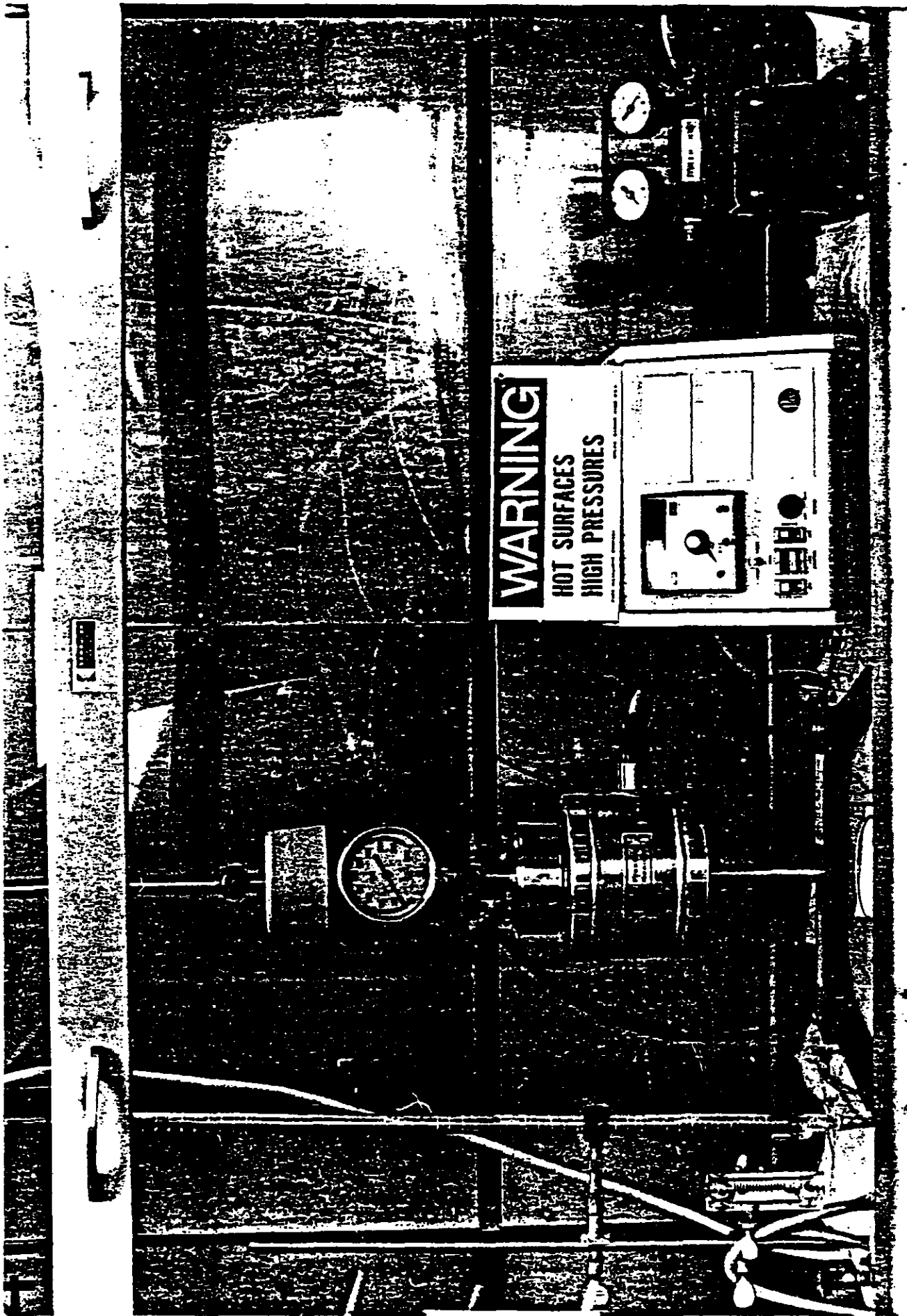


APPENDIX B

Experimental

The pressure reaction vessel (reactor) used to conduct the experiments indicated in this report is a stainless steel (T316 SS) 300 mL Parr® mini reactor, Figure B-1. The reactor is designed to perform reactions at pressures up to 2000 psig. The reactor itself, is equipped with a gas inlet valve, a liquid sample valve (both connected to a single dip tube which reaches to the bottom of the reactor), a gas sample (release) valve, an impeller type mechanical stirrer and a thermocouple. A controller, supplied with the reactor, operates the stirrer and regulates the reactor temperature allowing a continuous digital readout via the thermocouple. Prior to filling, the glass capillary tube filled with ethyl mercaptan is placed in the reactor, the reactor sealed, and a tare (empty) weight obtained. To fill the reactor with the liquified propane (LP), the gas inlet valve is opened fully and the gas release valve opened slightly, allowing the liquid to displace and purge the head space until the liquid itself is vented. The gas release valve is then closed followed by the gas inlet valve, effectively sealing the reactor. After reweighing the reactor, the LP is vented until just 100 g of LP (185 mL liquid) remained. Just prior to breaking the capillary tube, a sample of the liquid phase is taken to confirm the absence of interferences. Once confirmed the capillary tube is broken and the contents mixed using the mechanical stirrer, as the reactor is warmed. When equilibrated to 20°C, a sample of the liquid is vented into a two liter Tedlar® gas bag (representing 8 mL of liquid phase). Triplicate analyses were performed on each sample.

* Note: The author apologizes for any confusion resulting from the abbreviation of liquified propane [LP] vs. liquified petroleum gas [LPG] vs. the term "liquid phase", but these abbreviations appeared to offer the best options for clarity through the text.



WARNING
HOT SURFACES
HIGH PRESSURES

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ODORANT DEPLETION IN PORTABLE CYLINDERS

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ABSTRACT

Several research activities are underway in Canada under the sponsorship of the Propane Gas Association of Canada (PGAC) Residue and Odorant Committee. This group, with advisory representation by government agencies, was formed and actively supported by Marketer, Producer and Manufacturer members. This paper gives an overview of these activities, and describes in detail one of them, the research carried out on the depletion of ethyl mercaptan in small cylinders at the Esso Petroleum Canada Research Centre in Sarnia, Ontario.

The concentration of ethyl mercaptan and related sulfur compounds has been monitored in a variety of small steel propane cylinders ranging in size from 1 lb (disposable) to 100 lb (refillable) containers. The majority of the work was carried out with 20 lb barbecue cylinders made by different manufacturing methods and having different internal surface conditions. Evidence of ethyl mercaptan odorant depletion (fade) was found in several containers. Surface analysis of the metal interiors, and results on chemically cleaned or aluminum vessels suggests that the mechanism is dependent on the nature of the initial oxide layer. Incorporation of sulfur into or onto the oxide layer, and the appearance of sulfur compounds other than the primary oxidation product (diethyl disulfide) in the liquid phase indicates that the mechanism is not a simple oxidation.

ODORANT DEPLETION IN PORTABLE CYLINDERS

BACKGROUND

The nature of the Canadian propane business is similar to that of the USA, with major producers selling in bulk quantities to independent distributors and marketers. The major producers have limited contact with distributors, propane equipment manufacturers and end users, but as in the USA, are exposed to liability along with the latter.

In late 1984, several Canadian industry companies began to investigate various propane odorant and contamination issues as a result of litigation and user problems. Concern was expressed for the possibility of odorant depletion in small cylinders because of the rapidly increasing consumer use of propane in Canada and the large number of cylinders being manufactured and sold. There was renewed interest in the composition and source of solid and liquid contaminants sometimes found in portable propane containers and fixed and vehicle propane systems. Some of these deposits from vehicle tanks, filters, regulators and carburettors were identified as mixed iron oxide/sulfide (magnetic black powder), and elemental sulfur.

Of particular concern was the possibility that the phenomenon of odorant depletion was related to black deposit and elemental sulfur formation. Little was known about the reactions of ethyl mercaptan in liquid propane systems. However, studies on sampling and analysis of reactive sulfur compounds, and work on odorants in natural gas systems, suggested that similar reactions might occur, especially in small, high surface to volume ratio cylinders. In addition, differences in reaction mechanisms might be expected between natural gas (continuous flow) systems and propane (batch) systems. In particular, the occasional presence of higher and lower molecular weight sulfur species in the liquid, elemental sulfur deposits and formation of iron sulfide are difficult to explain.

It was apparent that resolution of these issues would require the combined efforts of producers, tank manufacturers, users and government regulatory bodies. A new working committee, the Propane Residue and Odorant Task Force, was formed under the direction of the PGAC, and has met regularly since mid-1985. This group has considerable representation by government agencies as a result of policies to encourage development of alternate fuels for the purpose of Canadian Energy self-sufficiency.

Several task force members have liaison functions with the related consensus standard and regulatory bodies that have responsibilities in other areas of propane production and use. These are outlined as follows:

- CGSB - Canadian General Standards Board
 - function similar to ASTM and/or GPA
 - publishes the CAN/CGSB-3.14 propane specification
- CGA - Canadian Gas Association
 - function similar to the NFPA
 - Publishes the CAN/CGA-B149.2 Propane Installation Code
- CSA - Canadian Standards Association
 - Publishes the CAN/CSA-B340 and related cylinder code
- OME - Ontario Ministry of Energy
 - Sponsor of the "Drive Propane" program
 - Supported conversion of cars to propane power with rebates toward conversion costs and elimination of road tax on propane fuel
- OMCCR - Ont. Ministry of Consumer and Corporate Relations
 - overseer of the Ontario Fuels Safety Branch
 - mandate for enforcement, public safety and education etc. Other provincial Gas Safety Branches are also active through CGA, CSA and CGSB committees, but Ontario, with the largest penetration of propane vehicles and programs has maintained active and direct involvement
- DND - Department of National Defence
 - combined Canadian Military Forces
 - maintains one of the largest fleets of propane powered vehicles at military bases accross Canada (3000 propane cars/trucks of a total of about 150,000 vehicles)
- EM&R - Energy, Mines and Resources Canada
 - Similar to the US Department of Energy
 - Supports a variety of government, industry and university research and demonstration programs in the areas of alternate fuels, off-oil initiatives, energy conservation etc.
 - Supported applied engine research through Chrysler Canada Engineering.

Other PGAC R&O task force members maintain an active monitoring role with ASTM and NLPGA.

As in the USA, accredited consensus standards may be recognized in various provincial and federal Acts and regulations, and become legal requirements. Government regulatory representatives maintain active involvement with the various consensus standard committees.

In addition to providing a forum for open exchange of information obtained by individual member initiatives, the PGAC R&O Task Force has sponsored and funded several research projects which are outlined as follows:

- 1) Survey of members for list of outstanding issues that should be addressed:
 - liquid residues ("skunk oil")
 - contaminants from manufacture and distribution
 - possible need for tighter contamination specs
 - "black deposit" in vehicle propane systems
 - odorant fade
 - possible need for alternate odorant systems.
- 2) Sampling and analysis of typical deposits found in the distribution system (contractor: Petro-Canada Research).
- 3) Collection and analysis of black deposit from a propane truck fitted with special filtration. (Project failed with loss of vehicle).
- 4) Test of 17 x 20 lb barbecue tanks for odorant fade (contractor: Esso Petroleum Canada Research).
- 5) Test of 13 new 1 lb disposable and 2 aluminum 33 lb tanks for odorant fade (joint study by ICG Liquid Gas Ltd. and Esso Petroleum Canada Research).
- 6) Metallurgical study of the nature of the oxide (millscale) layer in new and used 20 lb steel barbecue cylinders (study by Esso Resources Canada Research).
- 7) Test of 16 x 20 lb barbecue tanks with special heat treating and surface preparation for odorant fade (contractor: Esso Petroleum Canada Research).
- 8) 12 car fleet test to collect and analyze black deposit collected with special filtration, as well as any unusual deposits or residues that may be found over a period of 1-2 years. Iron oxidation state will be monitored by Mossbauer spectroscopy by the University of Manitoba. It is anticipated that a separate university research project will study the crystallographic nature of the black deposits that are collected. (Startup August 1987 - contractors: University of Manitoba, T. Eaton consultant and Government of Canada, Department of National Defence).
- 9) Development and testing of a field method for mercaptan odorants using the Gastec stain tubes and measurement method and the "baggie" method of collecting field propane samples. (Joint study with the CGSB Test Methods Committee - see Appendix I).

