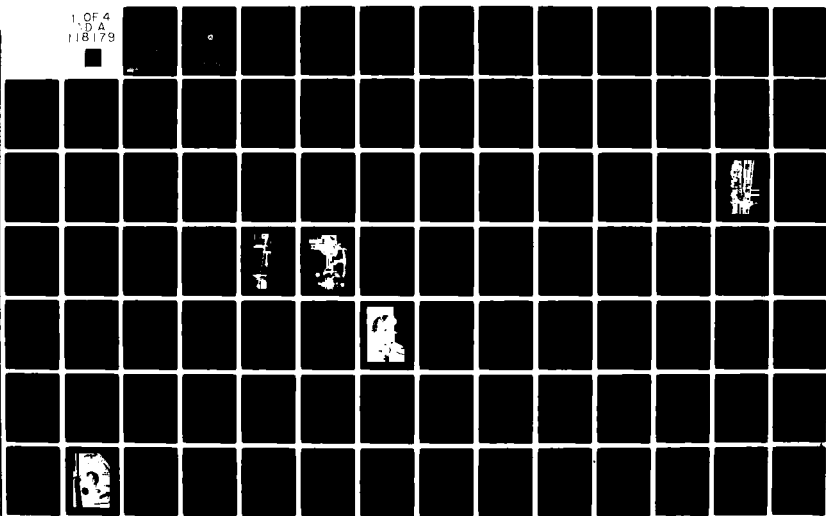


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A Crew Exposure Study - Phase I Volume II - At Sea

W. J. Astleford, et al

Southwest Research Institute
San Antonio, Texas

15 March 1982

Report No. CG-D-22-82

**A CREW EXPOSURE STUDY — PHASE I
VOLUME II — AT SEA**

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16. Abstract An assessment of worker exposure to potentially hazardous gases, vapors, mists, and dusts in the marine bulk liquid transportation industry is provided. Methodology for characterizing occupational exposures of crewmen to cargo- and noncargo-related materials during vessel operations in port and at sea was established. The major elements of the project included (1) a background study, (2) development of an experimental plan, and (3) trial implementation of the plan on one test at sea. The background study consisted of a search of the open literature and discussions with international maritime organizations for relevant industrial hygiene/occupational health study data. Also, two round-trip voyages aboard a product tanker and a gasoline carrier were conducted to document sources which may pose potential inhalation or dermal exposures. The background study was used to develop an experimental plan for characterizing the occupational exposures aboard bulk liquid carriers. Ten voyages were identified as necessary to reflect a representative data base covering variations in equipment, procedures, and cargos. The experimental plan was implemented in the Deck Department on one voyage of a chemical carriers. The remaining voyages are to be conducted in a Phase II follow-on to this project.					
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ACKNOWLEDGMENTS

A project of the scope of this Crew Exposure Study requires the commitment and participation of many individuals and organizations.

We wish to acknowledge the technical guidance, encouragement, and assistance of the U. S. Coast Guard personnel who have been involved with this project since its inception, especially the contributions of Lt. Guy R. Colonna, the project Technical Monitor, and Mr. Michael Morrisette of the Hazardous Materials Division. Also, special thanks are extended to Mike Flessner for his contributions during the early part of the project while he was still with the USCG.

The objectives of this project could not have been met without the direct participation and cooperation of ship owners, ship charterers, terminal operators, and the ship's crews. We gratefully acknowledge their commitment of time, personnel, and facilities, and we trust that their interest and involvement will continue in Phase II.

The written materials that were generated on this project were submitted for external review to an industrial hygienist, occupational physician, and a toxicologist, all of whom are board-certified and have prior experience in the marine work environment. Specifically, we appreciate the efforts of Professor James W. Hammond and Drs. Gordon W. Newell and Robert A. Wise.

Special thanks are extended to the many individuals at Southwest Research Institute who provided support services for this project, especially Mrs. Cathy Dean and Mrs. Dorothy Endicott for their skillful typing of this large manuscript.

EXECUTIVE SUMMARY

"A Crew Exposure Study - Phase I" is the title of a research project that has assessed the exposure of workers to potentially hazardous gases, vapors, mists, and dusts, in both the marine bulk liquid transportation industry and the offshore oil and gas exploration/production industry. Because these industries differ with respect to their basic operations, chemical substances in the work environment, exposure potential and work schedules, the results have been published in two volumes.

- o Volume I - Offshore
- o Volume II - At Sea

This volume addresses the At-Sea portion of the study.

