide</u> (ng/mL) [C]
.25	6.8	ND
2	11	ND
4	10	ND
6	8.4	ND
24	9.6	ND
48	7.7	ND
72	7.7	ND
96	12	ND
119	11	ND
120	8.7	ND
143	28*	ND

\*Increase due to depletion of liquid phase.

\*DL = Detection Limit of ethyl mercaptan (1.71 ng/mL) based on injection volume of 1.0 mL vapor by Hubaux and Vos with 95% confidence.

## LIQUID PHASE ODORANT OXIDATION

5th FILL W/ OXIDES

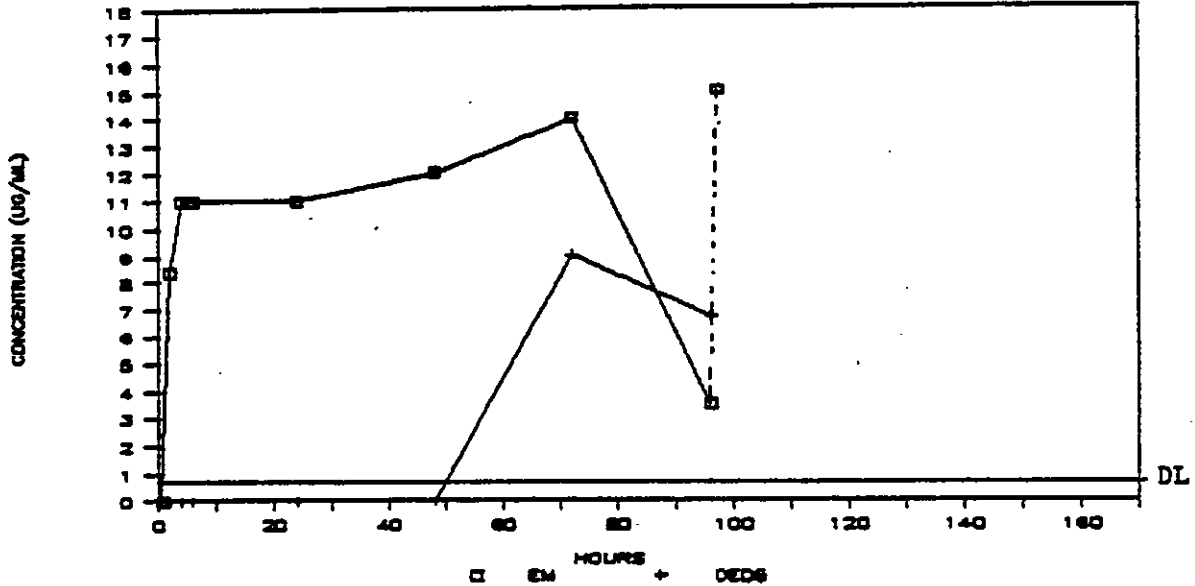


FIGURE 8

TABLE 10

Liquid Phase LPG Odorant Oxidation  
(5th Fill with Oxides)

Elapsed Time (hrs)	<u>Ethyl Mercaptan</u>		<u>Diethyl Disulfide</u>	
	Vapor Conc. [B] (ng/mL)	Calculated Liquid Phase [A] ( $\mu$ g/mL)	Vapor Conc. [B] (ng/mL)	Calculated Liquid Phase [A] ( $\mu$ g/mL)
0	ND	-	ND	-
.67	31	8.4	ND	-
2	42	11	ND	-
4	41	11	ND	-
6	40	11	ND	-
24	45	12	ND	-
48	53	14	ND	-
72	40	11	9.0	2.5
96	13	3.5	6.7	1.8
97	54	15	ND	-

\*DL = Detection Limit for ethyl mercaptan (.72 ug/mL) by Hubaux and Vos with 95% confidence based upon column limit at or below 2.68 ng/mL and an analysis of 1.0 mL vapor.