INTRODUCTION

The research that has been carried out at the Esso Research Centre in Sarnia has been in four phases which are described as follows:

Phase 1

The test of four 20 lb barbecue cylinders from each of two manufacturers along with a teflon-lined control cylinder. This experiment was conducted to document in a scientifically rigorous manner the phenomenon of odorant fade. Nine 20 lb barbecue containers were filled from a common source of commercially available HD-5 propane. Each cylinder was filled in the prescribed manner with five vapour purges. The contents were analysed by sulfur-specific gas chromatography to monitor the concentration of ethyl mercaptan and other low molecular weight sulfur species. The purpose of this test was to screen a number of cylinders for the occurrence of odorant fade. This test had the surprising result that all four cylinders from one manufacturer ('A') were stable towards ethyl mercaptan, while all four containers from the second manufacturer ('B') exhibited rapid and complete fade.

This initial result was so dramatic that it led to an immediate investigation of possible causes, and further tests of the same manufacturers' cylinders under a variety of conditions.

Phase 2

This phase involved the random testing of 13 one pound disposable propane containers (hand-held torch type) and two 33 lb aluminum cylinders (fork lifts) for ethyl mercaptan fade. This test showed that odorant fade had occurred in the majority of the one pound containers, and that the aluminum containers were virtually immune to odorant fade.

This led to the investigation of the nature of the steel surface layers as a possible explanation for odorant fade in some but not all small steel cylinders.

Phase 3

This phase involved the study of manufacturing methods utilized by various Canadian cylinder manufacturers, and the detailed surface analysis of the steel from new and used cylinders representative of the different types of manufacture. Cylinders from manufacturer 'A' were heat treated in an induction furnace which resulted in a very short exposure time to high temperatures in an oxidising environment. Cylinders from manufacturer 'B' were furnace heat treated, the more common heat treating method. It should be noted that this test was not meant as a "test" of alternate manufacturing methods.

It should also be noted that the 20 lb cylinders were selected for testing because they are an ideal model system, easily handled, and with a high surface to volume ratio to test the most extreme environment for surface catalysis, reaction or adsorption.

The surface analysis of the 20 lb cylinders showed striking differences depending on the method of heat treating, and led to a final phase of testing. This final test included interchanging cylinders from each manufacturer just before the heat treating step.

Phase 4

The final phase of testing included interchanging cylinders from each manufacturer just before the heat treating step, washing cylinders with inhibited acid, and superpurging the cylinders with propane vapour containing 1000 wppm ethyl mercaptan.

RESULTS AND DISCUSSION

Phase 1

Odorant Fade. The results from the first phase of the testing, which was intended primarily to be a scientifically rigorous demonstration of the phenomenon of odorant fade, are given in Table 1. These results clearly show that the four cylinders from manufacturer 'A' are resistant to odorant fade, while those from manufacturer 'B' rapidly show evidence of depletion, with no detectable ethyl mercaptan remaining in the liquid phase after only a few days.

Multi-filling. It was felt that these 'B' cylinders would eventually become passivated, and thus stabilized towards odorant fade. These four cylinders were therefore vented (liquid draw) and refilled. The results of four completed cycles of this refilling process are shown in Figure 1 for one of the four cylinders. Surprisingly, the cylinder appeared to stabilize during the second cycle, but in the third cycle, the ethyl mercaptan level again fell to zero. In the fourth cycle, the cylinder again appears to have been passivated. These results indicate that the mechanism of odorant fade is indeed complex.

Mechanism. The complexity of the mechanism is illustrated in the next 3 figures (Figures 2 - 4). Figure 2 is a G.C. trace of a newly-filled cylinder. Note the three peaks for LPG, methyl mercaptan (MeSH) and ethyl mercaptan (EtSH). (MeSH is often present in LPG from gas fields).

Figure 3 shows the G.C. trace some time later. Note the additional peaks for dimethyl disulfide (DMDS), diethyl disulfide (DEDS) and a higher molecular weight sulfur compound, believed to be diethyl trisulfide. Surprisingly, methyl ethyl disulfide is absent.

Figure 4 shows a similar G.C. trace, but with direct liquid injection into the G.C. in an attempt to pick up higher-boiling sulfur compounds which are believed to be involved in the mechanism. Note that three additional

sulfur peaks are indeed evident.

Further work on the mechanism of the fading of ethyl mercaptan, including the addition of oxygen and water to the system, has been started, and will be the subject of a separate report.

Phase 2

The results from the second phase of the program, the study of other cylinders, will now be discussed.

One Pound Cylinders. Table 2 highlights the results from a random sampling of one pound disposable cylinders. Note that in the majority of the samples, significant fading has occurred. (The "normal" treat level for ethyl mercaptan in LPG of 1 lb per 10000 USG is equivalent to 24 wppm).

Aluminum Cylinders. Two 33 lb fork-lift type aluminum cylinders were subjected to 4 x one monthly cycles of fade testing. The results are graphically illustrated in Figure 5 for one of the cylinders. Although there is some scatter in the data, the ethyl mercaptan appears to be stable in this system. This is borne out by the absence of diethyl disulfide in the G.C. traces.

Phase 3

The third phase of the test program consisted of a study of the different methods of manufacture used to make 'A' and 'B' cylinders, and a detailed metallurgical analysis of the interior surfaces of new and used cylinders from each manufacturer.

This study showed that manufacturer 'A' heat treated the cylinders in an induction furnace. X-ray analysis of the interior surface showed a continuous film of wustite (FeO). This presumably is produced as a result of the relatively short exposure time to the oxidising environment. Manufacturer 'B' used a conventional furnace for the heat treating process, resulting in an irregular surface of Fe_2O_3/Fe_3O_4 as revealed by the X-ray analysis. This is consistent with a longer exposure time allowing more oxidation to occur.

The X-ray technique revealed the further interesting fact that sulfur (elemental, sulfide, or sulfate - exact state not known) had been incorporated into the surface layer of used cylinders which had exhibited fade.

Phase 4

Inhibited Acid Wash. Since the interior surfaces of stable cylinders 'A' and 'B' were substantially different, one cylinder of each type was chemically washed with a solution

of inhibited hydrochloric acid. Each cylinder was then subjected to a fade test as before. The results are shown in Figures 6 and 7. Both cylinders are very similar after the acid wash, in that both rapidly lose about one-half of the ethyl mercaptan present initially, and then stabilize. These cylinders will be refilled and monitored for further evidence of odorant fade.

Heat Treatment Process. The significance of the heat treatment process in the fade phenomenon was demonstrated by interchanging cylinders from each manufacturer. Cylinders were removed from each production line just prior to the heat treating step, rapidly transferred to the other manufacturer, and the manufacturing process completed from the heat treatment step to the end of the production line in the normal way.

Two cylinders from each modified batch were tested for ethyl mercaptan stability in the usual way. The results are illustrated in Figure 8. The cylinders finished by manufacturer 'A' using the induction furnace were almost as stable to mercaptan fade as the regular production cylinders from that plant. Cylinders finished at manufacturer 'B', while not as prone to odorant fade as before, still showed evidence of severe fade, one of the two cylinders being much worse than the other.

Superpurging. Some earlier work had indicated that cylinders could be passivated by "superpurging"; i.e., using propane vapour highly enriched with ethyl mercaptan (1000 wppm) rather than normal propane vapour (5 wppm) as specified by the code.

Two cylinders from manufacturer 'B' were superpurged five times and compared to a similarly treated 'A' cylinder. The results are shown graphically in Figures 9 and 10. Figure 9 shows that the superpurge technique initially adds about 20 wppm ethyl mercaptan to the LPG. Not much change occurs during the first 3 days. (Unfortunately this test was prematurely ended). Both 'B' cylinders (Figure 10) rapidly lose ethyl mercaptan in spite of the superpurge. Refilling the containers in the conventional manner shows that they both are still susceptible to odorant fade.

CONCLUSIONS

The main conclusions that can be drawn from this study are as follows:

- Ethyl mercaptan fades in some steel cylinders but not all
- The mechanism of mercaptan fade is very complex
- Ethyl mercaptan does not fade in aluminum cylinders

- The interior surface of the steel is the most significant factor affecting fade
- The heat treating step significantly affects the fading of ethyl mercaptan in steel cylinders. Unfortunately, the induction heating method which, so far, produces the most stable 20 lb barbecue cylinders, is the least common heating process, and is not recommended for larger cylinders.

FUTURE STUDIES

There are several areas of research which need to be completed before the problem of ethyl mercaptan depletion can be completely resolved. These include:

- (a) A better understanding of the mechanism of odorant fade and the factors which affect it.
- (b) Evaluation of other odorant systems.
- (c) Methods of passivating interior surfaces.
- (d) A study of different heat treating processes.

TABLE 1

20 LB BARBECUE CYLINDERS

ETHYL MERCAPTAN IN LIQUID PHASE, WPPM

TYPE	DAYS ON TEST				
	0	1	3	7	9/10
TEFLON	23.0	-	23.4	24.4	23.9
A1	23.9	23.6	23.9	-	24.9
A2	23.9	23.9	-	22.9	25.4
A3	23.9	24.4	-	-	24.9
A4	23.9	22.4	-	-	21.9
B1	23.9	15.6	6.3	-	0
B2	23.9	10.0	0	-	-
B3	23.9	10.3	-	-	0
B4	23.9	14.0	-	0	-

TABLE 2
FADING ALSO OCCURS IN 1 LB DISPOSABLE CONTAINERS

<u>ETHYL MERCAPTAN IN LIQUID PHASE, PPH</u>		<u>MAY 22, 1986</u>	<u>JULY 28, 1986</u>	<u>SEPTEMBER 2, 1986</u>
CT-IDC-645		1.3	0	-
ICG-IDC-644	A	3.2	-	-
	B	10.0	5.0	-
	C	6.1	4.5	-
	D	9.7	10.0	11.0
	E	-	-	0
	F	-	-	0
	G	-	-	3.3
IDC/1107S	H	-	-	0
	I	-	-	0
	J	-	-	0
	K	-	-	9.2
	L	-	-	0

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Figure 1
Multi-filling of Cylinder B3

