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CHEMICAL SAFETY OF U.S. NAVY DIVER'S BREATHING GAS HOSES

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TECHNICAL REVIEW AND APPROVAL

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The experiments reported herein were conducted according to the principles set forth in the current edition of the "Guide for the Care and Use of Laboratory Animals," Institute of Laboratory Animal Resources, National Research Council.

This technical report has been reviewed by the NMRI scientific and public affairs staff and is approved for publication. It is releasable to the National Technical Information Service where it will be available to the general public, including foreign nations.

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Diver's breathing gas hoses manufactured according to a detailed military specification (MIL-H-
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lecent experience at the Naval Medical Research Institute (NMRI) suggests the need to clarify how
ıch hoses should be treated (i.e., when and how cleaning and chemical testing should be done).
imited chemical testing by NMRI indicated that at least some of the hoses introduced varying
mounts of several contaminants into the gas, the predominant species being toluene, a common
romatic hydrocarbon. Although we are unaware of any recent health or safety problems that can be
ttributed to chemical properties of diving hoses, this record of apparent safe use should not be used

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to minimize concern regarding hose safety. Particularly important may be the cumulative effect of low level exposures to toxic compounds that can occur over time and produce delayed responses, even years later. Unfortunately, the scarcity of data on the chemical properties of such hoses widely used for Navy diving raises questions regarding the adequacy of MIL-H-2815G to insure chemical safety.

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INTRODUCTION

Diver's breathing gas hoses manufactured according to a detailed military specification (MIL-H-2815G, 17 Feb 1989) are used throughout the U.S. Navy (1). These rubber hoses are designed to supply air or other gas mixtures from the surface to divers at depths up to 500 fsw. MIL-H-2815G details specific chemical offgassing requirements that the manufacturer of these hoses must meet. However, the U.S. Navy does not presently require a specific set of cleaning and/or testing procedures to be done by the user to insure that these hoses will not introduce potentially harmful chemicals into the breathing gas. Recent experience at the Naval Medical Research Institute not only suggests the need to clarify how such hoses should be treated (i.e., when and how cleaning and offgas testing should be done), but raises questions regarding the adequacy of MIL-H-2815G to insure the chemical safety of diver's hoses.

MIL-H-2815G AND CHEMICAL SAFETY

MIL-H-2815G requires that diver's breathing gas hoses have an inner core of natural or synthetic rubber and an outer cover of chloroprene. The fabric reinforcement should consist of two or more plies of braided cotton, rayon or polyester. The hose must contain the minimum quantities necessary of only the purest grades of rubber accelerators, both in the cover and inner tube, in order to be as free from odor as possible. No coupling lubricants or washer dressings, except water, may be used.

MIL-H-2815G requires the finished hose to pass a specific offgassing test, which is outlined below:

1. Hose to be tested will not have been flushed with gas or water, nor have been capped and stored at a temperature not less than 23 °C for at least 7 days.
2. Clean air is flowed through the hose at 28 ℓ/min (1 ft^3/min) with gas and hose at a temperature not less than 23 °C.
3. At the end of 15 min of gas purging, the air coming out of the hose is measured with a total hydrocarbon analyzer (hydrogen flame ionization detector).
4. Hoses that contaminate the air with greater than 100 mg methane equivalents/m^3 per 100 foot length or greater than 4 mg/m^3 per 4 foot length are unacceptable.

According to a representative from the manufacturer of the hose tested in this report, the company sends selected hose samples out to a commercial lab for the offgassing test just described and there normally isn't any problem with their diver's hoses passing this test. However, the manufacturer also has tested their diver's hoses in-house and has identified several offgassing species, one of which is toluene. The company was reluctant to provide more detailed information.