The objective of this study was to develop and implement, on a trial basis, methodology for characterizing occupational exposures of crewmen to cargo- and noncargo-related materials during vessel operations in port and at sea. Bulk liquid cargos were defined to include pure chemicals, gasoline, and crude oil, but excluded specialty products having proprietary composition. The vessels that transport these liquids include true parcel chemical tankers, product tankers that can carry chemicals as well as petroleum derivatives, ocean-going manned barges, and crude oil tankers.

Most tanker voyages consist of four operational phases:

- o Cargo loading
- o Laden leg to the discharge port(s)
- o Cargo discharge
- o Ballast leg

All four of these phases are included in this study, which represents a logical extension of other Coast Guard-sponsored research that has investigated marine terminal operations during product loading.

The major elements of this Phase I effort included (1) a background study, (2) development of an experimental plan, and (3) implementation of the plan on one full-scale test.

Background Study

The objective of the background study was to generate an information and experience base that would define the potential for occupational exposures at sea and lead to development of an experimental plan for characterizing the exposures.

Initially, the open literature was searched for reports on past and current industrial hygiene/occupational health studies on exposure monitoring in the marine chemical transportation industry. Domestic and international maritime organizations and agencies were then contacted to determine the extent of any similar research efforts and to obtain the relevant documentation. These activities produced the following conclusions:

- o The Crew Exposure Study does not duplicate current or past efforts of other organizations or agencies.
- o Studies of occupational exposures in the marine environment are not available in the open technical literature.

The background study was then expanded to include two round-trip voyages aboard a product tanker and a gasoline carrier with the objectives to

- o document sources that generate or release vapor, dust, mist, gas, and liquid into the work place and which may pose a potential for inhalation or dermal exposure; and
- o document work activities, the duration of these activities and the tankerman's proximity to the identified sources.

Walk-through surveys, emission inventories, and environmental monitoring (personal and area) were conducted in both deck and engine departments. Both cargo- and noncargo-related sources of exposure were considered. Vapor infiltration into living quarters was investigated. Entry into confined spaces (cargo tanks, ballast tanks, pump room) was observed, documented, and monitored.

The combined results that were obtained from these background voyages are as follows:

- o Airborne asbestos and oil mist concentrations in both Engine Rooms were below established exposure limits.
- o Extended work schedules existed on both vessels. While some crew members worked a standard 8-hour day, Deck Department operations during loading, discharging, and tank cleaning resulted in continuous work periods ranging from 13 to 30 hours.
- o On one vessel, vapor infiltration through the Engine Room ventilation system resulted in a peak total hydrocarbon concentration (as methane) of 27 ppm during loading which was roughly twice the level that existed while the vessel

was underway at sea. On the other vessel, measured concentrations were less than 10 ppm (as methane) in port and at sea.

- o The deckhouses on both vessels had closed, recirculating ventilation systems. However, cargo vapors infiltrated the deckhouses through access doors during loading, tank cleaning, and ballasting of cargo tanks.
- o On both vessels, environmental monitoring was conducted for the benzene fraction in gasoline vapor. For the gasoline carrier, occupational exposure and area concentrations were less than 8 ppm for sampling durations up to 6.5 hours (relative to the ACGIH TLV-TWA of 10 ppm). However, open tank gauging through tank top-off produced estimated time-weighted average exposures to total gasoline vapor that equaled or exceeded the ACGIH-recommended TLV-TWA of 300 ppm. On the chemical tanker, area samples in the pumproom and at the pumproom ventilation system exhaust, which was located in a work traffic lane, produced benzene concentrations that were roughly half of the ACGIH TLV-TWA. Both locations resulted in estimated total gasoline vapor concentrations that exceeded the TLV-STEL of 500 ppm during the sampling period. On a time-weighted average basis, the pumproom exhaust level exceeded the TLV-TWA for total gasoline vapor.
- o Occupational exposures to multiple chemical vapors were monitored during loading, discharging, and ballasting operations on the chemical tanker. The use of restricted gauging systems during these operations produced occupational exposures to individual chemicals that did not exceed recommended exposure limits. Exposures to vapor mixtures did not exceed 24 percent of the mixture Threshold Limit.
- o Crew members entered product tanks, segregated ballast tanks, and the pumproom to clean the bilge. Entry into gasoline product tanks following cleaning resulted in a benzene exposure level of 38 percent of the TLV-TWA for an 82-minute exposure and an estimated exposure level to total gasoline vapor that exceeded 500 ppm, the ACGIH TLV-STEL. When debris on the tank floor was disturbed, instantaneous total gasoline vapor concentrations exceeded 4,000 ppm as measured with a direct reading instrument (OVA). Entries into chemical product tanks resulted, in one case, in an exposure to ethyl alcohol of 20 percent of the TLV-TWA over a 30-minute period and, in another case, an 84-minute combined exposure to ethyl alcohol and epichlorohydrin (suspected leak from an adjacent tank) that represented 27 percent of the mixture Threshold Limit. Vapor levels in the segregated ballast tanks were not detectable. Benzene exposure levels in the pumproom did not exceed 1 ppm during bilge mucking.