## VAPOR PHASE ODORANT OXIDATION

5th FILL W/ OXIDES

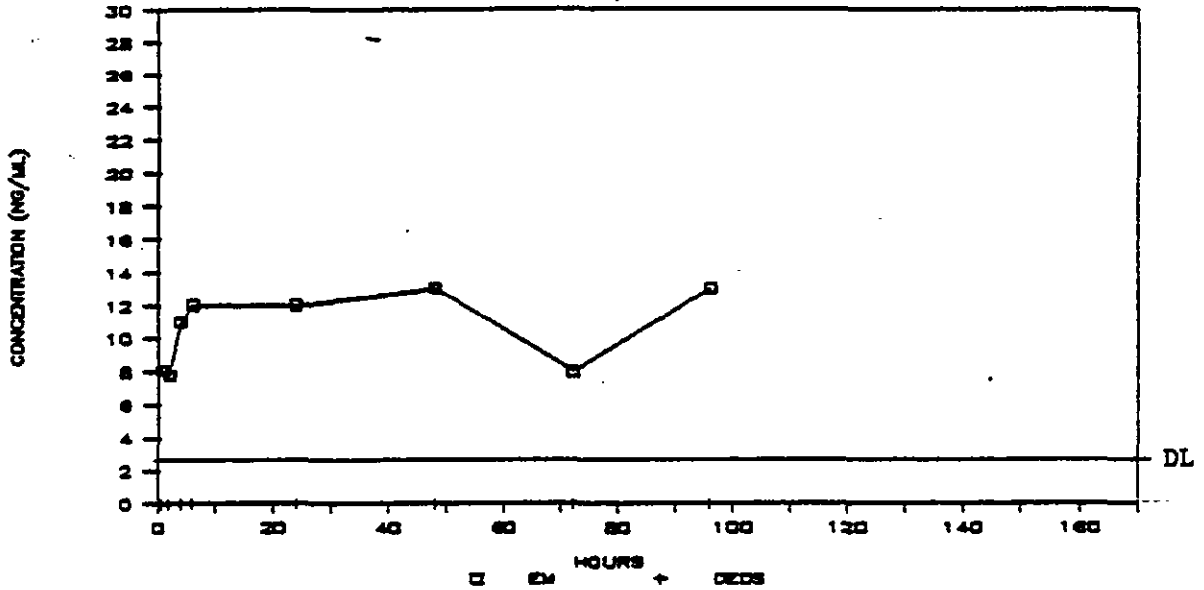


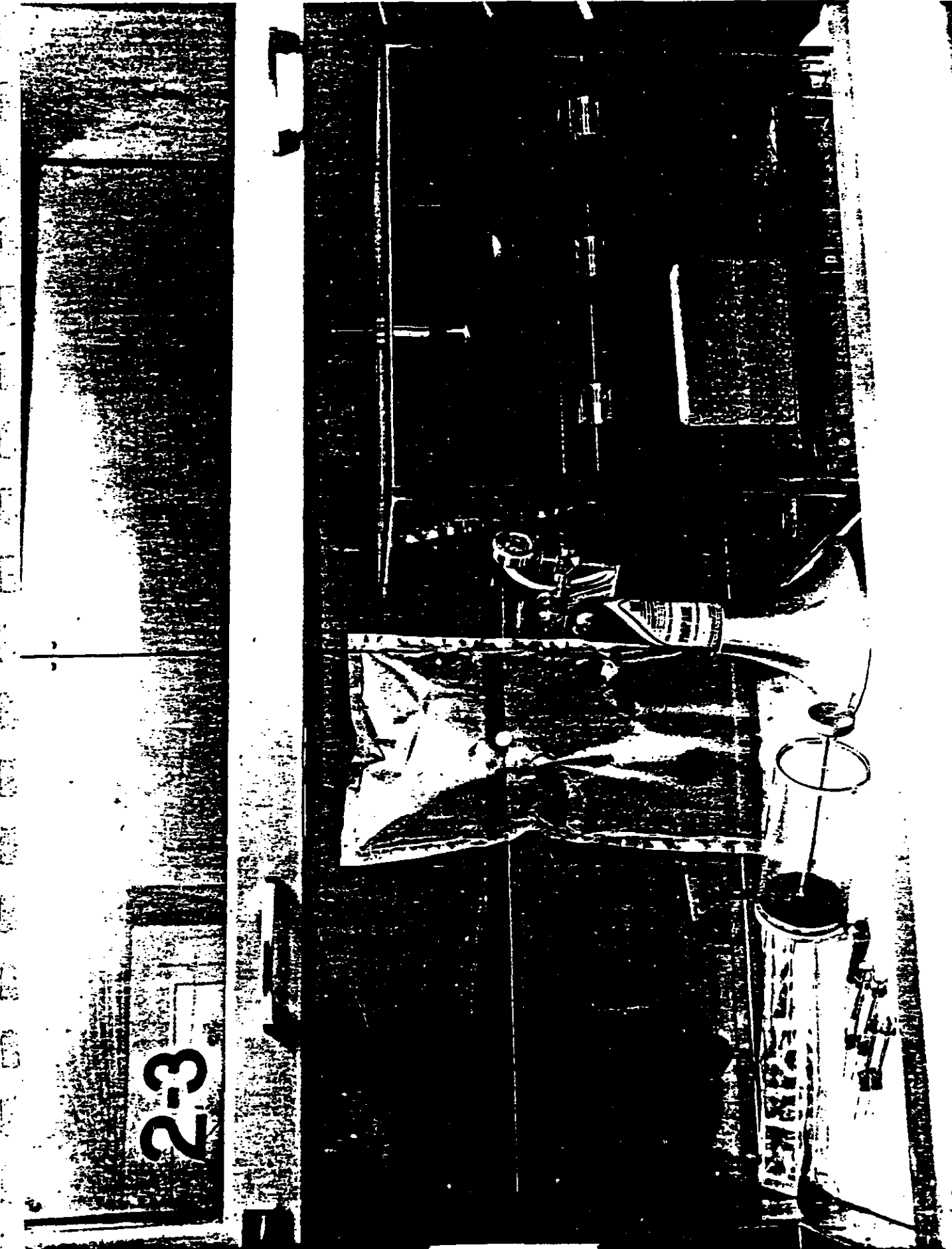
FIGURE 9

TABLE 11

### Vapor Phase LPG Odorant Oxidation (5th Fill with Oxides)

<u>Elapsed Time</u> (hrs)	<u>Ethyl Mercaptan</u> <u>Concentration</u> (ng/mL) [C]	<u>Diethyl Disulfide</u> <u>Concentration</u> (ng/mL) [C]
.67	8.1	ND
2	7.8	ND
4	11	ND
6	12	ND
24	12	ND
48	13	ND
72	8.0	ND
96	13	ND

\*DL = Detection Limit of ethyl mercaptan at or below 2.7 ng/mL vapor by Hubaux and Vos with 95% confidence based upon analysis of 1.0 mL vapor.