NMRI EXPERIENCE

Initial Hose Problems

In the Spring of 1991, the Diving Medicine Department (DMD) at the Naval Medical Research Institute (NMRI) obtained 6 diver's hoses for use in human research. These hoses (each approximately 50 feet long) were purchased without O_2-safe certification from the manufacturer via a local distributor. The in-house cleaning facility ("clean van") in DMD suspected contamination upon initial handling of the hoses based on a strong aromatic odor. As with all diving gear received at NMRI, four of these hoses were cleaned to remove any non-volatile hydrocarbons (e.g., hydrocarbon grease or oil) per Mare Island Naval Shipyard (MINSY) Process Instruction no. 0558-839F Ch-2, Par. 5.2.3.2 (2). Such cleaning is designed to make gear safe for use with high pressure O_2 by removing hydrocarbon contamination, thus minimizing the chance for combustion. Briefly, this procedure consists of a warm water (grade B) pre-flush, cleaning by flushing with a specified amount of 2.4% trisodium phosphate (TSP) solution heated to 120 °F, and a warm water post-cleaning flush followed by a warm nitrogen gas drying purge. Liquid rinse water samples are then taken to check for presence of trace non-volatile hydrocarbons and particulates. However, despite several repeated cleanings, odor problems persisted and the Gas Analysis Laboratory in DMD was requested to test the hoses for volatile hydrocarbons.

The four hoses that were cleaned were connected together in series using clean metal connectors and purged with hydrocarbon-free N_2 for approximately 15 min at a head pressure of 10.3 ATA. Flow was then stopped, hoses pressurized to 10.3 ATA to allow subsequent sampling, and valves at each end of the hoses were closed. After storage at room temperature (20 to 25 °C) for 60 h, the pressure remaining inside the hoses was measured so that analytical results determined at 1 ATA could be corrected for test pressure. A gas sample was then taken by attaching an evacuated stainless steel sample container (for container details see ref. 3) to one end of the hose, opening the valve on that end of the hose and the valve on the container, allowing the container pressure to equilibrate with the hose pressure, closing the valves, and then removing the container. A second sample was taken in similar manner immediately following the first. Samples were analyzed for volatile hydrocarbons using gas chromatography (GC) with flame ionization detection (FID) and mass spectrometry (MS) as previously described (4). Sample concentration was performed prior to GC/MS to facilitate identification of trace level analytes. Analysis results indicated significant toluene contamination (approximately 14 ppm absolute or 136 ppm surface equivalent value (SEV) after multiplication by 8.6 ATA to correct for the test pressure at time of sampling). Small amounts (< 1 ppm) of at least two unknown hydrocarbons were also detected.

We found the level of volatile hydrocarbons measured in the four hoses to be unacceptable for our use. Therefore, at our request, the supplier of the hoses agreed to furnish six new hoses of identical type. These were all cleaned and tested in similar fashion as before by connecting all six together in a series. Hoses were left pressurized for 42 h before sampling during the first test; only 4 h was allowed during the second test. Analysis results indicated that the new hoses also offgassed significant amounts of hydrocarbons. The 42-hour soak at pressure resulted in a buildup of approximately

25 ppm SEV toluene (corrected for 7.9 ATA, the pressure at time of sampling) and small amounts of other unknown chemicals. A 4-hour soak resulted in a buildup of approximately 15 ppm SEV of toluene (corrected for 6.3 ATA), which was surprisingly high considering the short time involved. Again, trace amounts of several unknowns were also detected.

Evaluation of these results was difficult because we had no prior hose data to use as a comparison. Our detection of significant amounts of toluene agreed with the information that the manufacturer had provided. Considering the hydrocarbon levels we observed from our hoses under no-flow conditions and the relatively high 28 ℓ/min test flow in the military specification, we thought at the time that it was likely that at least the second batch of hoses would have passed the MIL-H-2815G offgassing test. This conclusion assumed that these hoses were representative of this type of hose and that the contamination would be quickly removed by a minimal amount of flushing prior to use. The new hoses were, therefore, put into use with the recommendation that prior to actual inhalation of gas, hoses be adequately blown down (i.e., at least 5 min at normal flow rates) with the breathing gas as is standard practice during diving operations.

Offgassing Tests

Following the above incident, we continued our investigation into the safety of diver's breathing hoses. We were concerned that breathing hoses that appeared to meet MIL-H-2815G also seemed to be a constant source of a potentially harmful aromatic hydrocarbon. Because of this offgassing, we wanted to examine the effectiveness of purging hoses to remove contamination that had built up during storage.