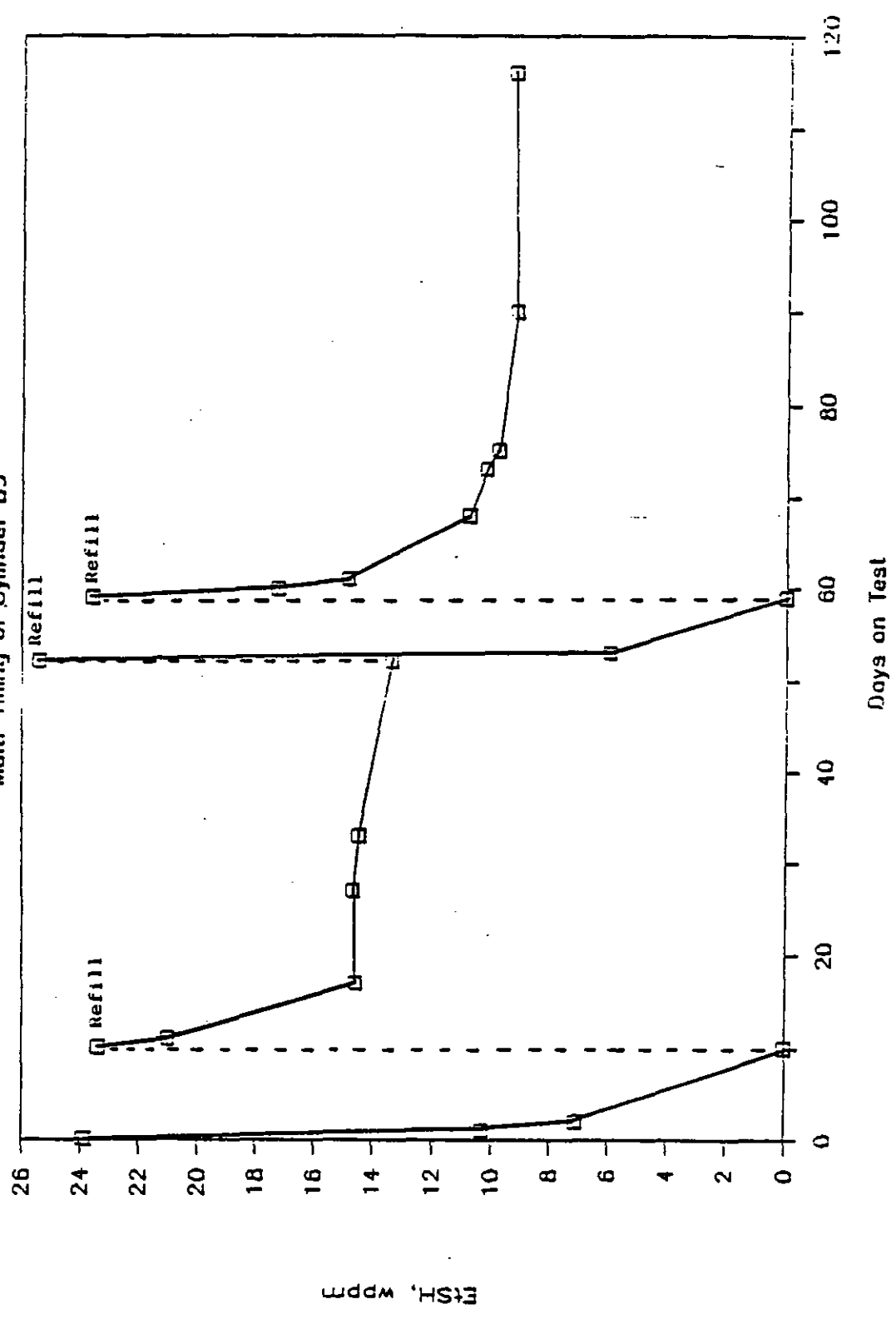


FIGURE 2

G.C. Analysis - Start of Test/Gas Injection

File: SM907R
FF = 0
IDC-A AFTER R100
Inst: 7 Ch: 0 Tray # 0
12:55:44
Page 1

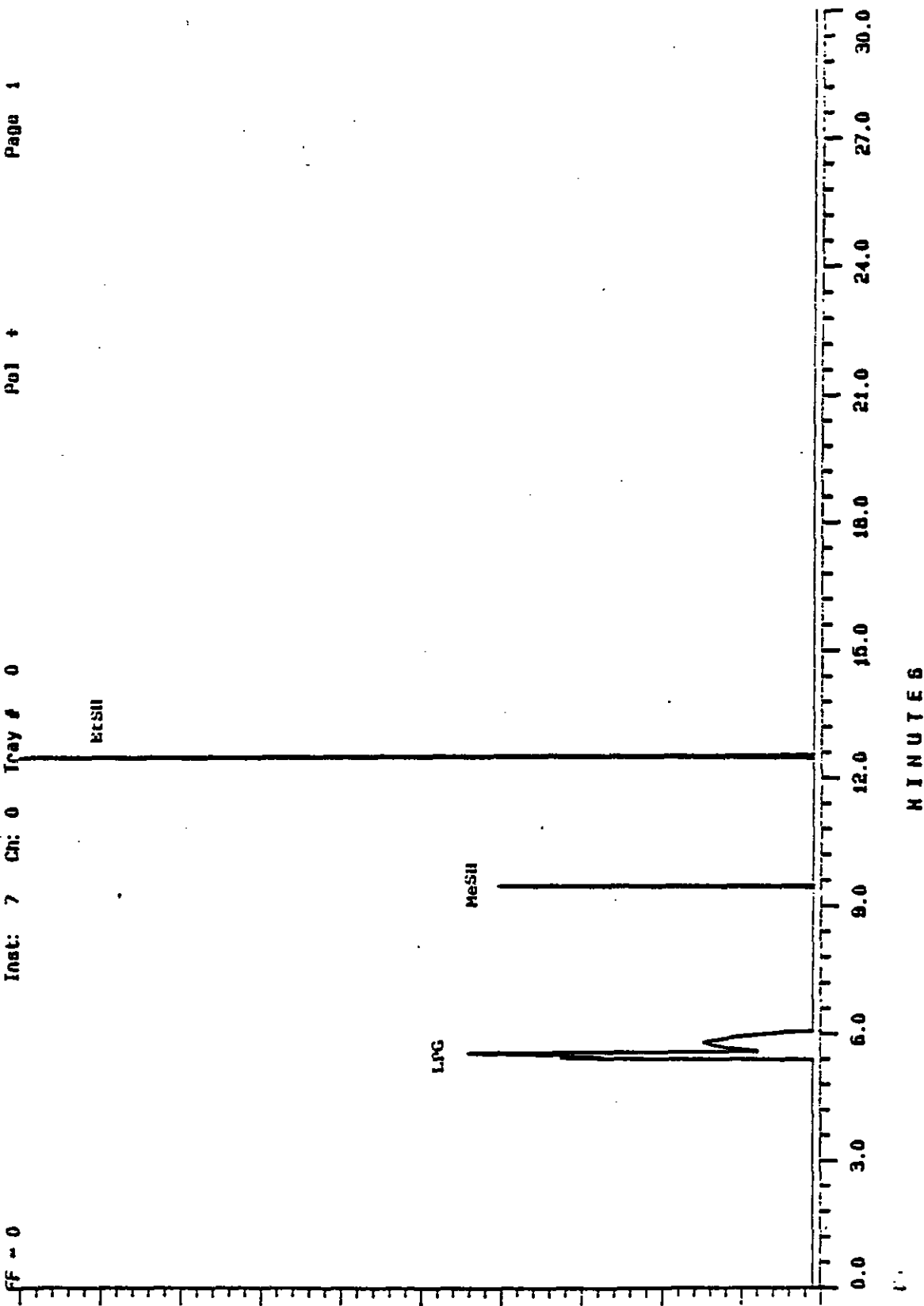
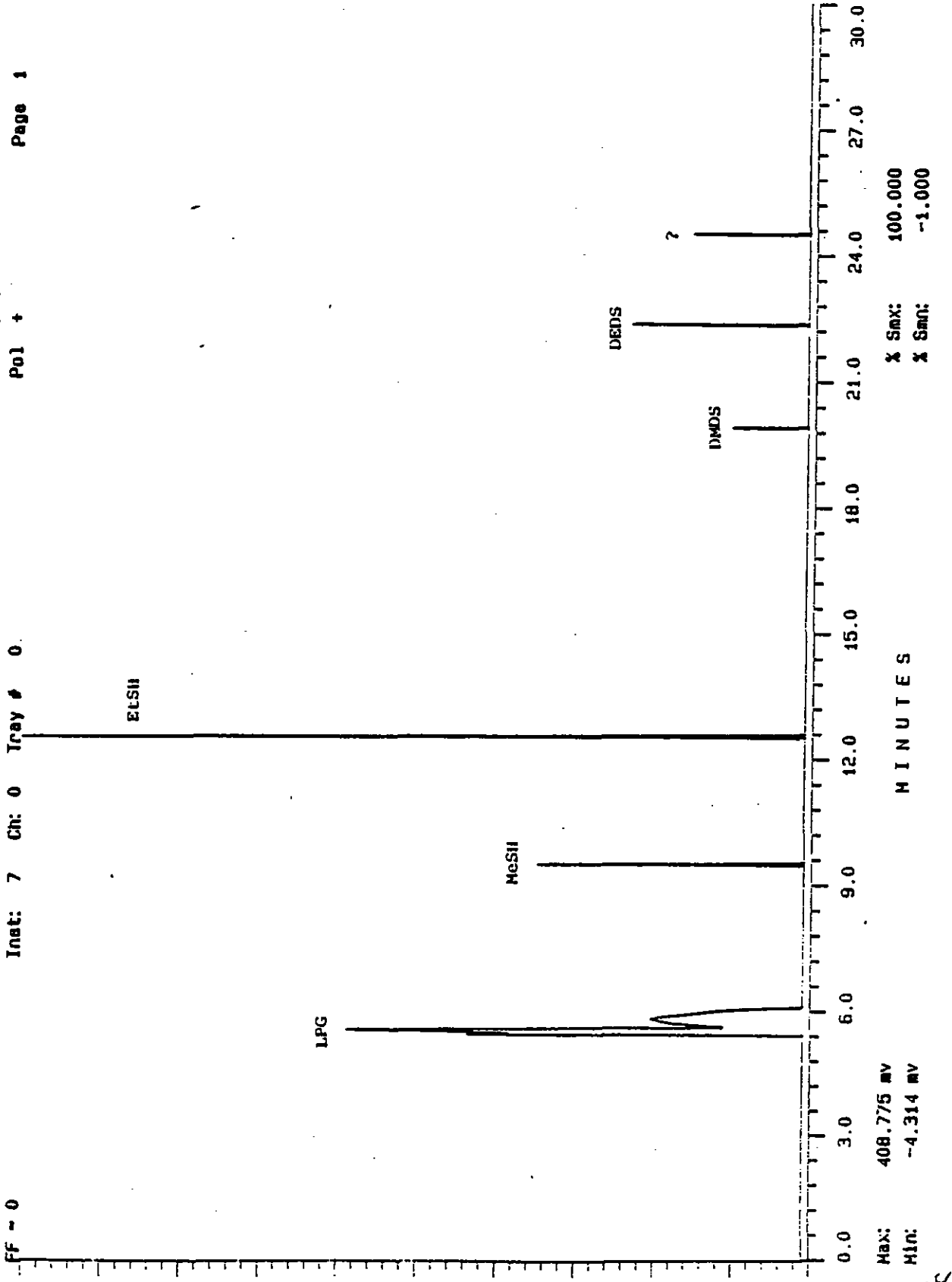