2-3

FIGURE 10 - MASONRY PROMOTED OMOGRANT FADING APPARATUS

31

30-50  $\mu\text{l}$  aliquot of the air. The initial trial run without masonry showed the chamber retained the test atmosphere reasonably well. As indicated in Table 12 and Figure 11A, the initial ethyl mercaptan concentration was .52 ng/mL air, corresponding to the level for 1.9% LP in air. After six hours in the blank chamber, the ethyl mercaptan was only depleted to 87% of its original concentration and the propane to 81% of its original level. After approximately 24 hours, the ethyl mercaptan level was .36 ng/mL (69% of original) and the propane at 56% of its original level.

Since information was not readily available concerning average sizes of exposed masonry surface for a typical user, an estimate was made based on a typical home dimension. For example, a typical home might have a 25' x 45' (7.62 m x 14.33 m) basement with a ceiling height of seven (7) ft (2.13 m). For this model, the interior volume is 7875  $\text{ft}^3$  (232.6  $\text{m}^3$ ), the surface area (walls and floor) is 2105  $\text{ft}^2$  (202.7  $\text{m}^2$ ) hence the ratio of area to volume is .267  $\text{ft}^2/\text{ft}^3$  (.87  $\text{m}^2/\text{m}^3$ ). This would be represented by a .1  $\text{m}^3$  (40 cm x 50 cm x 50 cm) gas exposure chamber with a concrete sample of 870  $\text{cm}^2$  surface area to the .1  $\text{m}^3$  volume.

Concrete (cinder) block samples obtained from a local masonry products supplier were normal weight natural concrete patio block (1 3/4" x 8" x 16"). The normal weight is the typical grade used in building construction. A sample of poured concrete was obtained from a local home renovation project in which parts of a ten year old basement foundation was being removed. To present the proper exposed surface area, the cinder block was scored and broken along one edge to yield the 870  $\text{cm}^2$  (i.e., 4.5 cm x 14.5 cm x 19.5 cm). The poured concrete sample required cutting with a diamond saw to obtain the proper surface area (i.e., 10 cm x 10 cm x 16.5 cm).

Using these samples, the ethyl mercaptan concentration was shown to decrease markedly over the test period as compared to propane. With the concrete block in place, the ethyl mercaptan concentration decreased to below detectable levels (< .4 ng/mL air) within five and one half (5 1/2) hours as indicated in Figure 11B. The propane, however, was still present at 1.2% after 24 hours, and after 46 hours was reduced to only 1.0%. The poured concrete sample reduced the ethyl mercaptan level to the detection limit of the FPD in approximately seven and one half (7 1/2) hours as indicated in Figure 11C.

### III. CONCLUSIONS

While there is some variability in the individual data points developed in this program, a general trend is discernible as to the fate of the ethyl mercaptan odorant in LPG under the conditions studied. Based upon the results in these experiments, it is apparent that the ethyl mercaptan in an LPG mixture in steel cylinders is subject to oxidation. The oxidation appears to occur regardless of the amount of iron oxides present in the cylinder. In fact, as noted by the results of the experiments without oxides added to the stainless steel reaction vessel, oxidation may take place even in a "clean" container. It also appears that the surfaces of a cylinder in continuous use may become deactivated with respect to reaction of the ethyl mercaptan or may at least cause a slower rate of reaction. Figures 12 and 13 present the previously shown concentration profiles grouped by liquid phase and vapor phase respectively, and support the premise that a container surface may be deactivated with repeated fillings.



TABLE 12

Masonry Promoted Odorant Fading Results

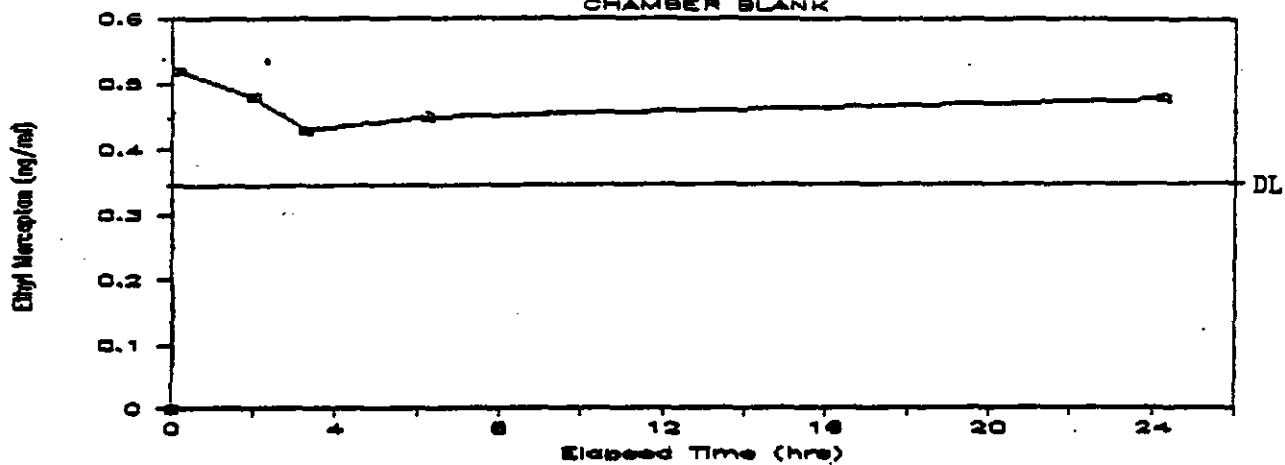
<u>Study</u>	<u>Elapsed Time</u> (Hours:Minutes)	<u>Ethyl Mercaptan</u> <u>ng/mL (DL)*</u>	<u>Propane</u> <u>‡</u>
Chamber Blank	0:10	.53 (.34)	
	0:30		2.0
	2:00	.49	
	3:15	.44	
	6:15	.46	
	6:45		1.6
	22:30		1.1
	24:15	.48	
Chamber with Concrete Block	0:10	.64 (.23)	
	0:40		1.7
	1:40	.44	
	2:30		1.4
	3:05	.39	
	4:00		1.2
	4:35	.32	
	5:40	ND	
	22:30		1.3
44:50		1.1	
Chamber with Poured Concrete	0:17	.35 (.20)	
	0:40		1.8
	0:53	.36	
	1:30		1.8
	1:47	.31	
	2:10		1.8
	3:21	.27	
	4:12	.23	
	4:17		1.8
	4:45	.23	
	5:50	.20	
	6:40	.21	
	8:20	.22	
9:00		1.6	