Six tests with four hoses from the original hose batch were conducted over a 3-month period. Two of these hoses had been previously cleaned as described; the other two hoses had not been cleaned. For purposes of discussion, these hoses have been arbitrarily numbered 1 to 4. Each test consisted of first purging and subsequently pressurizing each hose to 10.3 to 11.0 ATA with clean N_2 in a similar manner as before. Hoses were then stored at room temperature (20 to 25 °C) for 7-9 days. In four of the tests, two samples were then taken from each hose: an "outer hose" sample taken initially as before, and a second "inner" hose sample taken after the hose had been bled down to approximately one-half the starting pre-sampling pressure. No samples were taken during two of the tests.

Following sampling, all hoses were bled down to atmospheric pressure and set up to allow purging with clean N_2, while continuously monitoring the outflowing gas for hydrocarbons using a portable Photoionization Detector (PID, model PI 101, HNU Systems Inc., Newton Highlands, MA). In our application, a whip supplying N_2 was attached to one end of the hose via a clean stainless steel fitting, and a clean stainless steel T-connection (12-inch long, 1/4 inch o.d. pipe with a 2-inch long, 1/2 inch o.d. pipe side port) was attached to the other end. A flowmeter was connected to the outflow end of the 1/4 inch pipe of the T-connection whereas the gas was sampled by inserting the tip of the PID probe into the 1/2 inch side port.

The test was begun by turning on the N_2 and quickly adjusting the flow to approximately 12 to 14 ℓ/min as all flow was directed to the flowmeter by blocking completely the sideport. Flow adjustment generally took no more than 10 sec. The side port was then uncovered so that most of the gas flowed from it and the PID probe was loosely inserted to enable monitoring at 1 ATA for up to 40 min. Every 5 to 10 min, the flow was checked and adjusted, if necessary, after first temporarily closing off the side port as before. Flow never deviated more than 1-2 ℓ/min from the initial setting.

Before use, the PID was calibrated using a gravimetric standard of isobutylene/balance air at a concentration of approximately 12 ppm certified to ± 2% relative of stated value (Scott Specialty Gases, Plumsteadville, PA). Measurements were, therefore, in ppm of isobutylene equivalents in air. The PID, which is a general hydrocarbon analyzer, was equipped with a 10.2 ev UV lamp. This lamp gave it sufficient sensitivity to detect < 1 ppm of aromatic hydrocarbons, such as toluene. Although the PID is a fairly nonselective instrument that responds to a broad range of hydrocarbons, it can be used as an effective screening tool. In instances where the chemical contaminants have been identified (e.g., toluene in this case), quantitation may be possible if the sensitivities of the chemical species relative to the calibration gas (i.e., isobutylene) are known.

Initial PID readings ranged from 4 to 55 ppm isobutylene equivalents (Fig. 1). All PID readings reported here have been reduced by 1 ppm to correct for the PID response of hydrocarbon-free N_2, which was confirmed several times during each test. In all cases but one, PID readings fell by less than 50% following 15 min of purging at 12 to 14 ℓ/min. These small declines are surprising considering that each 50-foot hose was purged during this time by the equivalent of approximately 200 times its internal gas volume.

Table 1 compares the GC analytical results (i.e., toluene levels) to the initial and 15-min PID measurements of the gas flowing from the hose. For this comparison, PID measurements have been converted from ppm isobutylene equivalents in air to ppm toluene equivalents in N_2 (the purging gas) by dividing by 2.8, the correction factor as determined by our laboratory. GC samples and initial PID readings compare favorably, although not exactly, as would be expected as toluene was the predominant contaminant and produces a strong PID response. The influence of low levels of other hydrocarbons in the purging gas on the PID measurements would depend on whether they produce a strong or weak PID response. No relation between cleaning and relative level of chemical contamination is suggested by these limited data: the two hoses with the highest toluene levels (hoses 2 and 3) include one that had been cleaned and one that had not been cleaned. However, manufacturer representatives indicated in discussions with us in February 1992 that four of the original six hoses that NMRI received were from a defective lot of hoses that exhibited unacceptable levels of offgassing. Hoses 2 and 3 are from this defective lot.

As in prior analyses, several unknowns were detected at very low levels (< 1 ppm). In samples from at least three different hoses, one of these chemicals was identified by GC/MS to be carbon disulfide. This was confirmed by injection of a known sample of carbon disulfide into our analytical system.