FIGURE 3

G.C. Analysis - During Test/Gas Injection

File: SH936R
FF - 0
IDC A R100
Inet: 7 Ch: 0 Tray # 0
14:59:33
Pol +
Page 1



Max: 408.775 mV
Min: -4.314 mV

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FIGURE 4

G.C. Analysis - During Test/Liquid Injection

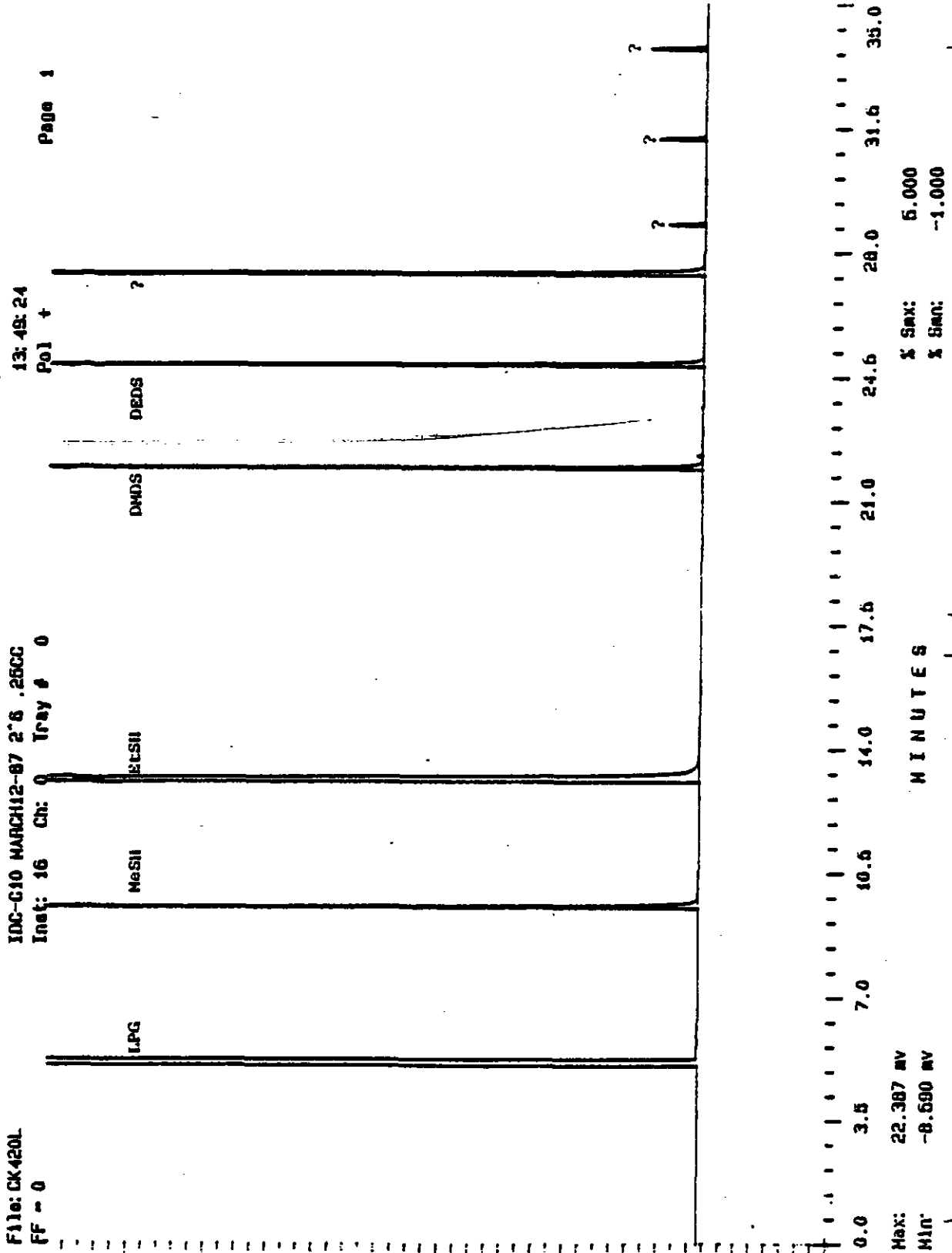


Figure 5
EtSH Stable In Aluminum Cylinders

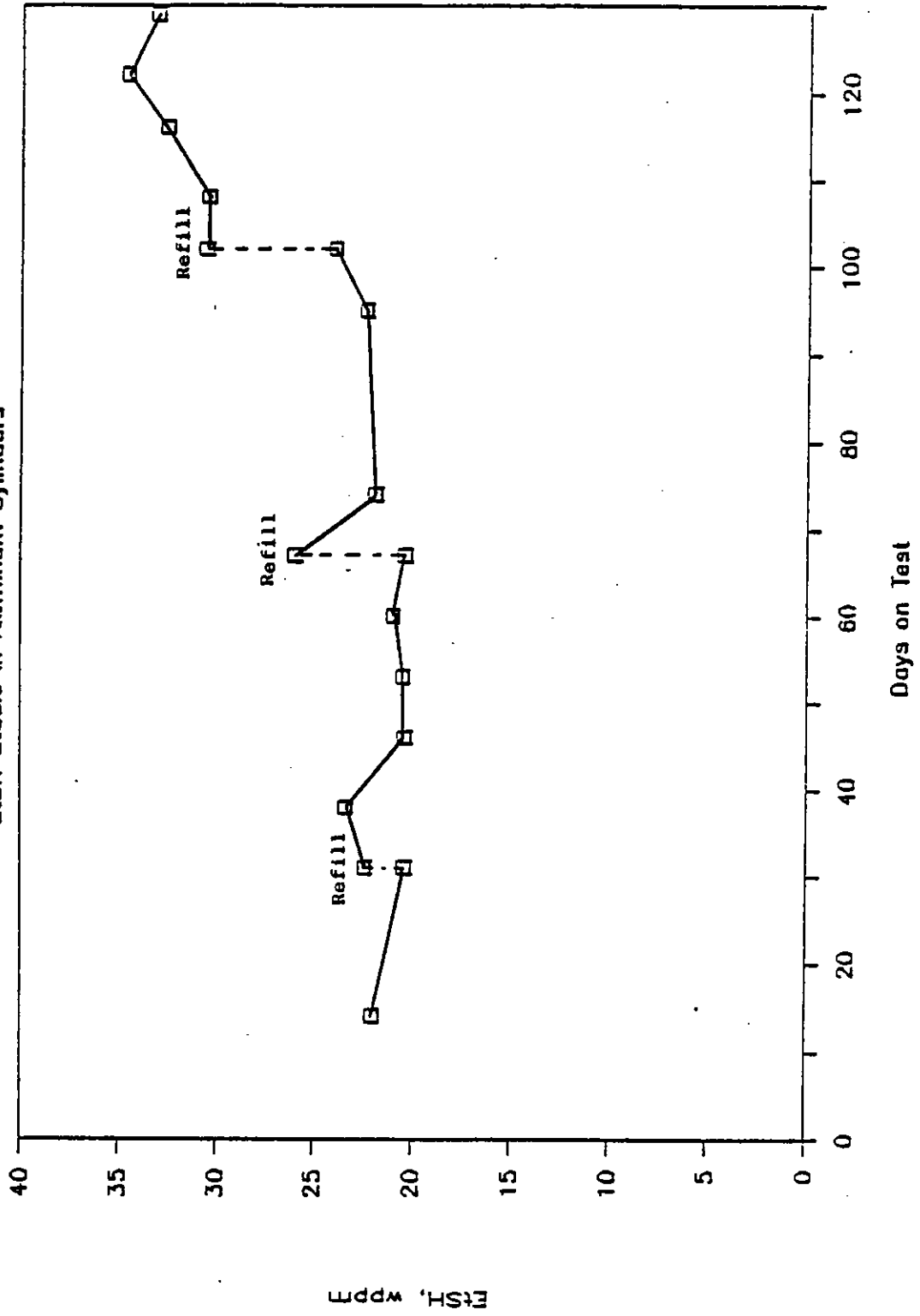


Figure 6

Cylinder A Acid-Washed

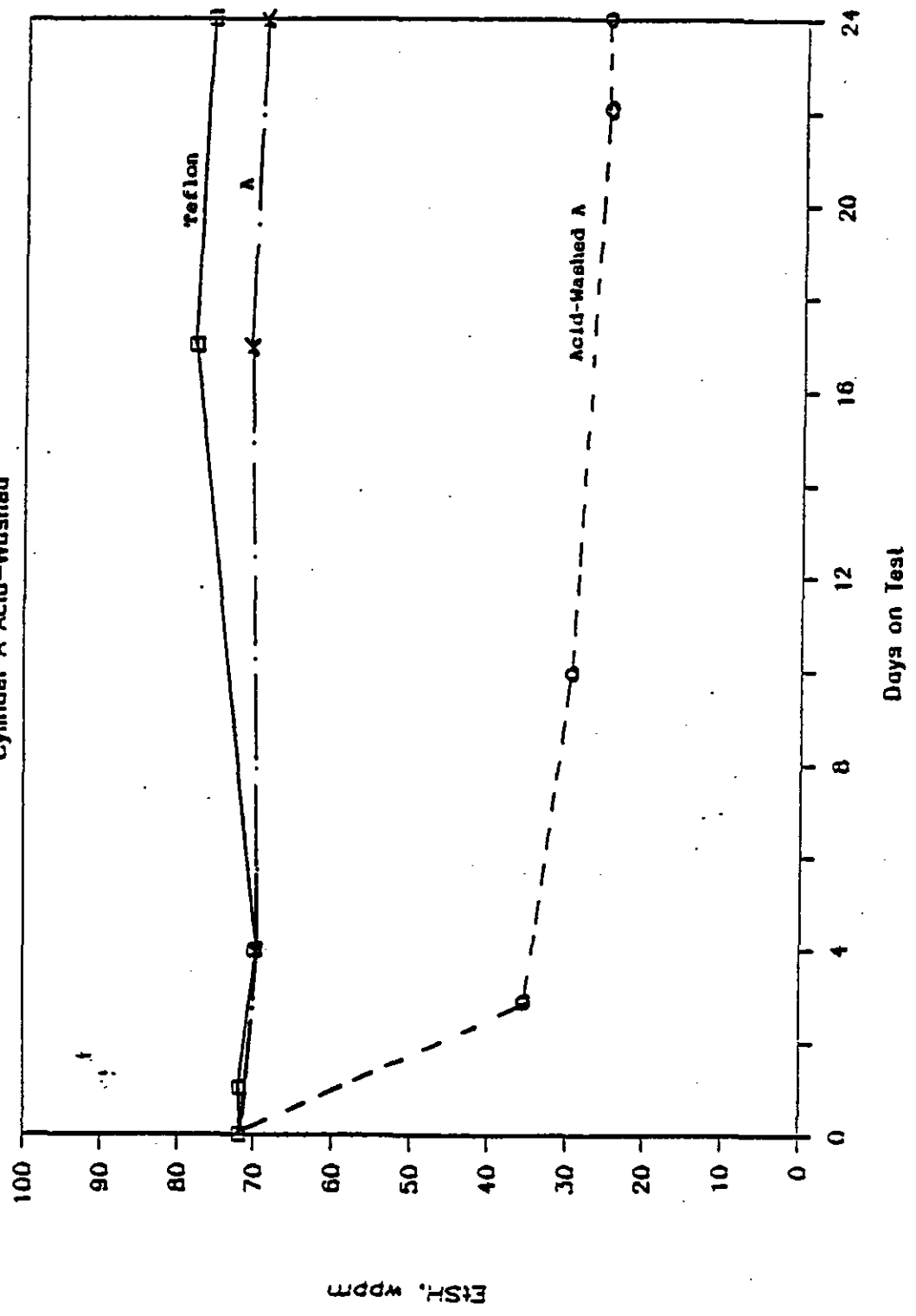


Figure 7

Cylinder B Acid-Washed

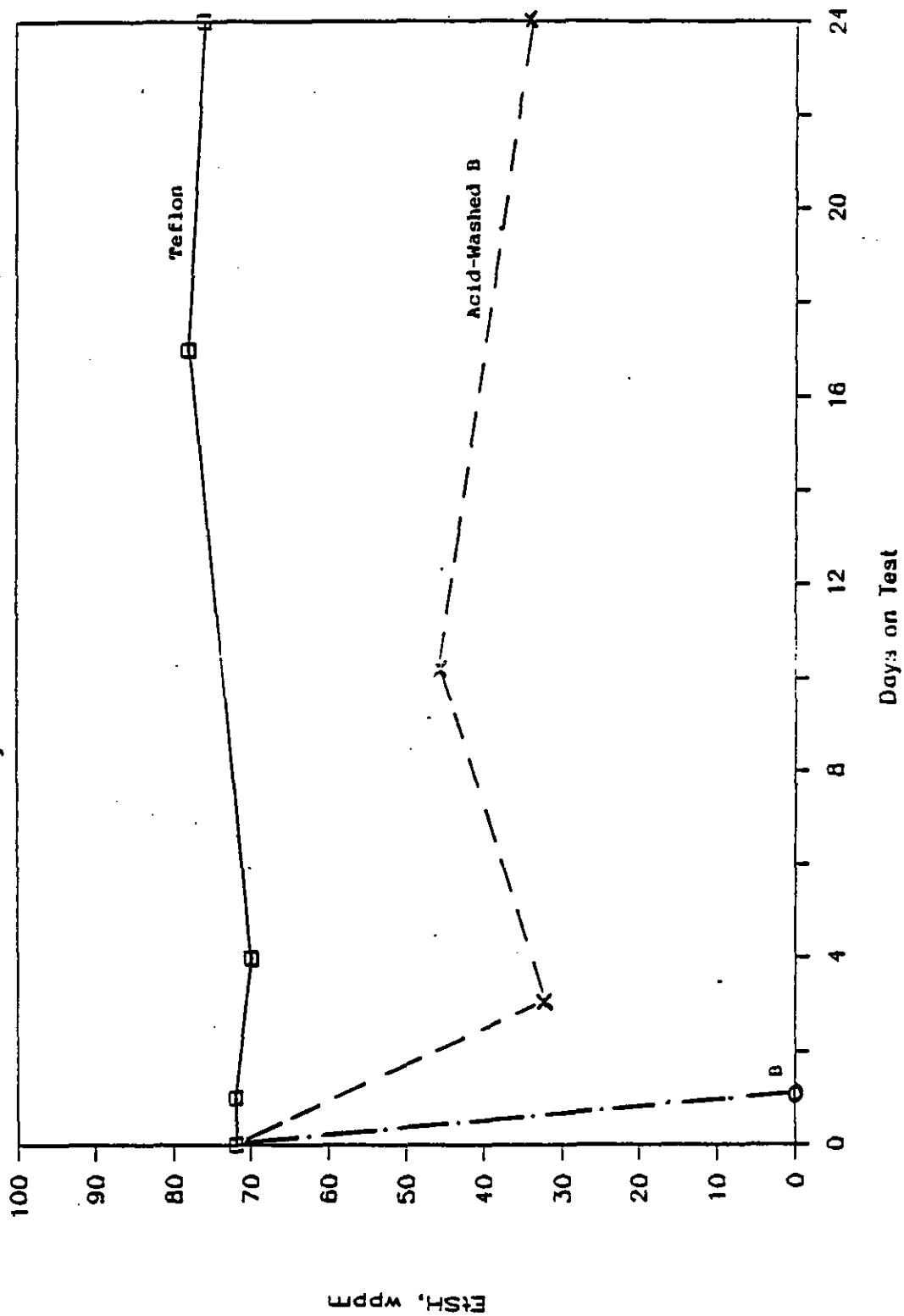


Figure 8
Effect of Interchanging Heat Treatment

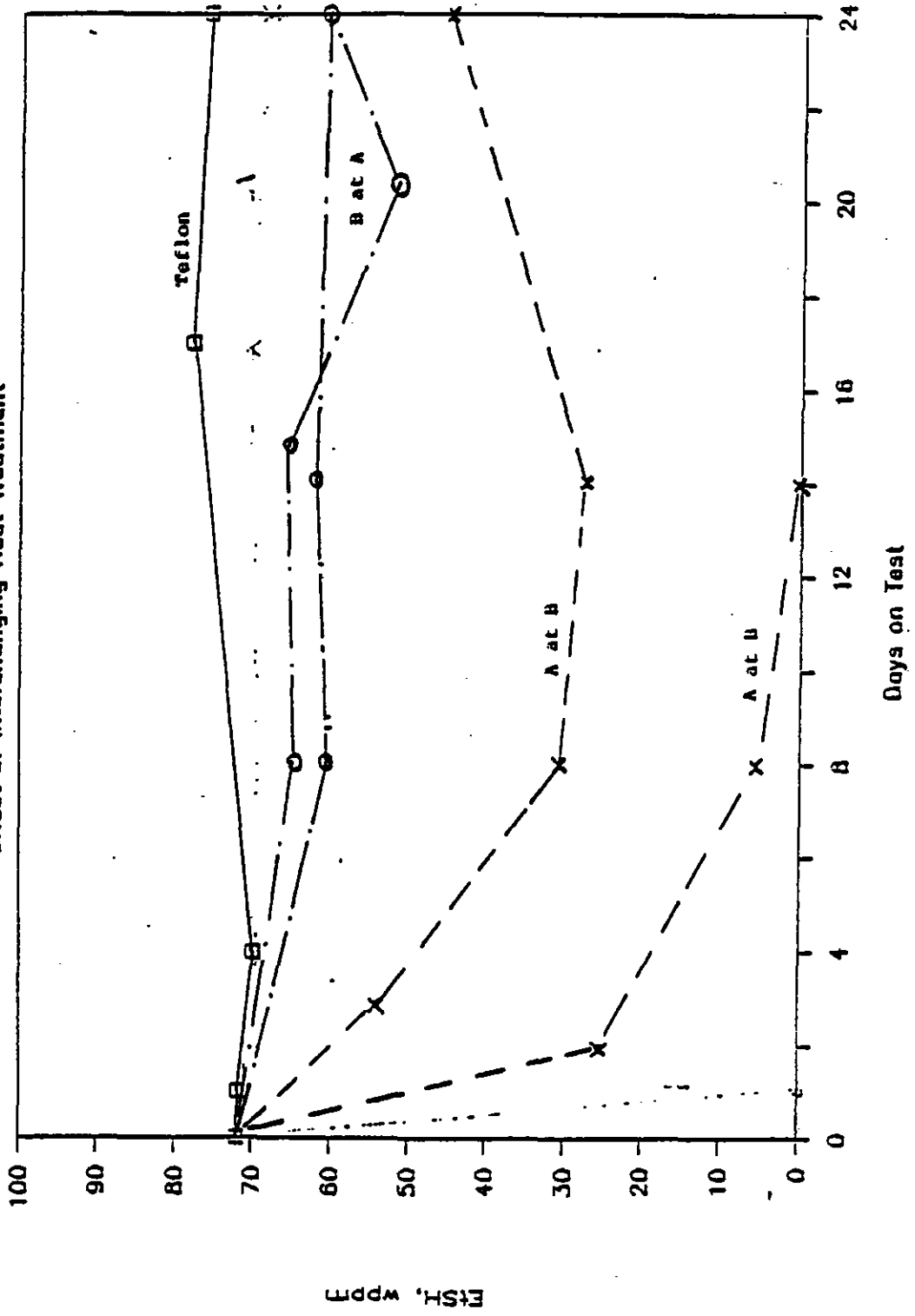


Figure 9
Superpurging of Cylinder A

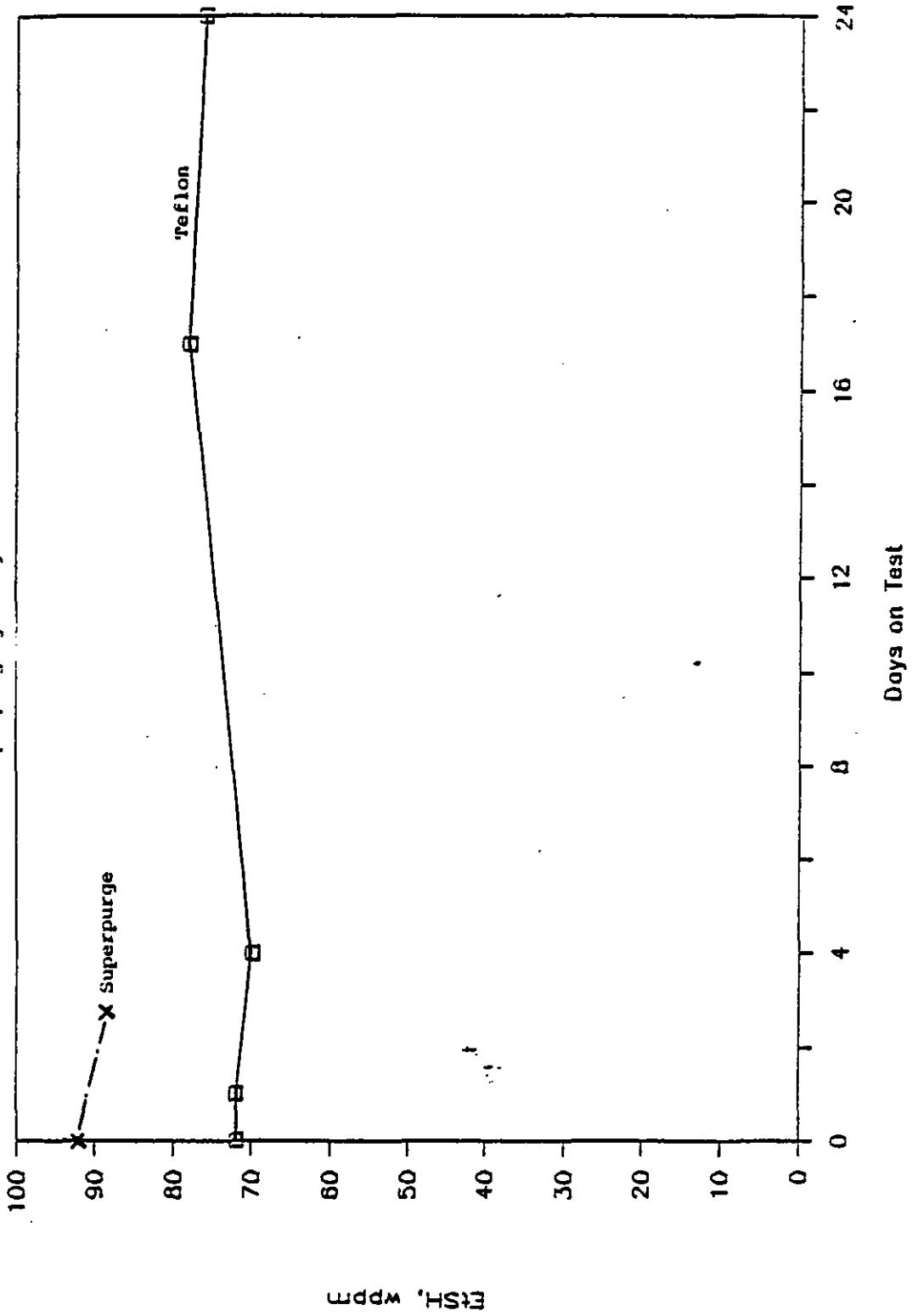
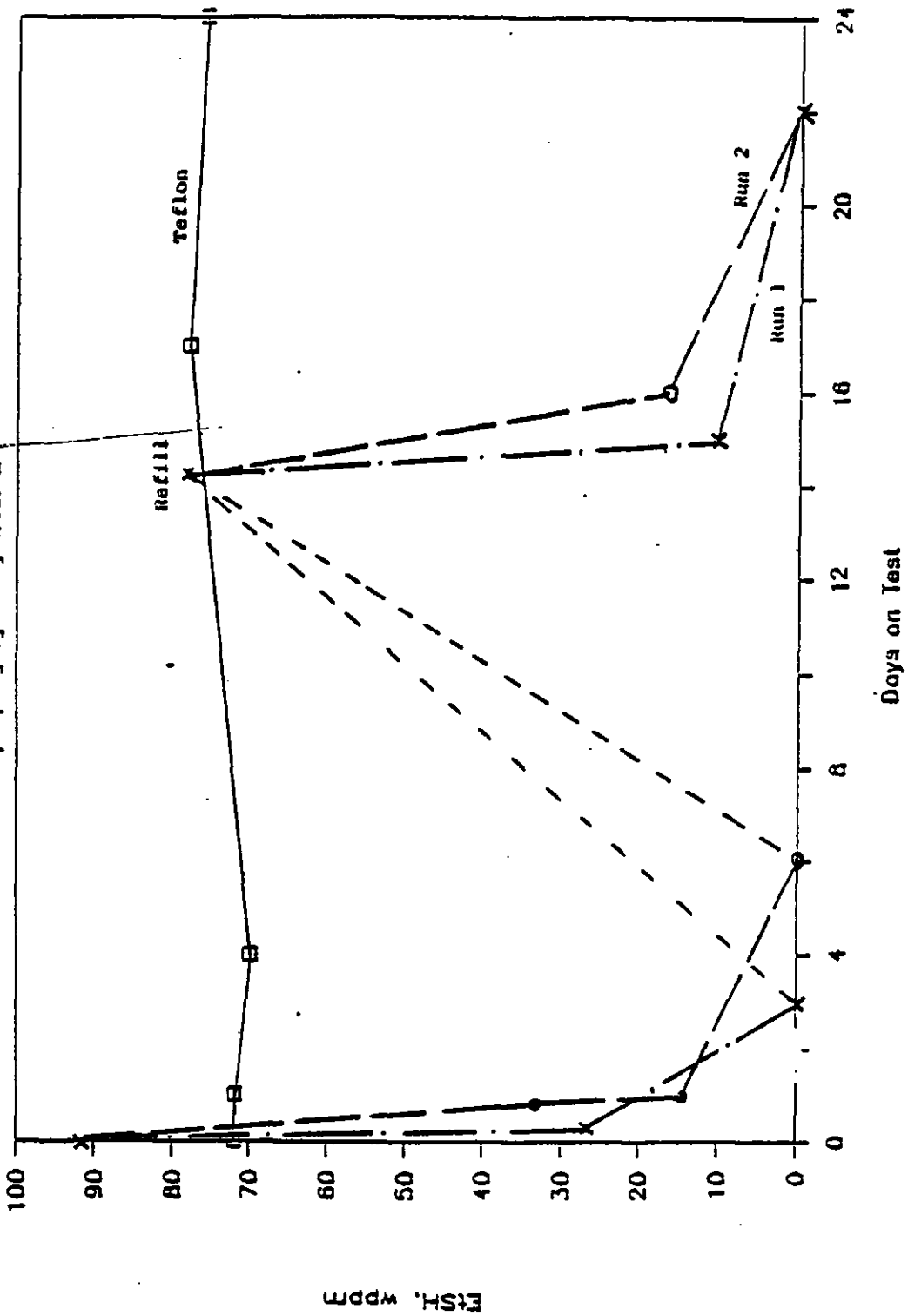


Figure 10
Superpurging of Cylinder B



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APPENDIX 1

SECOND DRAFT
July, 1987
A.L. Pickard

Proposed Method for PGAC
and CGSB
CAN/CGSB-3.0
No. _____

TEST FOR ETHYL MERCAPTAN
ODOURANT IN PROPANE, FIELD METHOD

1. SCOPE

1.1 This method is intended for the semi-quantitative (ie +/- 25%) determination of ethyl mercaptan odourant (within the range of 6 to 120 ppm) in propane. The method is intended for field application, and may be suitable for use by non-laboratory personnel. A gas chromatographic method should be used for more precise, quantitative determination of ethyl mercaptan in propane. (Note: The units of measurement (eg. vppm, mg/L, wppm) for ethyl mercaptan in propane by this method still need to be determined.)

1.2 Other low molecular weight mercaptans, such as methyl mercaptan, may interfere by giving a positive result.

Doc. # 0079y

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1.3 High concentrations of propylene may interfere, turning the "stain tube" gray. Thus this field method may not be suitable for some (commercial) propane containing significant levels of propylene.

2. APPLICABLE PUBLICATIONS

2.1 The following publications are applicable to this method:

2.1.1 Canadian General Standards Board (CGSB)
CAN/CGSB-3.14-M, Liquefied Petroleum Gas (Propane).

2.1.2 Canadian Gas Association
CAN/CGA-8149.2-M, Propane Installation Code.

2.2 The source for these publications is shown in the Notes section.

3. SUMMARY OF METHOD

3.1 A representative sample of liquid propane is completely vapourized by one of two procedures (a flowing stream of gaseous propane or evaporation of a sample in a plastic bag) and then tested for odourant concentration by use of a hand-held tester which utilizes a detector tube ("stain tube") specific for ethyl mercaptan.

4. SIGNIFICANCE AND USE

- 4.1 Propane, a colourless, odourless gas, is intentionally treated with an odourant, ethyl mercaptan, to allow propane gas leaks to be detected. However, the concentration of ethyl mercaptan in propane may decrease ("fade") over time due to adsorption on metal surfaces and oxidation, potentially leading to total odourant depletion. Therefore, a "field" test is required to allow determination of ethyl mercaptan in propane in the distribution system and at consumer's sites.