\*DL - 95% confidence detection limits (ng/mL) via Hubaux and Vos, differences in detection limits are produced by variation in detector response as determined on a daily basis.

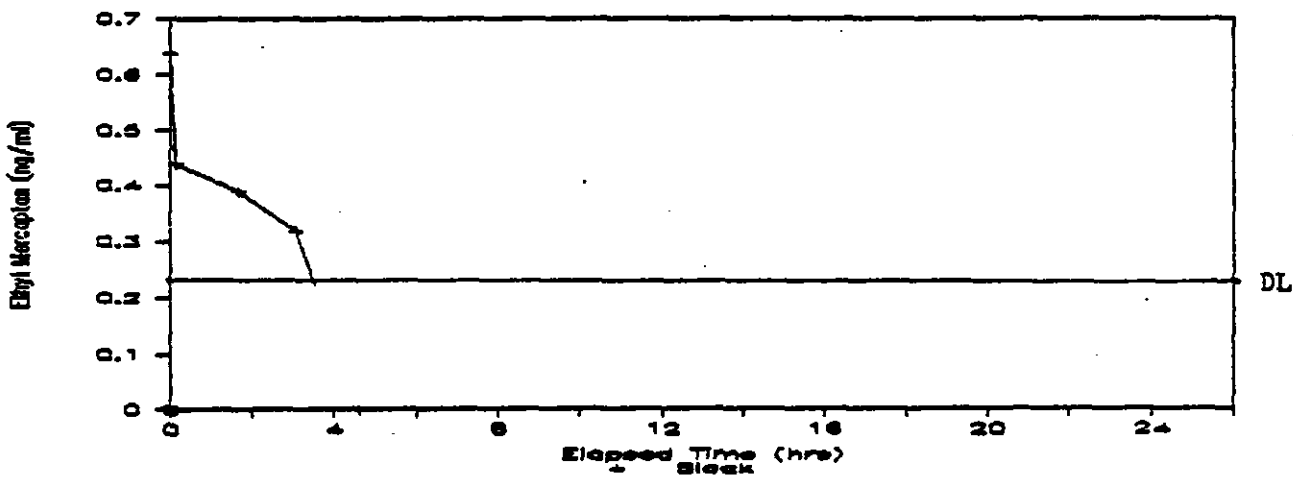
ND - none detected (no baseline deflection).

Figure 11

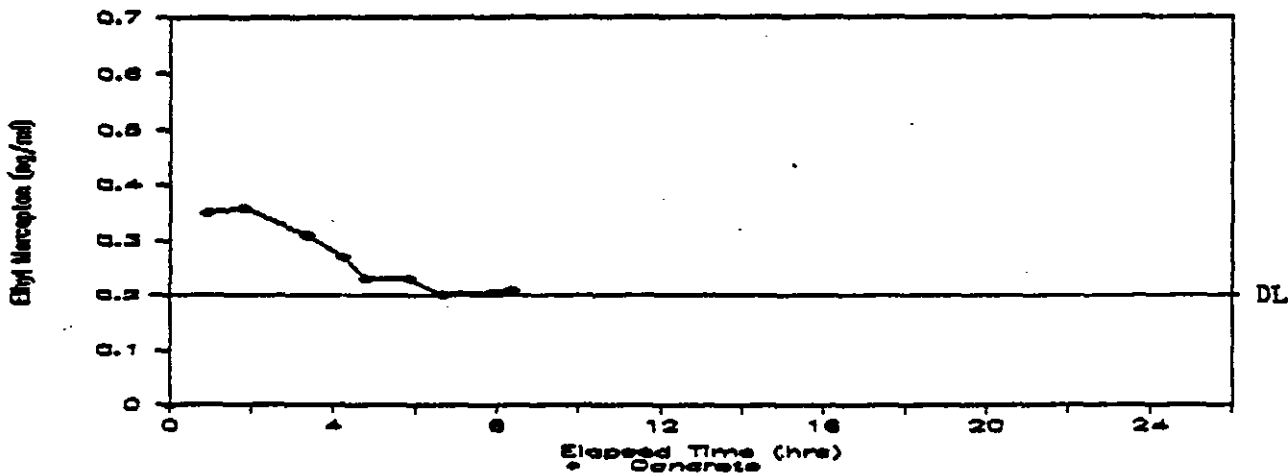
**MASONRY PROMOTED ODORANT FADING**  
CHAMBER BLANK



