

UNITED STATES GOVERNMENT
MEMORANDUM

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

JUL 11 1990

TO : The Commission

Through: Susan Birenbaum, Acting General Counsel
Through: Sadye E. Dunn, Secretary *Sadye E. Dunn*
Through: Thomas W. Murr, Jr., Acting Executive Director *Thomas W. Murr, Jr.*
Through: Douglas L. Noble, Director *Douglas L. Noble*
Office of Program Management and Budget (EXPB)

FROM : Jacqueline Elder, Project Manager
Household Structural Products Program, EXPB
James F. Hoebel, Program Manager *James F. Hoebel*
Household Structural Products Program, EXPB

SUBJECT: Final Contract Report on Long-Term LP-Gas Storage

The final report for the contract on "Long-Term LP-Gas Storage", prepared by MSA Research Corporation, has been completed and is available for review in the Office of the Secretary. An executive summary prepared by Donald Switzer, Directorate for Engineering Sciences, is attached. This report summarizes research conducted to define the effects of long-term storage on odorant concentration in liquefied petroleum (LP) gas containers. The information will be shared with the industry and other interested parties.

Attachment

NOTE: This document has not been reviewed or accepted by the Commission.

Initial rlu Date 7/11/90

CPSA 6 (b)(1) Cleared *7/12/90*

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CPSC Staff Executive Summary
MSA Research Corporation Report
LONG-TERM LP-GAS STORAGE
Contract CPSC-C-87-1256

Consumers involved in LP-gas accidents often assert that they did not smell the gas prior to the accident. Previous CPSC sponsored laboratory analysis indicated that the odorant, ethyl mercaptan (EtSH), added to LP-gas reacts or otherwise interacts with the inside surface of the storage container and appears to "fade". Industry asserts that this phenomenon is a problem only with new tanks. Over a period of time, EtSH reacts with all of the available surface area of the containers, causing used tanks to become "passivated". However, if air gets into the tank, the passivation may be lost. This contract examined the EtSH concentration in the vapor phase of LP-gas to determine the effects of long-term (9 month) residential storage. One unused and two used 500 gallon tanks were used.

EtSH concentration in the unused tank was 3.5 ppm at fill, but decreased to below the analytical detection limit in about four weeks. This EtSH concentration was below that recommended in the National Fuel Gas Code. However, we cannot say conclusively that the final odorant concentration was unsmellable, because most people can detect EtSH below the analytical detection limit.

The initial concentration in the used tanks was much higher, 6.5 and 10.0 ppm. During the test period, EtSH concentration in these used tanks varied with the temperature of the liquid LP-gas, measuring above 10.0 ppm at 90 degrees F and above 5.0 ppm at 10 degrees F.

A leak occurred in one of the used tanks during the project, after which the amount of gas in the tank slowly decreased and the EtSH concentration in the vapor phase increased. This observation supports the industry's field experience of increased vapor phase odorant concentration as tanks are emptied. Thus, little if any fade was observed in the used tanks. The odorant concentration did not fall below the level recommended in the National Fuel Gas Code. These results appear to support the contention that in-container fade is primarily an unused, not a used tank problem. However, if air enters a previously passivated used tank, the tank surfaces may again interact with the odorant.

The study recommends that a) the amount of odorant needed to passivate an unused container should be determined and b) the effects of "out of gas" occurrences on previously passivated containers should be investigated. Industry is currently investigating these steps.

CPSC staff believes that LP-gas added to previously unused tanks may not be adequately odorized. Some means should be developed to eliminate the loss of odorant in unused LP-gas containers.

MSAR 89-13
A-2180

FINAL REPORT

to

U.S. CONSUMER PRODUCT SAFETY COMMISSION
Directorate for Engineering Sciences, Room 760
5401 Westbard Avenue
Washington, D.C. 20207

on

LONG-TERM LP-GAS STORAGE

Contract No. CPSC-C-87-1256

12 October 1989

MSA RESEARCH CORPORATION
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P.O. Box 429
Pittsburgh, Pennsylvania 15230

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FINAL REPORT

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Directorate for Engineering Sciences, Room 760
5401 Westbard Avenue
Washington, D.C. 20207**

on

LONG-TERM LP-GAS STORAGE**Contract No. CPSC-C-87-1256****INTRODUCTION**

Maintaining proper odorant concentrations in LP-gas (vapor phase) is a major concern in the LPG industry. A CPSC study in 1982 indicated a higher number of accidents involving LP-gas fueled water heaters than would be expected based on the relative number of LP-gas versus natural gas installations. Odorant fade due to reaction with iron oxides in steel storage tanks is a known problem, the extent of which has not been characterized. If the odorant concentration of leaking gas falls below normal olefactory detection limits, serious safety concerns arise.

Although odorant fade in storage tanks is acknowledged by the LP-gas industry, it is believed to be a problem more specific to new tanks. Supposedly, tank surfaces become passivated with additional fillings to the point that odorant fade from typical fill concentration is no longer a problem with used storage tanks. CPSC, through a number of recent contracts, desired reliable documentation to characterize the occurrence and persistence of LP-gas odorant fade.

The objective of this work was to determine the effects of time and temperature on the concentration of ethyl mercaptan, the LP-gas odorant used almost universally in residential LP-gas. Information developed in this study will be shared with industry to assist them in improving odorants used in LP-gas. The ultimate goal is to improve the safe use and handling of LP-gas in the home.

MSAR conducted a program to determine the concentration of ethyl mercaptan, the odorant of choice in LP-gas, as a function of temperature and to characterize the odorant fade problem for ethyl mercaptan in commercial LP-gas containers as a function of long term storage and container materials. In both tests, the LP-gas was purchased from a local distributor and the ethyl mercaptan concentration was considered to be typical of commercial LP-gas.

The program, as outlined by the CPSC, consisted of the following:

- Using accepted laboratory procedures, characterize the concentration of ethyl mercaptan in the vapor phase of typical residential LP-gas as a function of temperature between -30°F and 120°F.
- Characterize the concentration of ethyl mercaptan in the vapor phase of commercially-available LP-gas containers as a function of time and container material - at ambient outdoor conditions - i.e. winter cold, hot summer sun. Other materials that will be identified during odorant concentration analysis are:
 - 1) LP-gas components.
 - 2) Degradation by-products of ethyl mercaptan.
- Design the studies so that the results provide answers to the following questions:
 - 1) What is the effect of temperature on the vapor phase odorant concentration?
 - 2) Given LP-gas properly odorized at reasonable ambient temperatures, will the vapor phase odorant concentrations fall below that specified in NFPA 58 at any temperature between -30 and 120°F?
 - 3) What is the relationship between odorant concentration and time after filling, as determined by chemical analysis over a 9-month period?

Two sets of experiments were conducted: 1) the ethyl mercaptan concentration/temperature relationship was studied using modified lab-scale storage containers; and 2) the ethyl mercaptan concentration/time relationship was studied using ASTM 500 gal LP-gas storage containers.

Duane V. Kniebes, formerly of the Institute of Gas Technology (IGT), was a consultant to the program, and was an invaluable source of information. Mr. Kniebes has over 35 years experience with IGT where he served as Assistant Vice President.

SUMMARY

The concentration of ethyl mercaptan in the vapor phase of a commercial supply of LP-gas was monitored for nine months in two used and one new 500 gallon tank exposed to western Pennsylvania ambient conditions. Concentration of ethyl mercaptan in the new tank was 3.5 ppm at fill, but fell below GC detectable limits (0.5 ppm) within 4 weeks. The concentrations in the used tanks started much higher (6.5 and 10 ppm) due to residual mercaptan from previous fills, and generally followed the temperature of the LP liquid phase, measuring above 10 ppm at the recorded high (90°F), and over 5 ppm at the lowest temperature (10°F) recorded.

A leak occurred in one of the used tanks about 5 months into the test, reducing volume from about 85% to 42% of fill. This apparently resulted in an almost continual increase of ethyl mercaptan in the vapor phase. An increase in ethyl mercaptan concentration similar to this would be expected during normal tank depletion.

In the separate temperature-controlled study, the concentration of ethyl mercaptan in the vapor phase of a commercial supply of LP-gas was monitored between the temperature limits of -30 to 120°F in stainless steel cylinders.

With the exception of the new tank, the ethyl mercaptan concentration at no time in either study fell below limits specified in NFPA 58.