5. PRECAUTIONS

- 5.1 Note the extreme flammability of propane and ensure that this test is performed in a well-ventilated area, free of ignition sources.
- 5.2 Liquid propane evaporates rapidly, and can readily freeze flesh. Avoid skin contact.

6. APPARATUS AND MATERIALS

- 6.1 Gastec Precision Gas Sampling pump (or equivalent), available from Levitt-Safety Limited in Canada (part no. IG 6800, which incorporates a "test complete" indicator).

6.2 Gastec Ethyl Mercaptan Detector Tube No. 72, 5-120 ppm (or equivalent) part no. IG 72.

6.3 Sample container suitable for collecting and holding liquid propane, and conditioned by prior exposure to propane odourized with expected levels of ethyl mercaptan to minimize adsorption of ethyl mercaptan from the sample. A sample cylinder of at least 500 mL capacity is required for Procedure A. The following sample cylinders (with outage tubes) have been found to be suitable:

6.3.1 Teflon-lined stainless steel pressure cylinders;

6.3.2 316 stainless steel pressure cylinders dedicated to stench propane service. Initial commissioning of new or cleaned/reconditioned steel cylinders should include charging the cylinder with stench propane, storing for at least 24 hours, and repeating this charging/storing process at least 5 times (Note 1).

Note 1: Sample cylinders for stench propane service should not routinely be left open to the atmosphere or cleaned (eg steam cleaning). A cylinder that has been exposed to oxygen or water (vapour) must be recommissioned as given in 6.3.2.

6.4 Vapourization device, depending on the particular sample preparation method chosen:

- 6.4.1 Heating bath (40 - 50°C - very hot tap water) with 3 m coiled 1/8" stainless steel tubing (see note after Par. 10.3), fitting for sample cylinder, and a flow meter and control valve (see Figure 1) or
- 6.4.2 Plastic food storage bags. Dow "Ziploc" 1.75 mil, 27 x 28 cm freezer bags have been found to be practical. The second choice is Glad-lock food storage bags, 25 x 33 cm (10" x 13").
- 6.4.2.1 Mark the "standard volume" of liquid propane to be put into each 27 x 28 cm bag by pouring 15 mL (one tablespoon) of water into one bag, and tilting the bag so that the water fills one corner of the bag. Mark a line diagonally across the corner of the bag to represent the 15 mL volume. Mark each plastic bag with a line at this determined location (but do not use a bag which has contained water for an actual ethyl mercaptan test).

7. PROCEDURE

CAUTION: This test procedure requires the release of combustible propane liquid and vapour. The user is warned to take proper safety precautions to prevent ignition and/or liquid burns. This procedure should never be performed in an enclosed building or near a source of ignition.