(A)

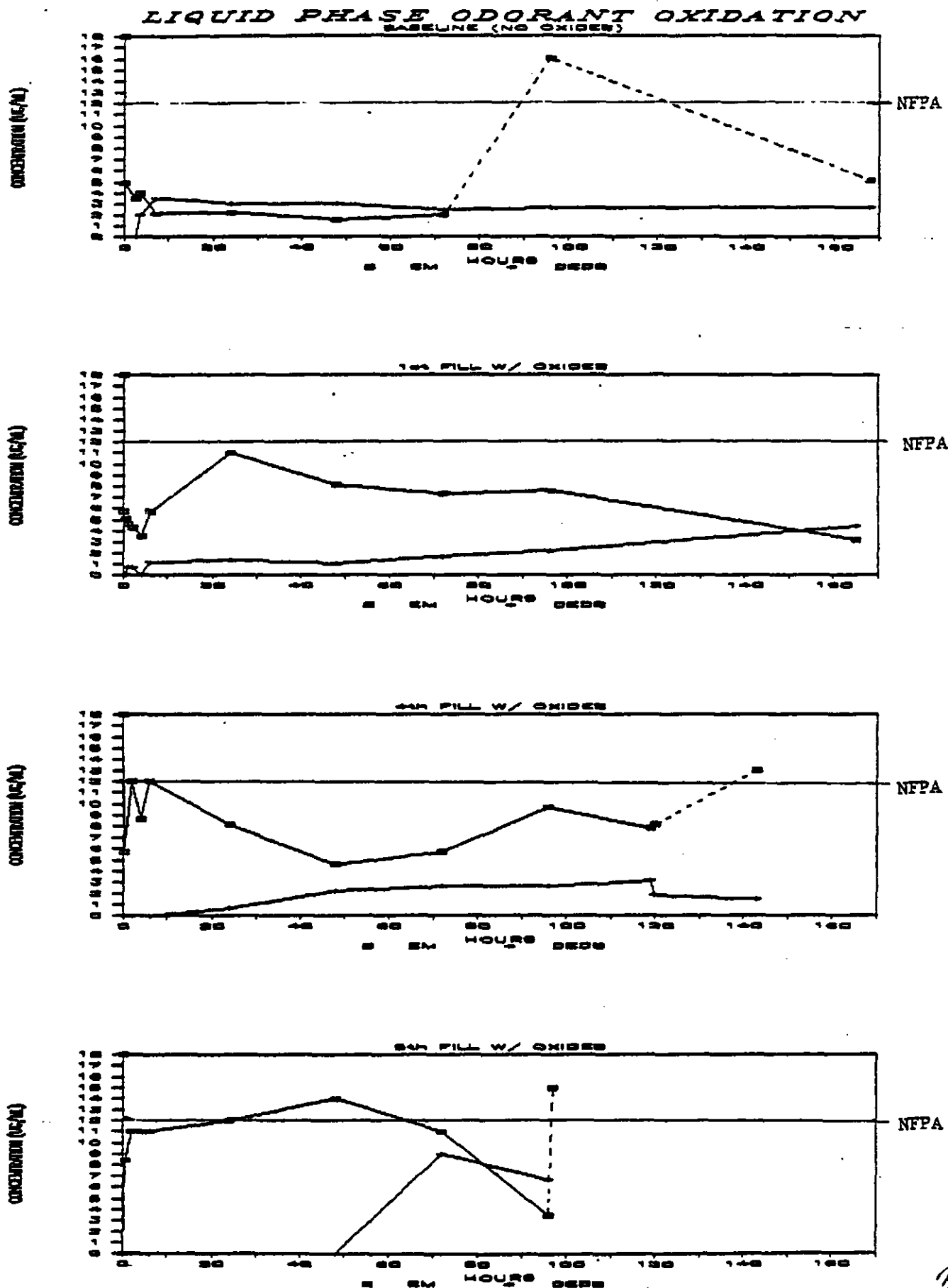


(B)



(C)