EXPERIMENTAL

LONG-TERM STORAGE STUDIES

Description of Experimental Set-up

Agway Energy Products, Butler, PA supplied the three 500-gal tanks for the study -- one new and two used. The descriptions of the tanks were as follows:

<u>Tank Serial No.</u>	<u>Date of Manufacture</u>	<u>Condition as Delivered</u>
1466272	1987 (unused)	White painted exterior - pre-purged with LP gas.
218815	1976	White painted exterior - approximately 5% of fill.
154550	1972	Considerable rust on exterior - approximately 5% of fill.

Pre-purging of the new tank was not done according to NPGA recommendations, which are:

- Add 2 quarts of methanol (for 500 gal tank).
- Pressurize to 15 psig. - release.
- Repeat above step three more times.

The actual procedure followed was the addition of liquid propane, allow it to vaporize and bleed off. This step was repeated three times.

The tanks were placed in the open about 10 feet apart, oriented east to west (Figure 1). The three tanks were instrumented for monitoring the temperature of the liquid propane. Each of the three tanks was equipped with a thermocouple attached underneath on the shady side of the tank. The resultant installation was then covered with about 1 in. of sprayed urethane foam over an approximate 1 sq ft area (Figure 2). A fourth thermocouple monitored the ambient shade air temperature at the same location.

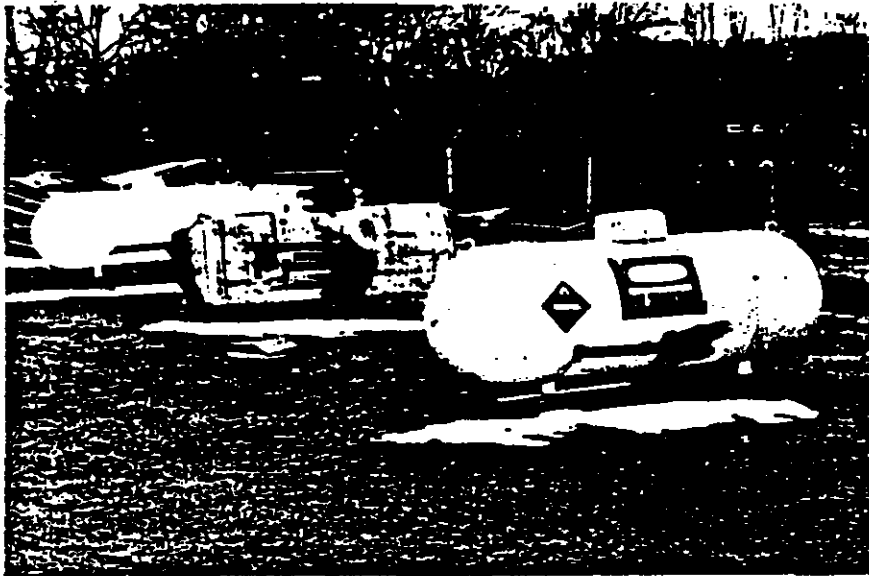


Figure 1 - Test Tanks

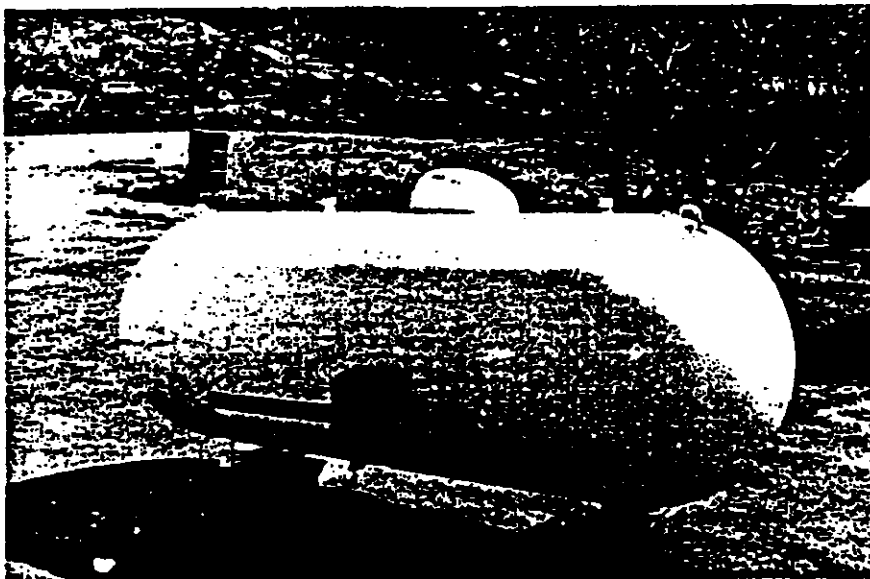


Figure 2 - Installation of Thermocouples

Data logging was done with a Molytec "Datalogger", reading the temperature every 2 seconds, and recording the temperature every 4 hours. A visual display allowed the technician to record the temperature at the time the sample was taken.

Experimental Procedures

Long term testing of the three 500-gal tanks was initiated on May 17, 1987. The tanks were charged by the vendor at 8:30 A.M. with approximately 400 gal of liquid propane. The temperature of the LP-gas in the tank truck was 73.4°F at the time of charging.

The LP-gas vapor samples were analyzed that afternoon and then for the next 39 weeks according to the following schedule:

<u>Week of Test</u>	<u>Sampling Frequency</u>
1 & 2	3 x per week
3	2 x per week
4	1 x per week
6 thru 12	once every 2 weeks
16 thru 39	once every 4 weeks

The initial ethyl mercaptan concentrations correlated with tank age, with the highest concentration (10 ppm) found in the oldest tank, about 6.5 ppm in the 1976 tank, and 3.5 ppm in the new, unused tank. It is unlikely that rapid odorant fade from 10 ppm to 3 ppm took place in the new tank on charging and aging over a period of several hours. The more likely explanation is that the higher concentrations in the aged tanks were the result of accumulated residual ethyl mercaptan from previous usage.

Sampling Procedure - The following tank sampling procedure was developed and followed consistently throughout the test period:

- Samples were taken from the vapor phase of the tanks in 250 ml glass tubes equipped with Teflon stopcocks, a syringe injection port and an "O" ring connector that mated to the propane valve outlet fitting (Figure 3). The tubes were previously cleaned by heating and purged with dry nitrogen.
- A 2 liter sample was purged through the tube at a measured rate of 1 liter/min. After the 2 liter purge, the tank valve was closed, and then the inlet