- o It is not feasible to use passive dosimeters as stationary monitors in crew accommodations because air velocities are less than the manufacturer's recommended operating limit.
- o Dermal contact with cargo liquids occurs during removal of flange blinds at the cargo manifold, hose hookup, hose disconnect, and when the ship's product transfer lines are drained. Accidental eye contact with gasoline occurred once.
- o Potential exposures to noncargo-related materials that were observed, but not quantified, occurred during sandblasting, spray painting, spraying of rust deactivators, and the use of general purpose cleaning solvents.
- o Consumption of soft drinks on deck during cargo transfer operations presents the potential for ingestion exposure.
- o Exposure monitoring is impeded when the sampling device is shielded from the exposure environment during heel stripping and when tankermen do not wear .

Experimental Plan

Based upon the results of the background voyages, a plan was developed for characterizing the occupational exposure profiles of tankermen aboard bulk liquid carriers.

The objective of the plan was to ensure that the exposure monitoring results would reflect a representative cross-section of the tanker industry with respect to equipment, procedures, and classes of liquid cargos. To this end, ten voyages were identified. Each voyage was associated with a specific vessel that exhibited combinations of configurational and operational variables that are known to or are assumed to influence the potential for occupational exposures. In the aggregate, these vessels transport pure chemicals, gasolines, and crude oils. While both the Deck and Engine Departments are represented in the plan, the emphasis is placed on the Deck Department.

Work schedules and the products carried will vary with each voyage. For this reason, the exposure monitoring plan contains a degree of generality; the plan can be made more specific when exact product loading plans and work schedules become known. The sampling plan is based upon a postulated voyage scenario and a number of assumed, but unspecified, cargos. Within this framework, it was possible to estimate the numbers and types of exposure samples (based on experience and NIOSH sampling protocols), as well as equipment requirements. The key elements of this sampling plan are summarized below.

- o Voyage scenario - 14-day round trip that includes loading, discharge, laden leg, and the ballast leg during which tanks are cleaned and entered.

- o Loading plan - Seven chemicals of interest in 12 tanks.
- o Two crew members would be monitored on each voyage. In the aggregate, all levels of licensed and unlicensed seaman would be represented.
- o Monitoring would include normal and extended work periods. A choice of instrumentation methods is suggested for monitoring the living environment in the crew's quarters during off-watch periods. In this latter case, the concern is for vapor infiltration into accommodation areas.
- o The plan acknowledges the extended or unusual work schedule and includes cargo-related exposures as well as those that are not cargo related, such as sandblasting and spray painting activities.
- o With respect to cargo vapor monitoring, the plan emphasizes the use of traditional solid sorbent methods (pumps and tubes). Passive dosimeters may be used in parallel with the tubes if logistics and costs permit. Some chemical vapors require the use of impingers for sampling. These devices are not really compatible with personal monitoring aboard ship, and they are best utilized as area monitors.
- o Sampling and analysis would be conducted in accordance with NIOSH-recommended procedures.
- o The plan includes short-term samples for high-probability exposure situations such as tank top-off with open gauging and tank entry for cleanup.
- o For other than the short-term cargo vapor exposures, the plan is based on product vapor samples of one hour in duration. This basis is consistent with the sampling duration for many chemicals as recommended by NIOSH. The plan, however, must be flexible so that durations can be extended in situations where it is known that the potential for exposure is low. In the final analysis, the plan must be fine tuned based upon the actual products that are involved, and it must respond to shipboard conditions that may differ from those in the plan.
- o In addition to inhalation exposures, dermal exposures are also evaluated.
- o Work activities of the selected crew members would be documented in conjunction with the personal monitoring tasks. Items of interest from an interpretation standpoint include the nature of the work activity and its duration, proximity to sources of airborne contaminants, and the use of any protective equipment.

- o Where multiple chemical exposures are likely, these would be duly noted and would be reflected in the sample analyses.
- o With respect to multiple vapor sampling, the key is noninterference with the work activity. A crew member can accommodate two sets of pumps/tubes and a passive dosimeter without reducing his work efficiency.

The experimental plan outlines a combined approach for interpreting exposure data.