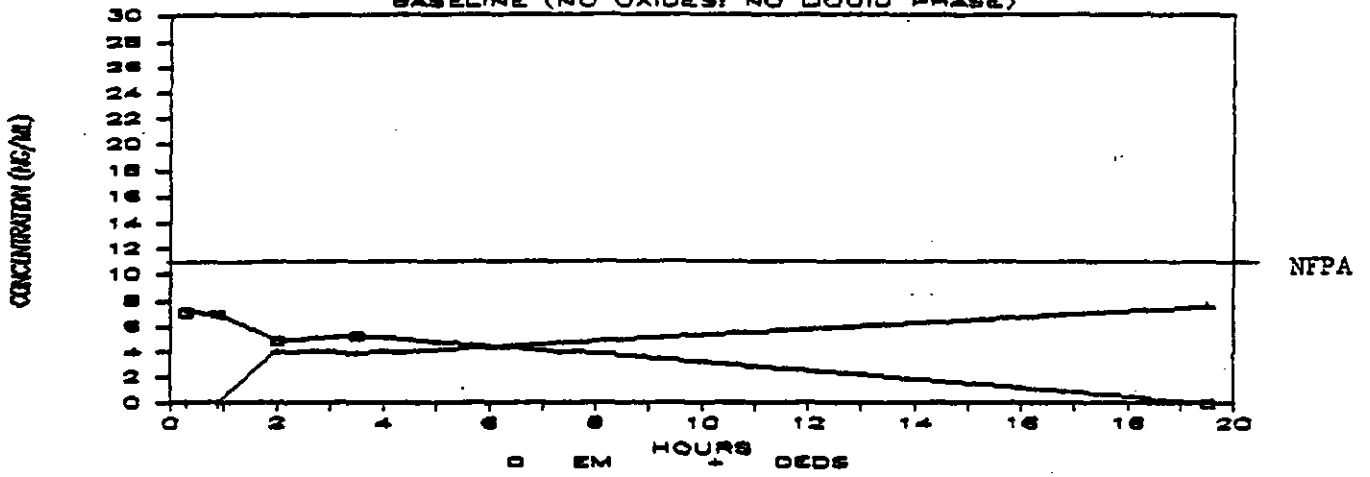
Figure 12



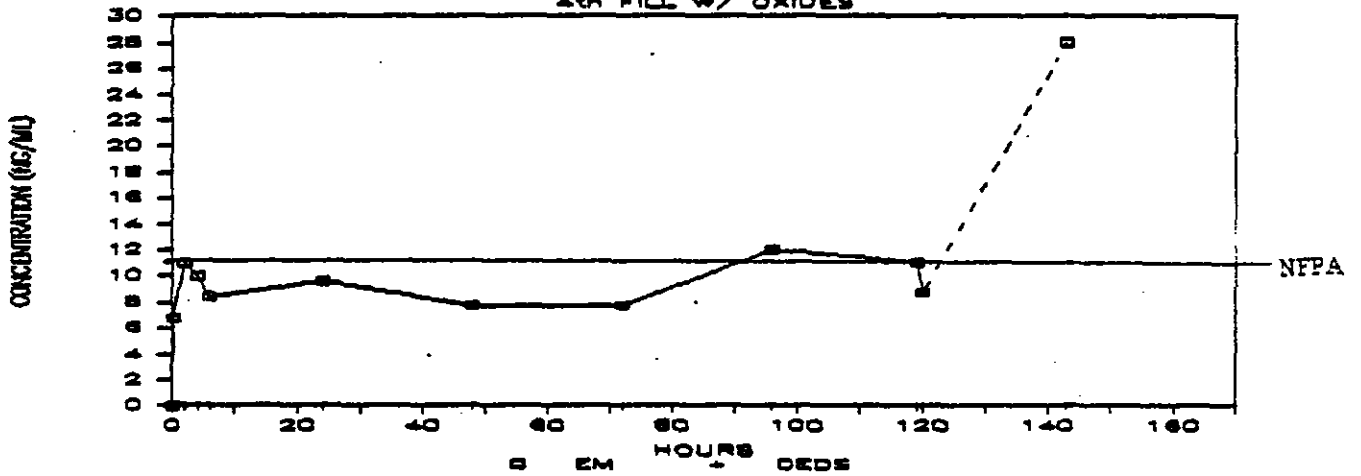
35

Figure 13

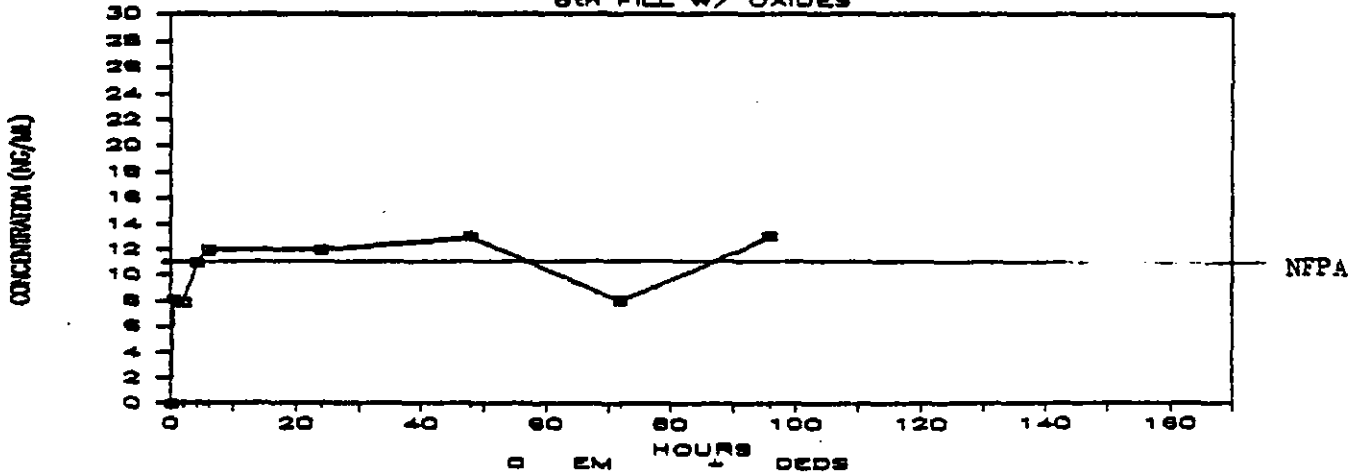
### VAPOR PHASE OXIDATION BASELINE (NO OXIDES; NO LIQUID PHASE)