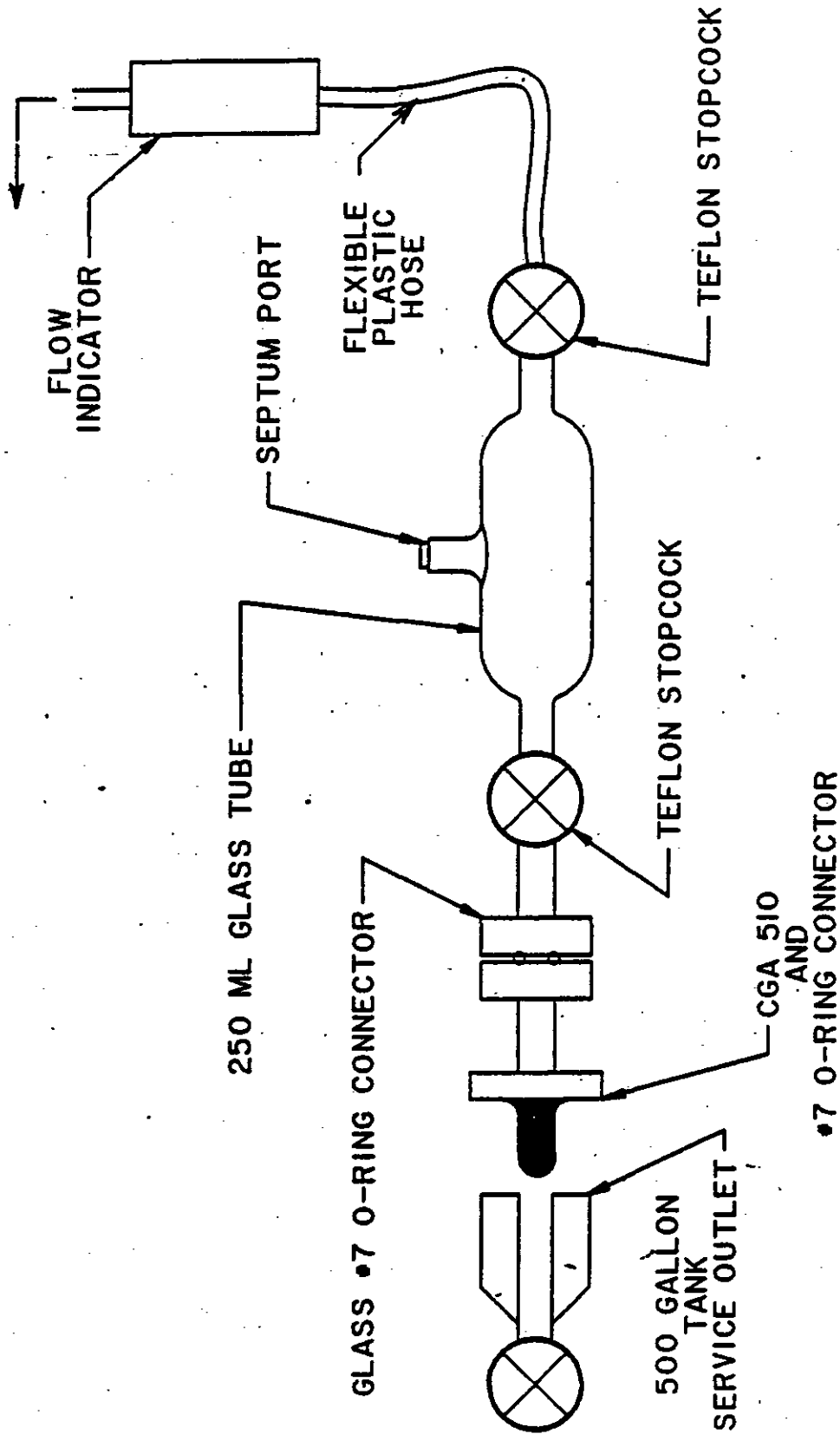


Figure 3 - Tank Sampling Apparatus

and the outlet stopcocks closed, in that order, leaving the sample in the tube essentially at atmospheric pressure. Consecutive 250 ml samples were withdrawn from a single tank, placed in a transport container maintained at 30°C, and returned to the lab without delay for GC analysis.

This procedure was repeated for each tank.

Standards were prepared and the GC calibration were done immediately before the tanks were sampled. Calibration standards were prepared to cover the range expected in the samples taken for the day, and generally consisted of ethyl mercaptan concentrations at 2.5, 5.0 and 10 ppm in propane.

Test Results and Discussion

Results and conditions of the long term tests are given in Table 1. The ethyl mercaptan concentrations recorded in the table show two values per sampling date. These values are the results of two separate samples per tank, and are the averages of at least two analysis per sample.

The tank temperature recordings show two additional values for the oldest tank (1972) starting in June. This tank had considerable rust on the top surface, and we became concerned that the ethyl mercaptan concentrations observed on hot sunny days appeared to be higher than we would expect for the bulk propane temperatures being recorded. Accordingly, we installed additional thermocouples to determine if a top-to-bottom temperature gradient was present in the liquid phase.

The additional thermocouples were installed against the metal of the tank; at positions 4 and 10 inches below the apparent level of the liquid (by feel), and well insulated from the environment with about a square foot of 1 inch thick sprayed polyurethane. The data from the three thermocouples on this tank are shown in the table as L-lower, M-middle, and T-top, and do show a significant differential, especially on sunny days when the top surface of the tank is rapidly heating.

In view of the data obtained for this tank that prompted our installation of the additional thermocouples, we believe that top-to-bottom temperature gradients are indeed present in the liquid propane on sunny days. We do not know, however, if the differentials indicated from our data on the insulated tank exterior are accurate for the liquid propane inside the tank. On the other hand, we don't believe that a

Table 1 - Tabulation of Long Term Storage Tank Data

Date	Time	Ambient Temp. (°F)	Tank Temp. (°F)			Ethyl Mercaptan ppm/vol					
			L	M	T	Tank 1987		Tank 1976		Tank 1972	
5-17-88	1245	64.3	64.3			3.48	3.49				
	1441	72.0	65.6					6.06	7.20		
	1330	73.0	67.5							9.60	10.99
5-18-88	1500	52.7	54.2			2.30	2.44				
	1620	53.7	53.0					4.90	4.80		
	1545	53.7	53.3							8.43	7.49
5-19-88	1135	60.8	55.1			2.35	2.36				
	1352	63.8	57.0					5.77	5.83		
	1245	61.1	55.8							7.14	7.53
5-20-88	1307	65.0	56.6			2.78	2.95				
	1442	63.2	58.5					6.88	6.81		
	1355	63.4	59.1							9.74	9.60
5-25-88	1309	49.1	47.3			2.63	2.56				
	1507	48.3	47.9					5.06	4.76		
	1359	49.4	49.1							6.51	6.91
5-26-88	1330	62.8	49.2			2.30	2.34				
	1522	65.6	55.5					7.28	7.10		
	1417	66.2	54.7							10.14	9.63
5-27-88	1257	73.9	58.7			2.28	2.12				
	1442	77.2	65.0					7.89	7.43		
	1350	75.5	64.6							10.36	9.64
6-01-88	1324	83.2	74.6			1.0	1.0				
	1517	83.9	78.8					7.9	7.8		
	1417	82.8	79.6	85.0	87.9					10.9	9.9
6-03-88	0954	47.3	49.8			0.7	0.7				
	1256	47.4	49.3					3.2	2.8		
	1107	48.9	50.8	50.9	51.2					5.8	5.4
6-09-88	1320	64.5	58.0			0.8	0.8				
	1439	65.8	60.4					8.0	7.7		
	1358	65.1	61.7	67.5	71.7					10.2	10.1
6-16-88	1337	73.4	68.5			<0.5	<0.5				
	1505	66.2	67.9					3.2	3.0		
	1417	66.1	70.3	69.4	71.4					8.2	7.3
6-23-88	1318	78.3	77.2			<0.5	<0.5				
	1453	79.8	80.0					9.4	8.9		
	1409	78.1	80.4	81.7	85.7					12.1	11.1

Table 1 - Tabulation of Long Term Storage Tank Data (continued)

Date	Time	Ambient Temp. (°F)	Tank Temp. (°F)			Ethyl Mercaptan ppm/vol					
			L	M	T	Tank 1987		Tank 1976		Tank 1972	
7-07-88	1316	94.5	78.8			<0.5	<0.5	10.3	10.0	12.2	11.6
	1429	96.7	85.0								
	1352	95.5	84.7	88.5	93.7						
7-21-88	1252	69.8	68.2			<0.5	<0.5	8.0	8.1	9.1	9.0
	1412	68.7	68.9								
	1332	69.0	68.7	70.2	71.6						
8-02-88	1309	95.1	84.9			<0.5	<0.5	8.8	8.8	10.5	10.1
	1420	98.4	89.4								
	1344	97.7	90.1	91.5	96.2						
8-31-88	1247	74.2	63.6			<0.5	<0.5	9.0	8.9	9.9	9.7
	1448	78.4	70.7								
	1348	76.7	70.5	71.9	77.1						
9-28-88	1319	73.0	61.8			<0.5	<0.5	6.0	6.0	9.0	8.7
	1042	66.9	55.4								
	1128	70.5	60.7	61.9	64.2						
10-26-88	1315	44.0	40.9			<0.5	<0.5	8.2	7.9	7.3	6.9
	1437	46.1	43.5								
	1355	45.1	44.5	46.8	49.2						
11-23-88	1317	45.2	34.7			<0.5	<0.5	8.7	8.8	7.5	7.4
	1435	45.0	37.0								
	1413	44.1	39.7	40.7	44.8						
12-12-88	1442	21.9	14.2			<0.5	<0.5	7.8	7.9	5.5	5.4
	1349	20.0	12.6								
	1303	18.4	10.4	17.1	21.2						
12-30-88	1323	32.4	18.7			<0.5	<0.5	9.7	9.2	6.3	6.4
	1429	33.6	21.7								
	1348	32.8	20.1	23.7	27.2						
1-26-89	1314	49.0	45.6			<0.5	<0.5	11.3	11.6	7.6	7.3
	1548	49.2	46.8								
	1408	49.1	45.9	46.6	47.0						

study to accurately measure the differential is indicated, since we do not foresee potential problems arising from the fact that such gradients occasionally occur.

Plots of the ethyl mercaptan concentration data for each of the three tanks as a function of weeks of storage, are given in Figures 4, 5 and 6. The corresponding tank temperatures are also plotted for comparison. General comments on the data are as follows:

- The ethyl mercaptan concentration in the new tank (1987) decreased to below detectable limits over a 4 week period. The ethyl mercaptan concentration started out at 3.5 ppm (64°F), slowly decreased, and, as the temperature went up, rapidly decreased in concentration to below detectable limits (<0.5 ppm). As one would expect, the rapid decreases occurred at periods of elevated temperatures, when reaction rates would be expected to increase.
- The concentration of ethyl mercaptan in the two older tanks essentially followed the temperature profile of the tank through the first 20 weeks (5 months) at which time an apparent anomaly became obvious. Whereas the concentration of ethyl mercaptan in the vapor phase of the 1972 tank followed the tank temperature as expected, the ethyl mercaptan concentration in the 1976 tank diverged from the temperature as it became colder, ending up as high as was recorded for the hot months.