DISCUSSION

The hoses that we tested appear to be a constant source of toluene, a common industrial solvent, as well as smaller amounts of other compounds including carbon disulfide, a relatively toxic species. Information from the manufacturer suggests that this offgassing phenomenon is characteristic of all of their diver's hoses. Although this property does not necessarily make such hoses unsafe, it does suggest that there is a potential for chemical problems with their use for diving. Our episode with the defective hoses suggests that there is a real possibility for unsafe hoses to reach the user. Surprisingly, we found that purging these hoses at flow rates similar to those that might be used during diving does not quickly reduce the hydrocarbon levels of gas leaving the hose. These observations raise at least two important questions relative to chemical safety of diver's hoses: 1) Is the current specification MIL-H-2815G appropriate for normal operational use? and 2) Should the user be required to perform any cleaning and/or testing of these hoses?

The most recent scientific evaluation of offgassing from diver's hoses that was found was done over 20 years ago by Vind and Mathews (5). This study reviewed the literature related to hose offgassing and performed limited experiments using a total hydrocarbon analyzer and a sulfur dioxide analyzer. Based on expected offgassing species and their relative toxicity, they proposed two hose-acceptance tests: one measuring total hydrocarbons in closed hoses and the other in hoses after being flushed. Concentrations of up to 50 mg of organic carbon/m^3/ft were permitted in air confined in hoses for at least 7 days; these concentration units are similar to methane equivalents. Their flushing test was similar to MIL-H-2815G but done at the higher rate of 3 ft^3/min for 15 min with a maximum permissible hydrocarbon of 0.01 organic carbon/m^3/ft of hose or a maximum of 4 mg/m^3 regardless of length. These limits appear to be considerably stricter than that of 100 mg/m^3 methane equivalents per 100 ft following 15 min flushing in MIL-H-2815G. Interestingly, Vind and Mathews (5) described poor success trying to clean up hoses that offgassed at high rates despite the use of high temperatures and long flushing.

Comparison of our data to the MIL-H-2815G limit of 100 mg/m^3 methane equivalents per 100-foot length requires conversion of the limit to ppm of toluene. To do this, mg/m^3 methane is first converted to ppm methane using the molecular weight of methane and the definition of ppm. The result is then converted to toluene equivalents based on the relative response of toluene to methane on a ppm basis. In this case, we divide by 6.9, the FID response factor of toluene relative to methane determined on our GC's; this factor would be expected to be similar for a total hydrocarbon analyzer. In this manner, the limit 100 mg/m^3 is converted into approximately 22 ppm toluene; interpolation for a 50-foot hose would yield approximately 11 ppm although MIL-H-2815G does not address such interpolation. Although suitable guidelines for chemical exposure limits do not exist for hyperbaric conditions, 22 ppm toluene is well below the time-weighted average (TWA) limit of 100 ppm toluene set by the American Conference of Governmental Industrial Hygienists (6) for a normal 8-hour workday/40-hour work week.

The highest level of toluene observed in our initial batch of hoses (which included two defective hoses) was approximately 136 SEV after storage under pressure for 60 h. Although this concentration was determined at pressure, comparable toluene levels might be expected to develop in hoses stored at 1 ATA. If this were the case, we would expect that some hoses of this initial batch, when connected together in pairs would not pass the offgassing test in MIL-H-2815G in view of the apparent ineffectiveness of gas purging to quickly reduce hydrocarbon levels. This situation would be likely if a phase equilibrium is occurring where toluene is diffusing from the inner core of the hose into the gas phase until its partial pressure equilibrates with the toluene dissolved in the rubber. The level of toluene that buildups in the gas would depend on the amount of toluene dissolved in the hose and the solubility coefficient for toluene in the rubber. Because toluene may not be homogeneously distributed in the hose, the equilibration chemistry may not be simple.

Because the rationale for the offgassing test in MIL-H-2815G is unclear, we can rely only on our findings to judge whether the test meets its objective of insuring hose safety. On this basis, we conclude that accurate screening by MIL-H-2815G can be assured only if the following conditions exist:

1. Toluene must be the principal offgassing species. Other compounds must be at negligible levels relative to their potential hazard or their impact on diver safety needs to be addressed.
2. The hoses that are tested by the manufacturer must accurately represent the chemical properties of hoses that are actually used.