### 4th FILL W/ OXIDES



### 6th FILL W/ OXIDES



This phenomenon would require experimental exposures longer than those examined in this study to be fully evaluated. The oxidation of EM was found to take place in both the liquid and vapor phases, but more rapidly and completely in the vapor phase. This phenomenon became clear in the experiments using only odorized vapor phase LP, and may be masked when liquid phase is present to dissolve any diethyl disulfide formed and replenish any EM lost. As described, diethyl disulfide was found to be the primary oxidation product of ethyl mercaptan, although additional products may form if other mercaptans are also present, e.g., methyl ethyl disulfide in the presence of methyl mercaptan. According to the general mercaptan literature, the oxidation reaction is reversible<sup>3</sup> (although we did not verify this experimentally) but the ethyl and methyl disulfides are relatively unreactive.

Because of the varying parameters present, i.e., temperature and liquid-vapor phase equilibrium and "odor-threshold" levels, acceptable levels of odorization in the pure vapor phase and at subsequent dilutions in air should be determined. The NFPA recommendation of 1.0 lb./10,000 gals. does not directly correlate to a delivered vapor phase concentration except by using the liquid/vapor equilibrium data, indicated by Hankinson and Wilson. The target would be approximately 11 ng EM/mL LPG vapor (4.0 ppm as delivered or about 15 ppb at 1/5 the LEL). Based upon the results of experiments with the liquid phase LP, the ethyl mercaptan concentration does not appear to stabilize and appear at the 11 ng/mL level until the 5th fill. Fewer fillings of the cylinder show erratic ethyl mercaptan concentrations in the LP(G) and are consistently lower than the target level until the cylinder is nearly expended.

It has been demonstrated that ethyl mercaptan is depleted much more quickly than the propane of an odorized LPG mixture in a steady state environment with masonry. In the presence of a concrete block, the ethyl mercaptan was shown to be undetectable within six hours, i.e., less than .09 ng/mL (32 ppb). Again, based upon the previous discussion of liquid-vapor phase equilibria, the recommended NFPA guidelines indicated above would correspond to a concentration of .21 ng EM/mL (76 ppb) air at the 1.9% LEL.

#### IV. RECOMMENDATIONS

Several recommendations became apparent as a result of this study:

- (1) The appropriate odorization level of ethyl mercaptan in LPG vapor and practices to achieve it may require better definition. The stated NFPA odorization level (1.0 lbs./10,000 gals.) does not address the final delivery concentration in the vapor phase. Considerations important to this determination include the liquid-vapor phase equilibrium of the original charge ratio, regional temperature effects, and potential losses to oxidation or other affects. Bullerdiak suggested that odorization at 1.2 - 1.5 lbs. EM/10,000 gals. LPG would yield 15 - 20 ppb at 1/5 the LEL. A study

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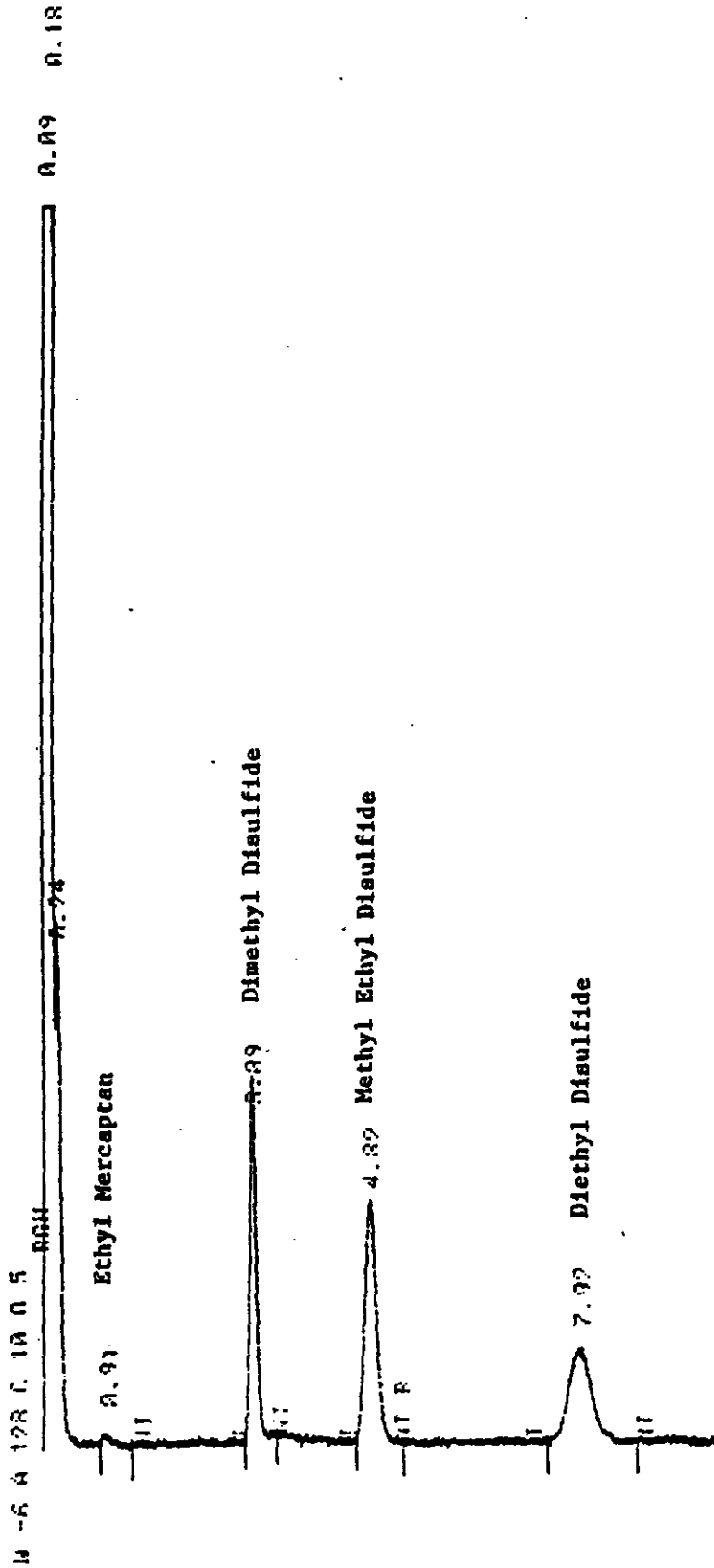
<sup>3</sup>Noller, Carl R., "Chemistry of Organic Compounds", W.B. Saunders Company, Philadelphia, 1951, p. 270.