- 7.1 Either collect a representative sample of liquid propane in an appropriate sample container, taking care to leave a vapour space in the cylinder (eg 20%) to allow for expansion of the liquid propane, or arrange for a fine flow of liquid propane at the sample point for testing "on site".

CAUTION: A fully charged cylinder, without "outage" (ie. 20% vapour space) will explode when allowed to warm up.

- 7.2 Proceed with the determination of ethyl mercaptan odourant by Procedure A or Procedure B. Both procedures achieve total vapourization of a portion of liquid propane, and allow measurement of ethyl mercaptan in the vapour phase. See Notes, para. 10.3.

7.3 PROCEDURE A - FLOWING PROPANE GAS STREAM ANALYSIS

- 7.3.1 Assemble the apparatus as shown in Figure 1, in a fume hood or other well-ventilated place, at an ambient temperature of 15 - 30°C.
- 7.3.2 Open the lower valve on the sample cylinder.
- 7.3.3 Carefully open the needle control valve to allow a gas stream of 500 mL/min to flow through the coiled tube, three-way valve and flow meter.

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- 7.3.4 Purge the tubing (eg for 2 minutes) and when the flow of propane gas has stabilized, readjust to 500 mL/min.
- 7.3.5 Turn the 3-way valve to cause the propane vapour to exit through the open, test port.
- 7.3.6 Prepare the Gastec detector tube as specified by the manufacturer (ie break both ends off by inserting them in the tube tip breaker of the pump) and insert the tube into the rubber inlet of the pump with the arrow on the tube pointing towards the pump.
- 7.3.7 Make certain the pump handle is all the way in. Align the red dots on the shaft and housing of the pump.
- 7.3.8 Place the open tip of the detector tube inside the open test port, in the flowing stream of propane gas, and draw back the handle all the way out for one full stroke, until it locks at the 100 mL mark. Keep the tip of the detector tube in the port for two minutes, to allow the correct volume of gas to pass through the tube. The current version of the Gastec pump has an indicator button to show when sampling is complete.
- 7.3.9 Immediately (within 30 seconds) read the coloured (yellow) portion of the tube.
- 7.3.10 If the reading is below 10 ppm, repeat the procedure (using the same tube) by turning the handle 1/4 turn in either direction and returning it to the starting point and repeat 7.3.7 to 7.3.9. Divide the reading of a double stroke test by 2.

Note 2: The Gastec ethyl mercaptan detector tube will give an erroneously low result if the temperature of the tube is much below 20°C. Keep the tubes in a warm place (20 - 30°C) before outside use in cool weather.

7.3.10 Close the sample cylinder and control valve and ensure the testing equipment and area are cleared of propane vapours.