The reason for the difference in tank behavior did not become clear until 34 weeks into the test, when it was noticed that the 1976 tank was leaking around the gauge gasket. The tank at that time was down to 43% of fill from the initial 85%. As a consequence, the ethyl mercaptan in the residual material would be expected to increase. The other two tanks were still at 82% and 83% of fill.

In looking at the plot of the data, the leak likely initiated during the first cold spell in early fall. Since the tank was the last in line, and generally downwind of the test technician, the leak was not noticed until it became visible on a rainy day.

Several additional points should be mentioned in regards to the tank storage data on the new tank.

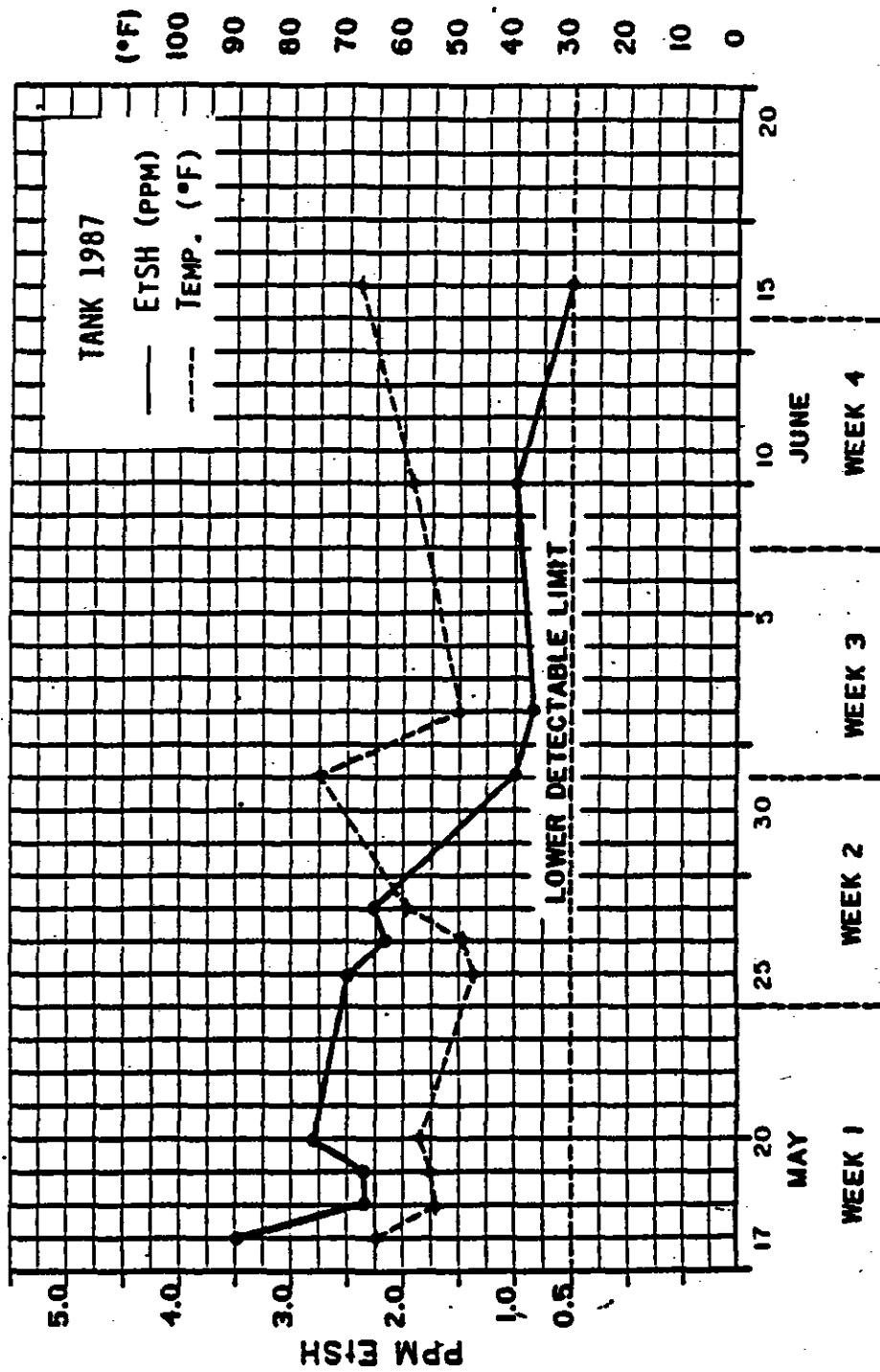


FIGURE 4 - TANK - 1987

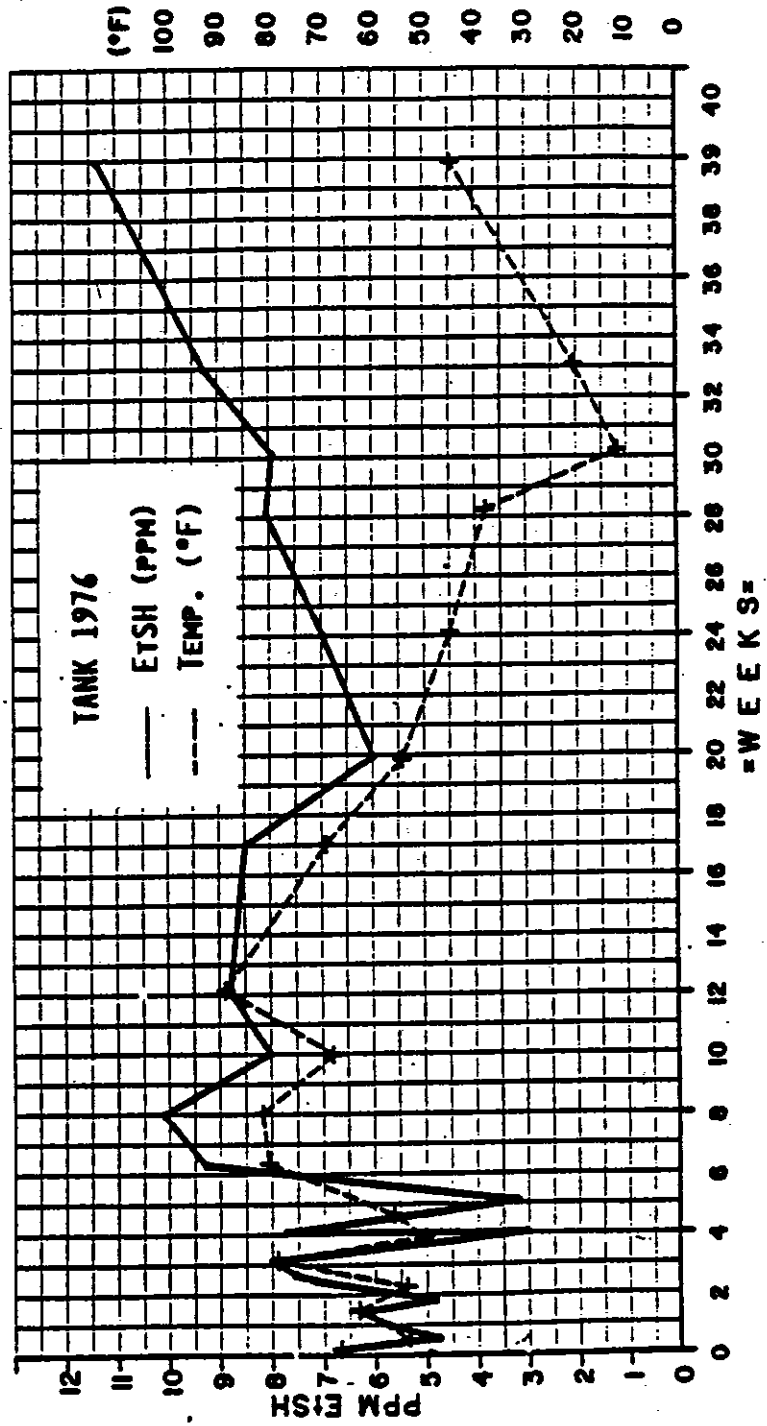


FIGURE 5 - TANK - 1976

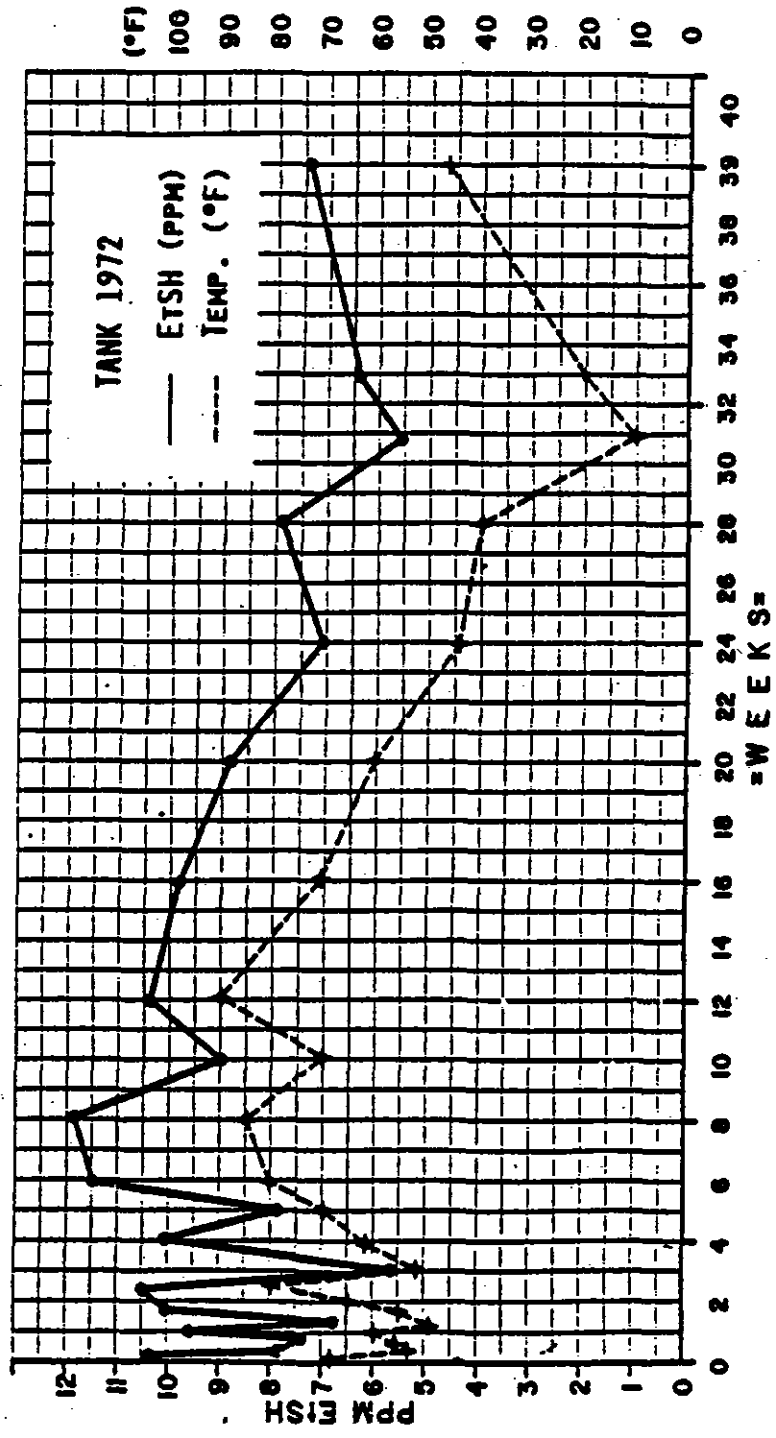


FIGURE 6 - TANK - 1972

- There was a significant amount of methyl mercaptan present in the odorant added to the propane which could, in part, be responsible for a faster-than-normal loss of ethyl mercaptan. Johnson⁽¹⁾ reported a synergistic effect on loss of odorant in pipeline materials for mixtures of methyl and ethyl mercaptan, such that the loss for a mixture was faster than for either alone.
- The practice of purging new tanks will contribute little to the passivation of the tank towards odorant fade. It has been the author's impression in discussions of our tests with several industry personnel that they believed that proper purging might have resulted in a much slower fade.

Purging of new tanks was introduced to rid the tanks of air and moisture to facilitate the fill and as a safety feature for the customer. Methanol is added to entrain moisture. The tank is then pressurized with propane to 15 psig and vented. This procedure is repeated four times over a period of several hours.

The above procedure will effect very little passivation. If one compares the amount of ethyl mercaptan present in the gaseous propane required for the total purging procedure (approx. 0.1 g @ 5 ppm conc.) with that present in a new 500 gal. tank filled to 85% with liquid propane (approx. 29 g @ 1.5 lb per 10,000 gal. loading) it is apparent that the ethyl mercaptan in the purging gas is a very small fraction (1/290) of that present in the filled tank. In our study, the ethyl mercaptan in the filled tank faded to below detectable levels in a four week span. And, we are still not certain that the tank is passivated. Our conclusion, therefore, is that the small quantity of ethyl mercaptan available in the purge propane could have but a very minor effect on the ultimate passivation of the tank.

EQUILIBRIUM STUDIES

The equilibrium studies were designed to measure the concentration ethyl mercaptan in the vapor phase of commercial LP-gas samples between the temperature limits of -30 to 120°F. The study was in effect, to duplicate and expand on a previous ethyl mercaptan/LP-gas

(1) Johnson, James L., "Stability of Odorant Compounds", Institute of Gas Technology, Chicago, Illinois, presented at 1965 A.G.A. Operating Section Production Conference.