3. Contamination levels in gas after 15 min flow at 28 ℓ/min under conditions detailed in MIL-H-2815G must relate well to hydrocarbon levels to which divers are exposed during operations using these hoses.

It is unknown how well conditions 1 and 2 hold. Our data suggests that toluene was the principal contaminant in the 10 hoses that we tested with GC; however, we have no data on any other hoses. Unfortunately, our detection of a highly toxic non-hydrocarbon such as carbon disulfide in gas from diver's hoses questions the approach of screening these hoses with only a hydrocarbon analyzer.

Company representatives have indicated that the manufacturing process for their hoses has undergone changes over the last few years. This raises the issue of differences among hoses that are currently being used in the Fleet and how well our results apply in general. The two defective hoses cannot be considered representative of normal hoses. Another factor is the age of the hoses; new hoses would be expected to offgas manufacturing chemicals more than old hoses. However, old hoses may have absorbed contaminants through use in the Fleet and could be a potential source of these chemicals.

MIL-H-2815G states that diver's hoses must be tested to insure that offgassing does not exceed the specified limit, but does not address testing frequency or circumstances that would require retesting, such as when changes are made in the manufacturing process. The fact that defective hoses were delivered to the supplier and then to NMRI suggests that chemical screening of selected hoses for quality control may not be routinely done by all manufacturers.

We believe, for a number of reasons, that hydrocarbon levels in the gas delivered from diver's hoses may at times exceed levels that would be measured during the MIL-H-2815G test. First, minimal purging of hoses prior to use may result in elevated hydrocarbon levels. This could easily occur if relatively rapid hydrocarbon buildup during stagnant conditions and slow decline during flow is characteristic of diver's hoses. Second, actual exposure levels might be further increased via pressurization as the diver descends to depth. However, the actual effect of pressure on hydrocarbon accumulation is unknown, for pressure may have hard-to-predict effects on the movement of solvents from the rubber into flowing gas. Here, pressurized gas is flowing through a hose and picking up contamination and exposure levels probably would not increase proportionally with pressure, as would be the case if we were considering pressurization of gas that was already contaminated. Third, diving under conditions where air and/or water temperatures exceed the lower test limit of 23 °C would promote greater offgassing from the inside of the hose by raising the vapor pressure and permeation rates of any solvents in the rubber. It is unknown whether any additional chemical species might be seen under the pressure/temperature conditions just described, which could differ markedly from test conditions in MIL-H-2815G.

At least two U.S. Navy instructions (2,7) detail procedures for O_2 cleaning of hoses so that non-volatile hydrocarbons are removed; unfortunately, these documents are not in agreement. Other U.S. Navy documents (8,9) are unclear regarding hose cleaning. As mentioned earlier, MINSY Process Instruction No. 0558-839F Ch-2 (2) calls for TSP cleaning of hoses. Charleston Naval Shipyard Process Instruction No. 0558-839-701-CH-4

(7) specifies hose cleaning by either TSP or Freon, as long as the hose components are compatible with Freon. Unfortunately, incompatibility is defined in terms of degradation of the hose rather than the potential for solvents to permeate into the hose material, resulting in offgassing at a later time. Although the literature is devoid of formal documentation of this problem, a letter report from the Naval Research Laboratory stated that hoses washed with Freon-113 deteriorated rapidly and contaminated the breathing gas with solvent (5). Our experience indicates that after softgoods (e.g., rubber, teflon, soft plastics) are exposed to organic cleaning solvents (e.g., alcohol, Freons, methyl chloroform), these materials will often offgas these solvents for a long time (e.g., weeks or months) afterwards. Therefore, it is our policy to recommend that no softgoods used for diving, including hoses and masks, be exposed to any organic solvents.

We are unaware of any recent health or safety problems that can be attributed to the offgassing properties of normal diving hoses. However, this record of apparent safe use should not be used to minimize concern regarding hose safety. We believe that existing U.S. Navy instructions and specifications for diver's hoses may not adequately reflect current legal and health aspects of chemical exposures. Particularly important may be the cumulative effect of low-level exposures to toxic compounds that can occur over time and produce delayed responses even years later. Underlying our concern is the scarcity of data on the chemical properties of hoses widely used for Navy diving.