7.4 PROCEDURE B: ANALYSIS OF PROPANE IN A PLASTIC BAG

7.4.1 Perform this test in a well-ventilated area, at an ambient temperature of 15 - 30°C.

7.4.2 Immediately before each series of measurements, test the pump for leakage as follows: insert an unopened tube and turn alignment marks off "lock" position; pull full stroke, hold for 5 seconds and carefully let vacuum return handle, making sure the return is back to original starting point. If it does not, look for vacuum leak and retest.

7.4.3 Clamp the sample cylinder in a vertical position. Attach a short tube to the lower valve (eg. 2 cm of 5 mm tubing).

7.4.4 Prepare the Gastec detector tube as specified by the manufacturer (ie break both ends off the tube by inserting them in the tube tip breaker of the pump) and insert the tube into the rubber inlet of the pump with the arrow on the tube pointing towards the pump.

- 7.4.5 Make certain the pump handle is all the way in. Align the red dots on the shaft and housing of the pump.
- 7.4.6 Take a new flat plastic bag (with a diagonal line across one corner to indicate a 15 mL volume) and open a short length (eg 2 - 3 cm) of the bag, minimizing the volume of the bag that is open to the air.
- 7.4.7 Crack the lower valve of the sample cylinder open and allow a slow stream of liquid propane to flow out before placing the bag for sample collection under the stream.

Note: Ensure there are no ignition sources in the area of the test. Avoid contact of stench propane with flesh or clothing. Wear gloves for steps 7.4.7 to 7.4.9.

- 7.4.8 Immediately collect about 15 mL of liquid propane (fill to the diagonal line) in the plastic bag, seal the bag and close the sample cylinder valve.
- 7.4.9 Shake or tumble the bag gently to aid evaporation of the liquid propane, and to mix the gases thoroughly.
- 7.4.10 As soon as the last drop of propane evaporates, proceed with the Gastec test by either:

NOTE: If bag has become drum tight, stop test and restart using new bag. If pressure inside bag breaks seal, restart test using new bag.

7.4.10.1 Puncture the plastic bag by "stabbing" it with the Gastec detector tube, and proceed with the test by drawing back the handle of the pump. (It may be necessary to press down on one part of the bag to give a taut "ballooned" bag to stab.)

7.4.10.2 Alternatively, open a small corner of the bag (eg 1 - 2 cm length), insert the ethyl mercaptan detector tube all the way and draw back the handle of the pump until it locks. Reseal the bag around the tube as much as possible. Keep the tube in place for 2 minutes to allow the correct volume of gas to pass through the detector tube.

7.4.11 Immediately (within 30 seconds) read the coloured (yellow) section of the tube.

NOTE: Leave the tube in the bag while taking reading in case a second pump stroke is required (see 7.4.12)

7.4.12 If the reading is below 10 ppm, repeat the test procedure (using the same tube) with a second 100 mL stroke, and divide the result by 2. Low level results (below 10 ppm) are not very reliable by this procedure, but should be indicative of a low odourant level.

NOTE: If the Gastec detector tube turns gray, it indicates a high level of propylene. Discontinue the test since it is not valid in the presence of propylene.

7.4.13 Destroy the sample bag by literally tearing it apart, and ensure that the test area is cleared of propane vapours. (A bag of propane vapour is a serious explosive hazard.)

8. REPORT

8.1 Report the ethyl mercaptan content in liquid propane to the nearest even whole number.

(NOTE: The units of measurement have yet to be resolved. While the Gastec result is probably in vppm, it may be preferable to convert the gastec reading to mg/L for direct comparison to specification requirements.)

9. PRECISION

9.1 To be determined by co-operative testing.

(Initial indications show a repeatability of +/- 15%.)

10. NOTES

10.1 The publication referred to in par. 2.1.1 may be obtained from the Canadian Government Publishing Center, Supply and Service Canada, Ottawa, Canada, R1A 0S9. Telephone (819)997-2560.

10.2 The publication referred to in par. 2.1.2 may be obtained from the Canadian Gas Association, 55 Scarsdale Road, Don Mills, Ontario, Canada, M3B 2R3.

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10.3 Ethyl mercaptan is very soluble in propane, but has a lower vapour pressure. Therefore, the equilibrium concentration of ethyl mercaptan in the vapour phase of a cylinder is much lower (possibly about one fifth) than the concentration of ethyl mercaptan in the liquid propane (depending on the temperature and amount of propane in the cylinder). Thus if a vapour sample of propane is taken from the vapour space of a cylinder, the amount of ethyl mercaptan present would generally be only a fraction of that measured on a sample of liquid propane by this method. Since this method is limited to about 6 ppm ethyl mercaptan, it is better to analyze a liquid sample (which is totally vaporized by this method) and thus expect to get a result in the range of 15 to 30 ppm.

NOTE: re 6.4.1, 7.3.3, 7.3.4: Apparently the average flow rate of gas into the Gastec tube is 200 mL/minute. However, the peak flow rate at the beginning of a stroke is much higher than 200 mL/min. Therefore, a flow rate of 500 mL/minute for propane vapour in the tube is suggested. Will a 3 m length of 1/8" tubing deliver 500 mL propane vapour per minute? For interest, an American odourant test uses a gas reservoir for the stain tube device as the point of test.

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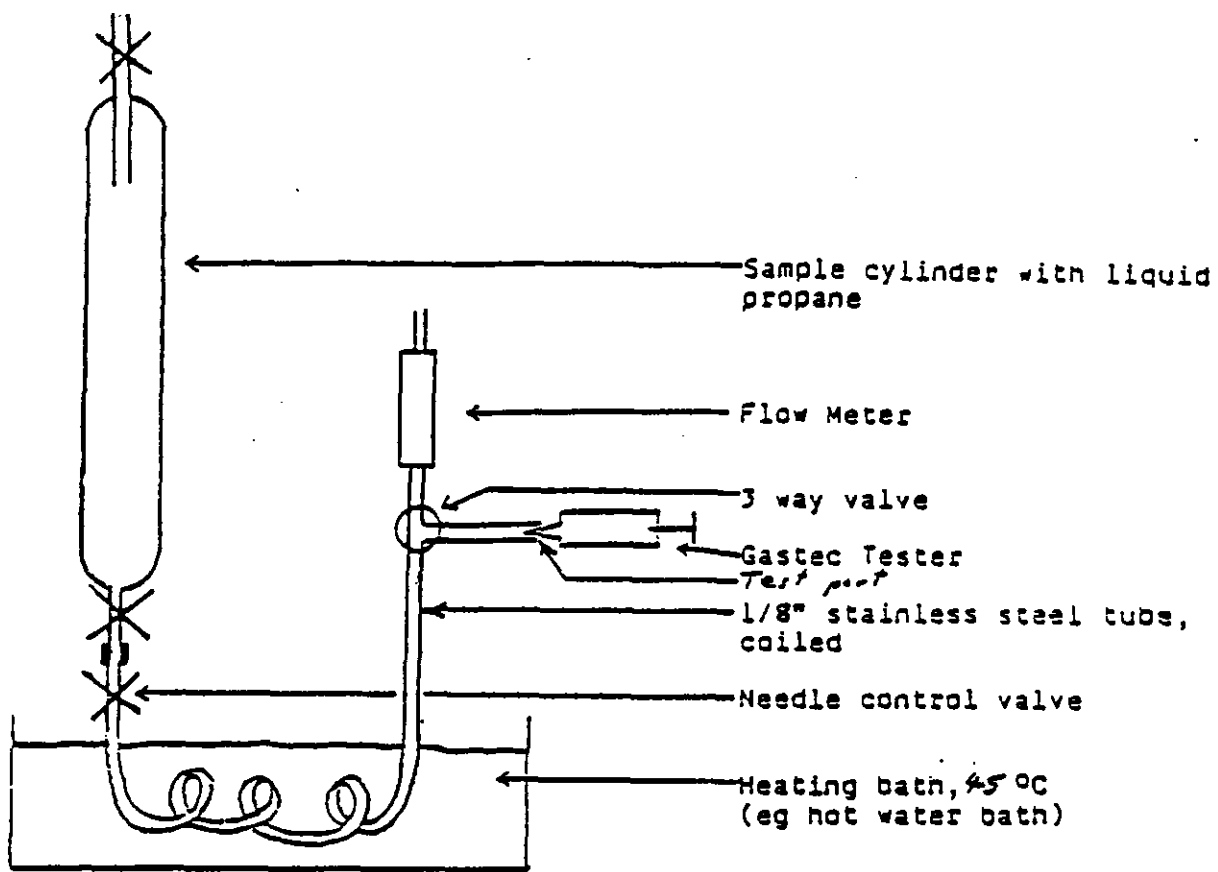


FIGURE 1. APPARATUS FOR PROCEDURE A, FLOWING PROPANE GAS STREAM

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Aging Impairs the Ability to Detect Gas Odor

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Abstract

Weakened smelling is common in age. Two studies here show that this phenomenon frequently reveals itself in inability to detect ethyl mercaptan, the warning agent most commonly added to propane (LP-gas). The first study compared 21 young (18-25 years) with 21 old (70-86 years) persons for (a) detection threshold (average ten times higher in the elderly), (b) suprathreshold odor strength (weaker for the elderly at all levels), and (c) ability to identify common odors (the elderly did worse). Seven of the 21 elderly failed to detect ethyl mercaptan at or above a concentration associated with the boundary between acceptable and unacceptable levels of propane. Three of these failed to detect the odorant at a concentration where accompanying propane could explode. In the second study 50 of 110 persons over 60 years failed to detect odor reliably in commercial odorized propane diluted to the Department of Transportation's safety standard (one-fifth the lower explosive limit). Six of 52 persons under 40 also failed. The elderly person would seem at high risk of LP-gas fire.

INTRODUCTION

IN A DATED (1957) BUT PROVOCATIVE STUDY, Chalke and Dewhurst¹ reported that 30 percent of Britons over 65 years old were unable to smell town gas. Since then town gas has universally given way to natural gas and liquefied petroleum gas (LP-gas), generally propane. Odorants are mixed with these gases, themselves odorless, to signal danger from potentially explosive leaks. The question here concerns the ability of persons, especially elderly persons, to detect the danger signal.² We focus here on one of these

References: Joseph C. Stevens, William S. Cain, and David E. Weinstein, "Aging Impairs the Ability to Detect Gas Odor," *Fire Technology*, Vol. 23, No. 3, August 1987, pp. 199-204.
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Key Words: Smelling and aging, gas odor detection, ethyl mercaptan, propane explosions.

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Detecting Gas Odor

odorants, ethyl mercaptan, the most commonly used warning agent for propane. In brief, we found that a large proportion of two samples of noninstitutionalized persons over 60 failed to detect it reliably at a level considered adequate for protection, compared with a much smaller proportion of samples of persons under 40. This result is consonant with the finding of many investigators that aging often weakens the sense of smell (for a review see Murphy).⁴

The National Fire Protection Association and the Department of Transportation specify that LP-gas shall be odorized so as to yield distinct odor when the gas is at or above a concentration in air of one-fifth the lower limit of flammability, also called the lower explosive level (LEL). The regulations state further that 1 pound of ethyl mercaptan per 10,000 gallons of LP-gas has been found by experience to serve effectively. One-fifth the LEL occurs at 0.47 percent propane in air. Based on an activity coefficient of 0.2 (ratio of vapor to liquid concentration), a fresh cylinder of LP-gas should yield about 14 ppb ethyl mercaptan at one-fifth the LEL. (The activity coefficient was found to vary from 0.13 to 0.26 for temperatures ranging from -10°C (14°F) to 35°C (95°F). The coefficient equals 0.2 at about 11°C (52°F).⁵)

We made two studies of the problem, the first in the psychophysical laboratory, the second outside under conditions more typical of everyday life. The first was a comparison of 21 young (18-25 years, $\bar{X} = 20.7$, $\sigma = 1.55$) and 21 elderly subjects (70-85 years, $\bar{X} = 73.5$, $\sigma = 4.56$) for:

(a) absolute detection threshold to ethyl mercaptan (the source was an aluminum cylinder containing 1.1 ppm ethyl mercaptan in nitrogen, [redacted]);

(b) the perceived suprathreshold strength of ethyl mercaptan, and the ability to identify common odorants.