concentration-versus-temperature study conducted by Whisman, et al.(2) The temperatures chosen for sampling were at approximately -30°F, 7.5°F, 45°F, 82.5°F and 120°F.

The test apparatus and procedure were similar to that employed by Whisman. The LP-gas samples were contained in two stainless steel cylinders equipped for ease in sampling the vapor phase above the liquid. The systems were static, that is, only samples for GC were withdrawn from the cylinders during the study. Sufficient liquid was charged to the cylinders to ensure that subsequent sampling would not significantly affect the ethyl mercaptan concentration in the liquid phase throughout the complete test period.

Description of Test Apparatus

The equilibrium samples were contained in two 3-liter stainless steel cylinders equipped with a Hoke ball valve (B) and a stainless steel sampling reservoir with volume of about 8 cm³ (Figure 7). The reservoir was equipped with a Hoke needle valve (A), and terminated with a high-pressure septum. Heat tape and insulation was used to hold this reservoir above the test temperature for the elevated temperature studies (a minimum of 130°F for 120°F test series) to avoid condensation of ethyl mercaptan in the sampling section.

Propane sample weight was about 1.75 pounds, occupying about one-half of the cylinder volume. At 120°F, system pressure was approximately 240 psi, or about .16 atmospheres, allowing for about 25 liters of equilibrated gas for sampling. At this pressure the SS sample reservoir holds about 130 cm³ of sample at STP, and thus, removed about 0.5% of the equilibrated gas volume. At the lower test temperatures, the pressure, and thus amount of sample removed was reduced accordingly.

Sampling Procedure

Considerable effort was taken to establish a sampling system/procedure that would give consistent data; and give data that we had faith in as being representative of the equilibrated vapor mix. Testing was initiated at 120°F in order to rapidly passivate the cylinders and sampling apparatus. System passivation and procedures were demonstrated over several weeks of testing, and is detailed here for the 120°F test series.

(2) Whisman, M.L. et al, "A New Look at Odorization Levels for Propane Gas," BERCI-77/T, Bartlesville Energy Research Center, Bartlesville, OK (1977).



Figure 7 - Equilibrium Test Cylinders

Initial attempts to sample a smaller stainless steel reservoir (ca. 1/cm³) met with wholly unsatisfactory and erratic results, both with the system at room temperature, and especially at 120°F. Success on both counts was finally achieved when we installed the larger stainless steel reservoir (approximately 8 cm³) shown in Figure 8, and incorporated a glass sampling tube into the procedure. The glass tubes were used in our 500 gal storage tank sampling procedure and had demonstrated ability to contain a stable tank mixture for an hour or more. They served as a check on the passivation of the stainless sampling reservoir. Once passivation was demonstrated, the glass tubes were eliminated from the procedure.