CONCLUSIONS

a. The rationale behind the offgassing test in MIL-H-2815G is uncertain. Such a specification should be designed to screen for all potentially hazardous chemical species known to offgas into the hose gas. This screening should be based on the actual operational conditions (e.g., gas flow, ambient temperature ranges, pressure ranges) and procedures (e.g., amount of pre-use purging, how hoses are stored between operations) of hose use. Worst case situations should be considered. MIL-H-2815G does not appear to address these issues.

b. MIL-H-2815G does not detail requirements of offgas testing in terms of frequency of testing (e.g., what percentage of hoses) to promote detection of chemically unsafe or defective hoses. Certainly, increased frequency of testing might be appropriate in certain circumstances as when changes in manufacturing processes have occurred.

c. U.S. Navy instructions on O_2 cleaning of hoses are not in agreement and, thus, cause confusion. In our view, Freon cleaning of hoses is inappropriate and may make hoses unsafe for use due to permeation of the solvent into the hose and later offgassing into the breathing gas.

d. Relatively simple chemical testing (such as that described here with the PID) may be effective for initial and periodic screening hoses by the user. The usefulness of such testing should be evaluated and any suitable procedures provided to the user.

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TABLE 1

OFFGASSING TESTS WITH 4 HOSES

Toluene levels reported in ppm, uncorrected for test pressure following 7 to 9 day storage under pressure at 10.3 to 11.0 ATA. GC results are compared to PID readings that have been corrected to toluene equivalents in N_2. Six tests over a 3-month period are presented; sample dates are noted. Hoses 1 and 3 tested 2 different times. Outer samples taken initially; inner samples taken after bleeding down to one-half starting pressure.

	GC (ppm toluene)	PID (ppm toluene - purge time)
14 May 1991		
hose 1 - not cleaned	no samples	2.6 - 4 min 2.1 - 15 min
hose 2 - cleaned	no samples	19.6 - <1min 6.8 - 15 min
29 May 1991		
hose 3 - not cleaned	10.0 - outer 14.0 - inner	7.9 - 2 min 4.3 - 15 min
hose 4 - cleaned	0.8 - outer 1.4 - inner	1.4 - 4 min 1.0 - 15 min
7 Aug 1991		
hose 1 - not cleaned	0.6 - outer 0.8 - inner	1.3 - <1 min 0.9 - 15 min
hose 3 - not cleaned	1.6 - outer 4.7 - inner	2.5 - 1 min 1.4 - 15 min

FIGURE LEGENDS

Fig. 1a/b: Hydrocarbon levels decline slowly with time as 4 hoses (#1-4) are purged with 12 to 14 ℓ/min N_2. Hoses #1 and #3 were tested 2 different times as detailed in Table 1. Measurements were made with a PID.

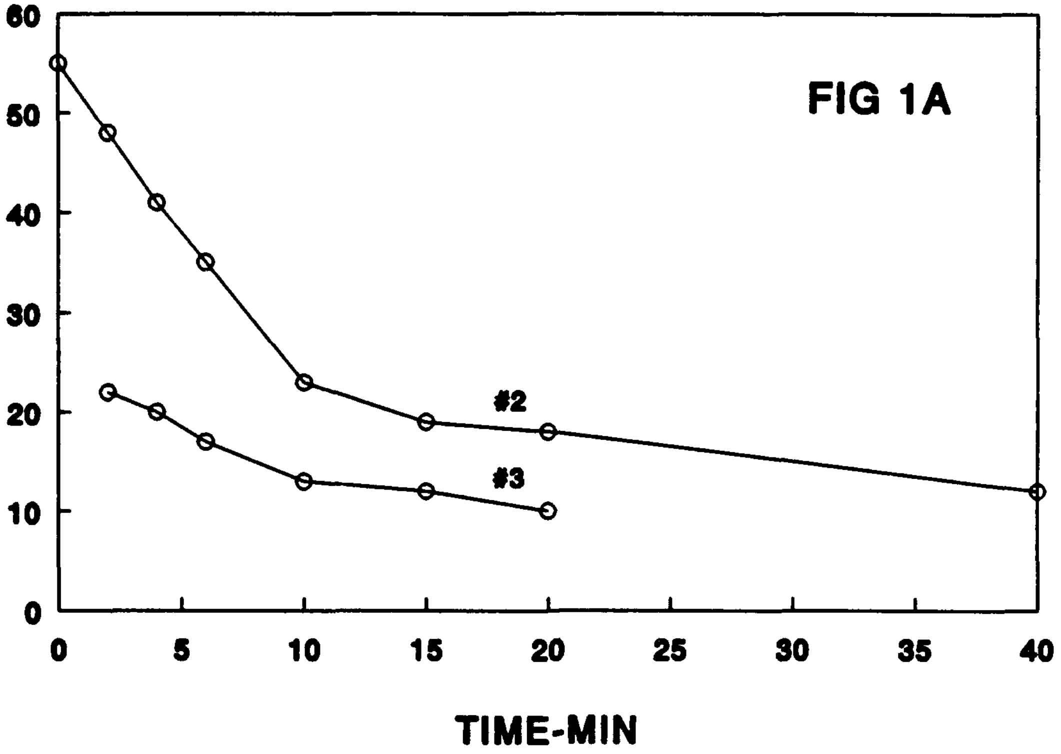
PPM HYDROCARBONS
60
50
40
30
20
10
0
#2
#3
0
5
10
15
20
25
30
35
40
TIME-MIN