Each age group contained 11 men and 10 women; all were nonsmokers and able to breathe freely through the nose. The second study compared 110 persons over 60 with 52 persons under 40 for the ability to detect reliably the smell of commercial, odorized propane. Here selection by sex and patency of nasal airways was intentionally avoided to more nearly approximate the conditions of everyday existence. The sample of young contained 26 of each sex, the sample of elderly 23 males and 87 females. About 15 percent of both groups were smokers.

LABORATORY STUDIES

Thresholds were taken using an air dilution olfactometer.⁶ On each trial the subject had to decide which of three glass nozzles emitted odorant as opposed to just plain air. Flow rate was 3.0 ± 0.3 L/min from each nozzle. Eight concentrations of odorant, spaced by a factor of three between 0.18 and 394 ppb, were available. Testing began at the lowest level, 0.18 ppb. Whenever a

⁶ The use of trade names in this report is for identification purposes only and does not constitute endorsement by the authors.

subject chose incorrectly, the next higher level was presented; whenever correctly, the same level. That level at which the subject responded correctly four times in a row defined the threshold. This basic ascending forced-choice procedure has been extensively used in the clinic to distinguish various degrees of smelling losses.⁶

Figure 1 displays all the thresholds along a logarithmic axis. The geometric mean threshold of the elderly exceeded that of the young by 10-fold ($t = 5.94$, 40 d.f., $p < 10^{-6}$). Seven elderly subjects gave thresholds near or above 14 ppb, which would correspond to concentration of ethyl mercaptan present at one-fifth the LEL of propane, and three at 70 ppb, which would correspond to the concentration present at the LEL itself. The averages for the young (0.74 ppb) is a little higher than found in some other studies⁷ probably because our starting level was relatively high; this was necessary in order to provide concentrations high enough to measure the threshold of the least sensitive elderly subjects.

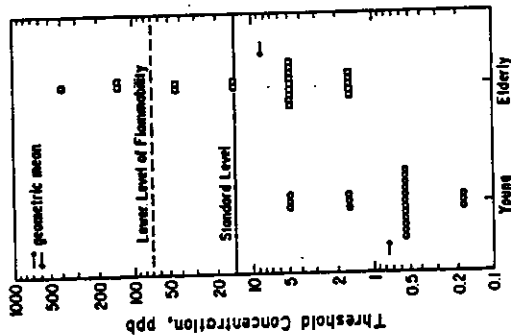


Figure 1. Detection thresholds of 21 young and 21 elderly subjects for the gas warning agent, ethyl mercaptan. The standard level refers to the concentration of ethyl mercaptan (14 ppb) that would be achieved when a leak of propane from a freshly filled cylinder achieves a concentration of 0.17 percent (one-fifth of the lower explosive limit).

differences reflect themselves in suprathreshold odor strength. To do this we called on the same subjects to make numerical magnitude estimates⁹ of the odor strengths of the top five concentration levels (4.9 to 394 ppb) compared with the taste strengths of five NaCl solutions between 0.08 and 0.40 molar on a common scale of perceived magnitude, each presented twice. The salt solutions were made up from reagent-grade NaCl and deionized. H₂O (DHOH) at room temperature, sipped from small cups and then expectorated, followed by a DHOH rinse. Tastants and odorants were presented in alternation and random order as to level. This procedure, called magnitude matching,⁹ takes advantage here of the report that suprathreshold saltiness remains relatively intact in old age.¹⁰ The basic, simple question asked here is how strong do the odors seem relative to the tastes of young persons compared to older persons? To make the comparison quantitative, the saltiness estimates were used to "normalize" the odor estimates, i.e. each odor estimate was multiplied by a normalization factor that made each subject's mean taste estimate equal 10. This procedure has successfully served to reveal age-related losses in odor perception for several different compounds.^{11,12,13,14}

The mean normalized estimates are plotted in the log-log coordinates of Figure 2. The functions are very flat, signifying that it takes a tremendous increase in concentration to strengthen the odor by much (typical of olfaction).¹⁴ The horizontal separations of the functions are on the order of 3- to 8-fold—a little less than the 10-fold threshold difference, but substantial, nevertheless. The smaller difference at lower concentrations may reflect the older subjects giving 13 false-positive responses to subthreshold levels. It should be noted also that any suprathreshold weakness to NaCl that may have eluded earlier investigation would operate in the direction of underestimating suprathreshold olfactory weakness in the elderly.

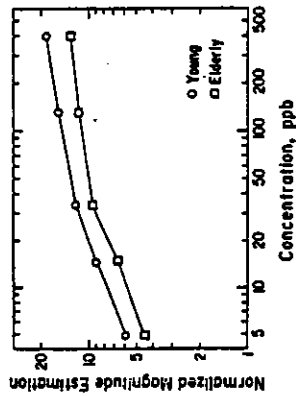


Figure 2. Average magnitude estimations of the odor strength of ethyl mercaptan gas relative to salty taste strength, comparing young and elderly estimates. The magnitude estimations were normalized by means of saltiness estimates using a procedure described in the text.

ODOR IDENTIFICATION

Ten common odors, e.g., rubbing alcohol, tea, and orange, were sniffed from containers covered with gauze to prevent seeing. On the first of two runs

the subject tried to name each odor without prompts; on the second run, to select the correct name from among four alternatives. On the unprompted run the young correctly identified an average 5.62 odors; the elderly, 2.52 ($t = 5.17$, 40 d.f., $p < 10^{-4}$). On the prompted run the young correctly identified 8.95; the old, 7.52 ($t = 3.35$, $p < 0.001$). The loss of ability to identify odors is thus compounded the problem faced by older persons when it comes to gas warning agents and other hazards signaled by olfaction. It is one thing to detect a smell and another to identify it and act on it. Ultimately the relation among detection threshold, recognition threshold, and action threshold is a subject of great practical importance in this domain.

IDENTIFICATION OF ETHYL MERCAPTAN IN EVERYDAY SETTINGS

In practice, odorization of propane often exceeds the minimum level specified. For example, 1.5 pounds per 10,000 gallons is commonly added by design. Furthermore, refilling a cylinder before it is empty can increase odorant above design levels. With this in mind, we chose a 20-pound tank of commercially obtained propane as the odor source in the second study. Because the partial pressures of ethyl mercaptan and propane differ, the emitted ratio of ethyl mercaptan to propane actually grows as a tank empties (unfortunately, a newly installed, full tank constitutes the greatest hazard because relatively less ethyl mercaptan is emitted). To make our tests realistic we drew samples at five levels of fullness: 100, 87, 63, 39 and 22 percent. At each level the vapor phase concentration of odorant in the undiluted gas was measured by a gas chromatograph equipped with a flame photometric detector. The samples were drawn and analyzed immediately at TRC Environmental Consultants, Inc., in East Hartford, Connecticut. The measured concentrations were 6.45 ppm (average of three separate samples—6.56, 6.48, 6.32 ppm—as a reliability check), 7.86, 12.6, 36.0 and 43.7 ppm.

For psychophysical testing of the commercial propane, samples were bled off at each tank level and were mixed with breathing air via a Matheson Mass Flowmeter so as to produce a concentration of 0.47 percent propane in air, or 1/5th the LEL. The corresponding concentrations of ethyl mercaptan were for the five levels: 30.3, 36.9, 59.2, 169 and 209 ppb, all well above the standard level of 14 ppb. Such samples (or plain breathing air for comparison) were placed in 5-L gas sampling bags (Analabs Co.) that were filled in the same day at four testing sites: the laboratory, two senior citizens' centers in New Haven, and Jonathan Edwards College at Yale University. The subjects were 110 persons over 60 ($\bar{x} = 72.1$, $\sigma = 6.26$) and 52 persons under 40 ($\bar{x} = 23.5$, $\sigma = 4.33$). Each subject was tested at only one tank level. The average age for the five groups of 20 to 25 elderly subjects was nearly the same, as was the average age of five groups of 10 to 12 young subjects.

The subject sat at a table with the nose at a distance of 2.5 cm from the stainless steel valve of the bag. At a ready signal the experimenter pressed the bag so as to eject the odorized or plain air for 2 to 4 seconds at a flow rate of

3.4 L/min (±0.6). The subject had to choose which one of three bags contained an odorant. The instruction was to choose the sample that smelled like gas or simply smelled different than the other two. Thus the task called for correct detection only, identification not being required. This procedure was repeated four more times.

The binomial probabilities of chance performances for at least 0, 1, 2, 3, 4 or 5 correct responses were respectively: 1.0, 0.87, 0.54, 0.21, 0.045 and 0.0041. For the purposes here it was decided that four or five correct responses constituted reliable performance. Under this criterion, 45 percent of the elderly failed the test (50 out of 110) and 1.0 percent of the young (6 out of 62). It is clear, therefore, that aging places a person in far greater jeopardy. One should also note that although the absolute number of young persons who cannot smell the warning agent could in principle be very large, the sample size is far too small to estimate that number accurately.

ANCILLARY VARIABLES

Neither the first nor second study revealed any significant sex difference. On the average, women usually have been shown to outperform men at odor identification,^{14, 15} but our test was doubtless too easy or short to show the difference. No effects emerged from smoking or from use of the home.

Our samples do not represent the population of propane users in detail. For example, users of propane for home heating are more often rural than urban. Also, the two senior citizens' centers seemed to differ somewhat—even though both showed large detection failure. The first two tank levels were tested at one center, where the number of unreliable detectors were 12 out of 20 both times. The last three levels were tested at the other center, where the number of unreliable detectors were 19 out of 25, 10 out of 23, and 2 out of 22, respectively (showing that increasing the concentration of ethyl mercaptan can substantially increase the number of persons who detect it). Since only six young persons failed to detect it, no effect of tank level showed up. Although the individual sample sizes are relatively small, the difference between the two centers may be large enough to suspect that olfactory detecting could possibly be influenced by a number of demographic factors, e.g., occupation, health care, neighborhood pollution, etc., and that an epidemiological survey may be warranted to single out high-risk factors.

DISCUSSION

The peril of propane usage is serious. With only about one-third of U.S. fire departments reporting, 2,227 LP-ignited fires were reported in 1984, with 19 fatalities and 372 injuries, sometimes disfiguring.¹⁶ Injured persons and bystanders often insist that they smelled nothing before an explosion. Inability to detect ethyl mercaptan at the levels emitted undoubtedly accounts for some proportion of such incidences. Although the risk of natural gas explo-

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sions is lower relative to the amount consumed, some of the same concerns raised here also apply to it.¹⁷

The elderly should be educated by their physicians, by directors of senior citizens' centers, by appropriate literature from the distributor, or whatever, that aging frequently brings about hyposmia. Unfortunately, the elderly often fail to observe that their sense of smell has weakened.¹⁸

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