The sampling procedure employed for demonstrating system passivation, referring to Figure 8, was as follows:

- Evacuate glass sampling tube via glass vacuum system and manometer.
- Evacuate stainless steel sample reservoir through the glass sampling tube by connecting the two with a double-ended hypodermic needle penetrating the septums on the reservoir and sampling tube.
- Pressurize sample reservoir by closing valve A and opening valve B momentarily.
- Close off vacuum pump from system. Leave system open to mercury-manometer.
- Open valve A to expand pressurized reservoir sample into glass sample tube.
- Close valve A, repressurize reservoir, and expand into sample tube the second time. Allow system to bleed to atmospheric pressure through mercury bubbler.
- Sample reservoir and sampling tubes for GC through septums using 1 ml gastight syringe.

Verification of System Passivation

Verification of the sampling system passivation and sampling procedure was demonstrated by data for cylinder #1 (Table 2). Samples were taken over the first two days after the cylinders had been equilibrated at 123°F for one week.

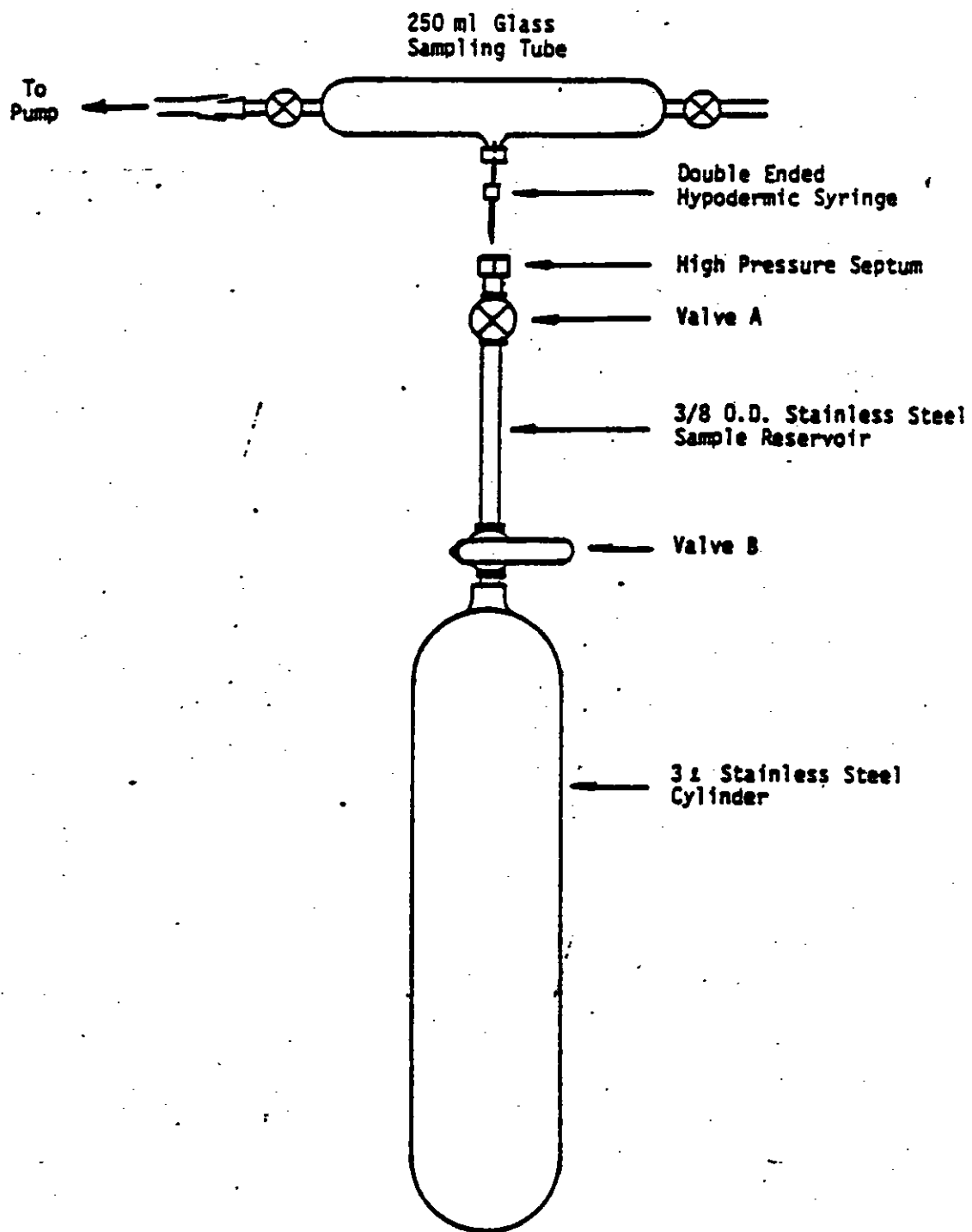


Figure 8 - Schematic of Apparatus for Equilibrium Study with Glass Sampling Tube

Table 2 - GC Analyses Data for Cylinder #1 as
Function of Exposure to Ethyl Mercaptan

<u>Day #1</u>	<u>Sample Number</u>	<u>Time</u>	<u>Area Units - GC</u>	
			<u>SS Reservoir</u>	<u>Glass Sample Tube</u>
	1	11:10	28,529	55,533
	2	11:25	104,280	180,860
	3	11:44	360,460	188,578
	4	13:28 14:14	80,094(1) 0,000(2)	222,860
	5	14:31 14:44	451,880(1) 162,590(2)	314,100
	6*	15:26 15:34	618,600(1) 486,980(2)	584,720
	7	15:48 15:55	520,470	506,150 523,250
<u>Day #2</u>	1	9:34	500,350	496,710
	2	9:53	608,020	513,510
	3	10:20	555,130	556,420
	4	13:48	555,560	-
	5	15:31	543,120	-

*System sampled for GC under pressure.

A measure of faith in the values as being representative of the vapor mix in the cylinders was attained by the rapid achievement of a constant value on Day #2, as represented by data for Samples 3, 4 and 5, and verification of the SS reservoir sample analyses by analyses from the glass sample tube. The average of data such as this (Samples 3, 4 and 5) for Day #2 was considered one point for the equilibrium value at 123°F if it was verified by a second set of similar data for the next day (or next sampling period). The equilibrium value reported for any one temperature, therefore, was the average of at least 6 such individual analyses taken over a 2 day period. This data, converted to ppm, are shown graphically in Figure 9.

The data also demonstrate that although stainless steel is considered to be a suitable container for sampling and/or studying mercaptan-propane mixtures, the early samples in the SS reservoir held at about 130°F show rapid reaction with the mercaptan. The GC value for the initial sample was only 28,529 units (1.5 ppm), but rapidly increased to 360,460 units (6.5 ppm) with the 3rd sampling. The speed at which the loss of mercaptan was occurring in the sampling reservoir is evident in Samples 4, 5 and 6 of Day #1, which show large decreases in mercaptan in the SS reservoir over periods of 46, 13 and 8 minutes, respectively. This mercaptan fade is depicted by the broken lines in Figure 9.

The degree of passivation was apparent with each successive sample. First, the values increased; secondly, the values in the SS reservoir and glass sampling tube began to come together. This observation culminated with those values for Day #2 in which the two samples were essentially identical.

Test Results and Discussion

Test data for the equilibrium study are shown in Table 3. These data show breaks in continuity for cylinder #1 at 45°F, which represents problems with a leak in the test cylinder valving. A similar leak in the #2 cylinder occurred at -30°F, necessitating a change in valving for both cylinders, a refill, and a repeat of limited data for a second commercial charge.

A summary of the ethyl mercaptan/temperature data is shown in Table 4. The table shows the data as a function of the ethyl mercaptan concentration in the commercial propane as charged, although the 30 ppm value shown for the initial charge represents only a preliminary analysis.