FIG 1A

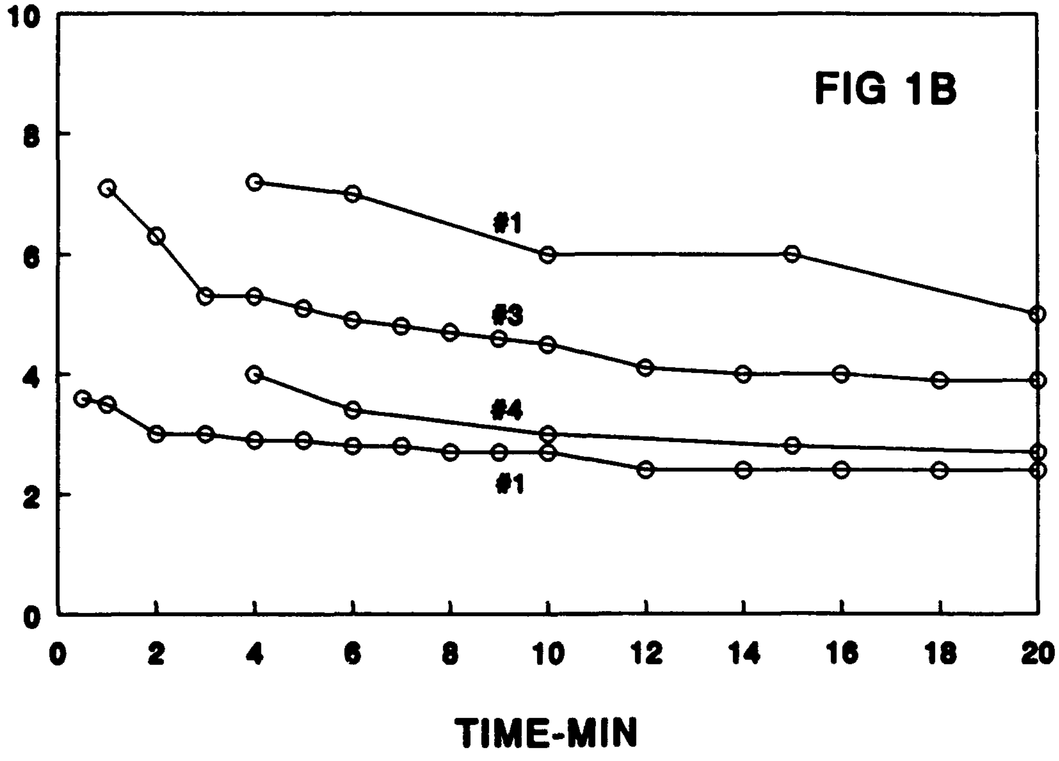
10
8
6
4
2
0
#1
#3
#4
#1
0
2
4
6
8
10
12
14
16
18
20
TIME-MIN

FIG 1B