correlating the odorization level with final delivery concentrations by both chemical and sensory analysis may be appropriate.

- (2) While a trend of odorant oxidation in storage of LPG in steel cylinders appeared to occur during our short term study (5 - 7 days/test), a longer term study should be initiated. The oxidation taking place in the environment of the steel cylinder should be studied over weeks or months to gain a fuller understanding of the phenomenon. It might also be of interest to determine whether or not there are practices or techniques available to mitigate the oxidation produced by the storage container, e.g., whether or not a polymer coating might be effective. Similarly, polymer coatings (paints) on masonry might be important inhibitors of odorant loss. In this latter case, it should also be recognized that in actual practice, a dynamic situation exists, and relative rates of loss and replenishment become important.
- (3) During the course of this program, the potential for odorant loss at cold temperatures (near freezing) in the vapor phase concentration of the LPG was suggested. A study to determine whether or not this effect is real would be appropriate. The temperature/concentration profiles in the steel cylinders, as well as storage duration and use frequency might be examined. For example, it is possible that regular use at colder temperatures would produce near normal odorization in the vapor phase but the odorant will more readily condense out of the vapor phase with infrequent use (such as might be found in seasonal or rental properties).



FILE 143 RUN 1 STARTED 11:29.0 87/03/20 CPSC 0000 FADING  
 % METHOD 1 CPSC 0000 FADING LAST EDITED 11:27.1 87/03/20



FILE 143 RUN 1 STARTED 11:29.0 87/03/20 CPSC 0000 FADING  
 % METHOD 1 CPSC 0000 FADING LAST EDITED 11:27.1 87/03/20

RT	AREA	HEIGHT	RC	AREA PERCENT	HEIGHT PERCENT
0.18	6122624	6499.9175	T	39.2628	85.1866
0.24	1761916	435.5100	U	11.2493	5.7698
0.91	267264	12.9556	U	1.3383	0.1716
3.09	2340361	348.1306	U	15.2753	4.6122
4.89	2812965	299.6281	U	16.1582	3.0497
7.99	2202794	91.9010	U	14.2150	1.2175

FIGURE A - SAMPLE CHROMATOGRAM BY FPD

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### Calibration

Calibration standards were initially prepared for both ethyl mercaptan and diethyl disulfide in the vapor phase (nitrogen matrix). Numerous problems were encountered with the reproducibility of the diethyl disulfide (DEDS) in the vapor phase. The problems stemmed from the DEDS condensing onto the walls of the Tedlar® bags used in the study. The problem was initially resolved by gently warming the bag in an oven (50-60°C). Ultimately the standards for the two compounds were prepared separately, ethyl mercaptan in the gas bag (nitrogen matrix) and diethyl disulfide standards prepared in hexane.

Calibration data for the ethyl mercaptan after four weeks showed a relative standard deviation of approximately 5%. The average slope of the regression lines for the EM data was 232 (ng on column vs. square root of area) with a standard deviation of 10.5. The correlation coefficient for each curve was better than .997. Typical calibration data showed a detection limit of 2.25 ng at the 99% confidence level (1.55 at 95%) according to the Hubaux and Vos<sup>4</sup> calibration method, a very conservative method of determining acceptability of data. Presence of compounds can routinely be determined at levels below the indicated statistical detection limit value. This line indicated a slope of 236, a y-intercept of -4.0836 (y-value of 5937.8 at 25.17 ng EM) and a correlation coefficient of .9983 for forty-four (44) data points run over four days (range 1.26 ng - 25.2 ng). For three sets of diethyl disulfide standard curves prepared in gas bags over three days the regression line had a slope of 99 (ng on column [x] vs. square root of area [y]). A correlation coefficient of .998 and a y-intercept of 550. For a set of standards prepared in hexane, the results were very similar: slope = 110, y-int. = 285, c.c. = .998.

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<sup>4</sup>A. Hubaux and G. Vos, "Decision and Detection Limits for Linear Calibration Curves," Anal. Chem., 42 (8), 849-855 (1970).