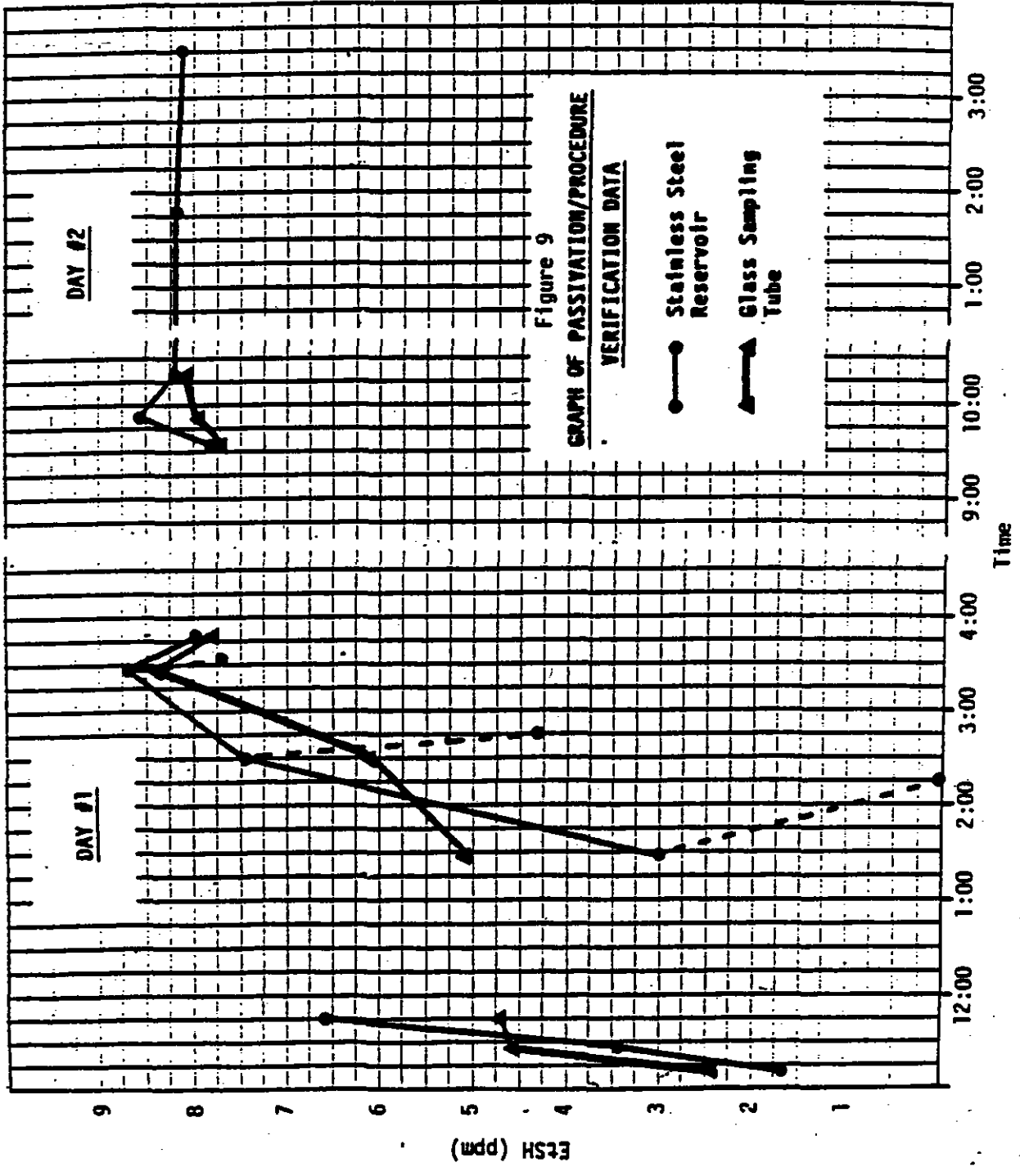


Figure 9

GRAPH OF PASSIVATION/PROCEDURE

VERIFICATION DATA

- Stainless Steel Reservoir
- Glass Sampling Tube

Table 3 - Equilibrium Test Data

<u>Test Date</u>	<u>Sample No.</u>	<u>Bath Temp.</u>	<u>Vapor Phase Conc'n (ppm EtSH)</u>	
			<u>Cyl. #1</u>	<u>Cyl. #2</u>
<u>122°F</u>				
Jan. 5	1	123	7.6	7.6
	2	122	7.6	8.0
	3	122	8.1	8.1
	4	122	8.3	8.3
Jan. 6	1	121	8.4	8.2
	2	122	8.3	8.2
	3	121	8.3	8.2
<u>83°F</u>				
Jan. 11	1	83	6.4	6.5
	2	83	6.8	6.4
	3	83	6.6	6.3
Jan. 12	1	83	6.1	6.2
	2	83	6.5	6.1
	3	83	6.4	6.2
	4	83	6.3	
<u>45°F</u>				
Jan. 27	1	45		4.7
	2	45		4.3
	3	45		4.6
	4	45		4.7
	5	45		4.5
Jan. 30	1	44		4.3
	2	44		4.2
	3	44		4.8
	4	44		4.5
Jan. 31	1	46		4.2
	2	45		4.5
	3	45		4.4
	4	45		4.3

Table 3 - Equilibrium Test Data (continued)

<u>Test Date</u>	<u>Sample No.</u>	<u>Bath Temp.</u>	<u>Vapor Phase Conc'n (ppm EtSH)</u>	
			<u>Cyl. #1</u>	<u>Cyl. #2</u>
<u>7.5°F</u>				
Feb. 2	1	7		3.4
	2	7		3.0
	3	7		3.1
	4	7		3.2
	5	7		3.2
	6	7		3.1
Feb. 3	1	8		3.2
	2	7		3.0
	3	7		2.7
	4	7		2.9
	5	7		2.7
Feb. 6	1	8		3.1
	2	8		3.1
	3	8		3.1
	4	8		3.2
	5	8		3.1
<u>-30°F</u>				
Feb. 24	1	-30		1.3
	2	-30		1.3
Feb. 27	1	-31	1.3	1.2
	2	-31	1.2	1.1
Feb. 28	1	-28.5	1.4	1.4
	2	-30	1.1	1.2
	3	-30	1.0	1.3
Mar. 1	1	-30	1.7	1.3
	2	-30	1.5	1.1
	3	-32	1.4	1.2
Mar. 2	1	-32	1.5	1.3
	2	-32	1.5	1.2

Table 4 - Summary of Equilibrium Test Data

Temp. (°F)	Conc'n of EtSH in Liquid Phase of LP-gas Supplied (ppm)	Conc'n of EtSH in Vapor (ppm)		Conc'n of EtSH* at 0.43% Propane (ppb)
		Cyl. #1	Cyl. #2	
122	30	8.08 ±0.34	8.08 ±0.23	35
83	30	6.44 ±0.22	6.28 ±0.15	27
63*	26.5	4.7	4.9	21
60	26.5			
45	30	---	4.46 ±0.20	19
7.5	30	---	3.07 ±0.18	13
-30	26.5	1.36 ±0.21	1.24 ±0.09	5.6

*Based on average values for cylinders 1 and 2, where available.

Table 4 also shows the calculated values for ethyl mercaptan in the commercial LP-gas samples at one-fifth the lower explosive limit in air ($2.15\% \times 0.2 = 0.43\%$). At all temperatures, they well exceeded 1 ppb, considered to be detectable(2), and even at -30°F exceeded it by a factor of five.

ANALYTICAL

Analyses were conducted on a Varian Model 3300 gas chromatograph equipped with a J&W GS-Q 30 meter x 0.53 mm I.D. capillary column. This column demonstrated sufficient resolution to separate propane and ethyl mercaptan and a sensitivity to less than 0.5 ppm with a 1 cc syringe-injected sample.

The flame photometric detector response to sulfur was a square root function of the electrometer output. Propane was found to have a quenching effect on the output, so all working standards were prepared in odorant-free propane. Since we were using an integrator, the response was measured as the area of the ethyl mercaptan chromatographic peak. The square root response becomes non-linear as the amount of ethyl mercaptan seen by the detector increases.

Calibration and analysis over the expected concentration range (<1 - >15 ppm by volume in the vapor phase) was accomplished by adjusting the sample size so that the amount of ethyl mercaptan seen by the detector was within the linear range. Thus, a 1 cc sample was used for both the standards and samples for low vapor concentrations (0.5 to 5 ppm) and a 0.5 cc sample size was used for higher values. The following chromatographic conditions were used for the analyses:

Gas Chromatograph: Varian 3300 with dual flame photometric detector in the sulfur mode.

Column: J&W Scientific GS-Q fused silica 30 meter x 0.53 mm I.D.

Conditions:

Nitrogen Carrier Gas	10 cc/min
Nitrogen Make-up Gas	20 cc/min
Hydrogen	240 cc/min
Air #1	80 cc/min
Air #2	170 cc/min
Column Temperature	140°C
Detector Temperature	200°C

Injection Port: Teflon insert 1/8" O.D.

Sample: Gas tight syringe, 1 cc or 0.5 cc vapor injected into injection port.

Calibration standards were made up in glass containers equipped with a septum and several pieces of Teflon to facilitate mixing. Standards were prepared from freshly prepared stock solution by injecting a measured amount of stock mix into a propane matrix using glass-Teflon, gas-tight syringes. The concentrated stock mix was prepared by injecting liquid ethyl mercaptan in a known volume of nitrogen. As with the sampling tubes, all standards were mixed and maintained at 30°C.

Figure 10 shows a calibration curve for ethyl mercaptan in propane using a 1 cc sample injection. Figure 11 shows chromatograms of duplicate samples taken from the new (1987) and a used (1972) tank during the second week of testing. The ethyl mercaptan peaks, at 2.62 were calculated to be concentrations of 2.2 and 10.0 ppm, respectively. Note also the strong peaks for methyl mercaptan in the 1972 tank samples at 1.41, which are not in evidence in the new tank samples shown. A peak for methyl mercaptan, however, was present in chromatograms of the LP-gas, as supplied, but disappeared over the first two weeks. This is not surprising, in view of work by Johnson⁽¹⁾, that showed methyl mercaptan to fade even faster than ethyl mercaptan when exposed to pipe-line materials..

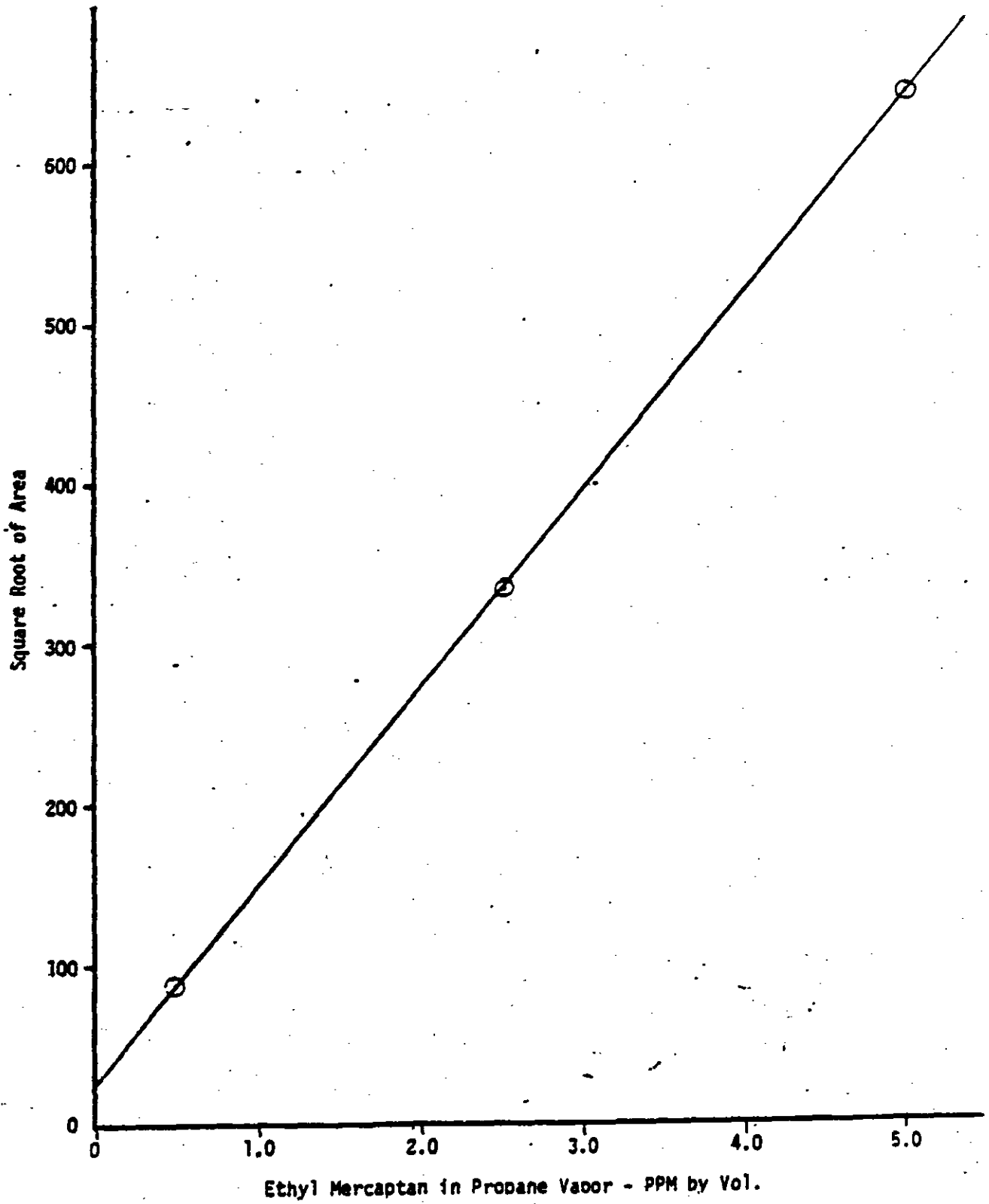
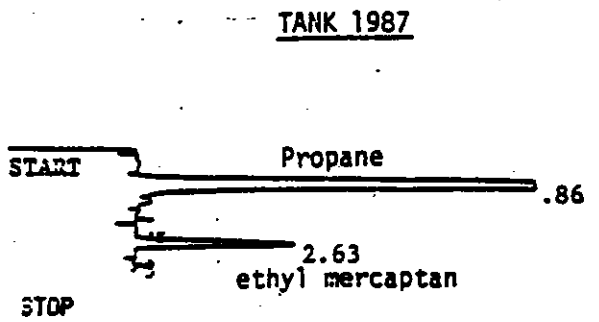
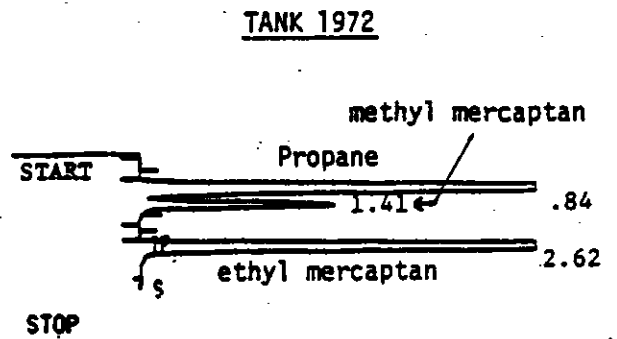


Figure 10 - Calibration Curve



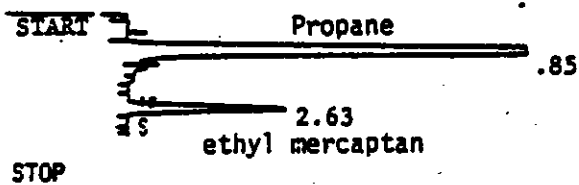
RUN # 198 MAY/27/88 13:27:01

AREA#	RT	AREA	TYPE	AR/HT	AREA%
	0.86	230300	VV	0.188	89.939
	2.63	25763	SPB	0.166	10.061



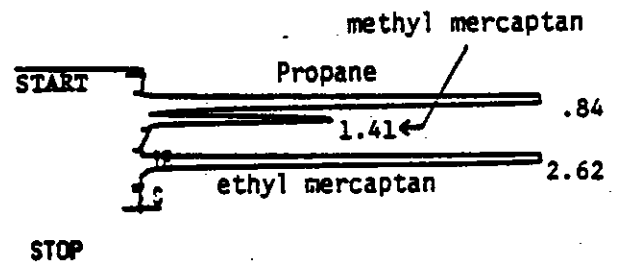
RUN # 202 MAY/27/88 14:13:35

AREA#	RT	AREA	TYPE	AR/HT	AREA%
	0.84	245360	PV	0.186	33.699
	1.41	35312	VB	0.189	4.850
	2.62	447420	SPB	0.166	61.451



RUN # 199 MAY/27/88 13:31:36

AREA#	RT	AREA	TYPE	AR/HT	AREA%
	0.85	226990	PB	0.186	90.046
	2.63	25072	SPB	0.164	9.954



RUN # 203 MAY/27/88 14:18:56

AREA#	RT	AREA	TYPE	AR/HT	AREA%
	0.84	247130	PV	0.186	34.923
	1.41	36195	VV	0.195	5.132
	2.62	422820	SPB	0.172	59.945

Figure 11 - Chromatograms of Tank Samples

RECOMMENDATIONS

Several recommendations became apparent as a result of the long term storage study:

- The study should be repeated in the new tank to determine the number of refills required to produce a completely passivated tank. The ethyl mercaptan concentration in the vapor phase of the new tank fell below detectable levels (<0.5 ppm) in only four weeks, and may indeed have completely reacted over the life of the program. Is the tank passivated, or are there still sites available to react with EtSH in subsequent refills?
- The study on the two old tanks should be repeated following an apparent "gas out" situation. The two old tanks are apparently passivated. There are instances in which air can possibly reenter the tank, such as a valve change out, or when a consumer runs completely out of gas. If these conditions persist, the tank can breathe, allowing air to reenter the tank. Will this reactivate sites, and if so, to what extent?