- o Apply the ACGIH methodology for time-weighted average exposures to single chemicals during selected 8-hour periods.
- o Apply the ACGIH additivity criterion for vapor mixtures.
- o Assess ceiling exposures in the usual fashion and interpret the TLV-STEL as an MAC (Maximum Allowable Concentration).
- o For a single chemical exposure during an extended work period, apply the OSHA compliance criteria based on calculated upper and lower confidence limits.
- o Where appropriate, interpret extended work period exposures relative to limits that are derived from mathematical models for TLV-TWA adjustment factors.

Implementation of the Experimental Plan

The experimental plan was implemented in the Deck Department on one voyage in Phase I with the remaining voyages to be conducted in Phase II. The test was conducted aboard a vessel that exhibited the following selection criteria:

- o Maximum crew size,
- o Double-bottom product tanks that are free of internal structure,
- o Single aft deckhouse,
- o Closed gauging system on all product tanks,
- o B/3 vents on all product tanks, and
- o Vapor return system on selected cargos.

Two additional operational variables were encountered which had not been included in the test plan.

- o Short-loading of product tanks, and
- o Shore-stop on cargo transfers.

The voyage consisted of docking at eight terminals in seven days for the purpose of loading 19 products and discharging one product. Of these 20 products, 13 were included in the sampling plan. Two able-bodied seamen who worked cargo transfer watches were monitored. In addition to this primary objective, additional operations that were documented and/or monitored included tank cleaning and tank entry. The major results from this voyage are as follows.

- o The vast majority of the vapor concentrations that were obtained from the occupational exposure samples during cargo transfer were not detectable. This result reflects the combined effect of shore-stop, short-loading, and a gauging method that involved standing on the expansion trunk hatch cover. For these cases, individual exposure limits and mixture threshold limits were not exceeded.
- o Of the products loaded, only the carbon tetrachloride tank was filled to near capacity without the aid of a vapor return system. On one occasion, the data indicated that the mixture threshold limit for simultaneous exposure to carbon tetrachloride and 1,1,1-trichloroethane may have been exceeded.
- o Exposures during tank entry did not exceed the TLV-STEL. Time-weighted average exposure levels were less than the TLV-TWA.
- o Gas chromatographic analyses of the deckhouse environment revealed that there were no detectable peaks corresponding to the products that were transferred.
- o Loaded, closed tanks emit fugitive vapors to the work environment. These emissions were eliminated when the tanks were sealed with an epoxy resin, which was used to protect gasket materials.

Closure

Occupational exposure profile monitoring in the marine environment is feasible. The experimental plan was implemented, and only minor modifications are indicated for the Phase II study. The results from the first implementation test represent a valid data point in the total spectrum of tanker operations.

TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES	xvii
LIST OF TABLES	xviii
GLOSSARY OF TERMS	xix
GLOSSARY OF CHRIS ABBREVIATIONS FOR VOYAGE CHEMICALS	xx
 I. INTRODUCTION	
I.1 Background	1
I.2 Objectives	1
I.3 Perspective	3
 II. BACKGROUND STUDY	5
II.1 Literature Search	5
II.2 Related Occupational Health Investigations	5
II.3 Pertinent Regulations	8
II.4 Chemical Cargo Property Data	9
 III. PRELIMINARY VOYAGE OBSERVATIONS	11
III.1 Observation Objectives	11
III.2 Manned Barge - Gasoline	12
III.2.1 Voyage Overview and Observation Plan	12
III.2.2 Summary of Project Activities	13
III.2.3 Environmental Monitoring - Methods and Results	13
III.2.4 Data Interpretation	18
III.2.5 Summary of Important Results	24
III.3 Parcel Chemical Carrier	28
III.3.1 Voyage Overview and Observation Plan	28
III.3.2 Summary of Chemical Tanker Activities	29
III.3.3 Environmental Monitoring - Methods and Results	29
III.3.4 Data Interpretation	32
III.3.5 Summary of Important Results	40
III.4 Work Schedules	43
III.5 Work Practices	46
 IV. DEVELOPMENT OF AN EXPERIMENTAL PLAN	49
IV.1 Approach to Plan Development	49
IV.2 Elements of the Experimental Test Plan	50
IV.2.1 Vessel and Voyage Selection Criteria	50

	<u>Page</u>
IV.2.2 Sampling Plan	52
IV.2.3 Data Interpretation	55
IV.3 Impact of Analytical Modeling on the Experimental Plan	57
V. IMPLEMENTATION OF EXPERIMENTAL PLAN	59
V.1 Vessel Selection	59
V.2 Voyage Summary	60
V.3 Assessment of Operations	61
V.4 Potential for Occupational Exposure	65
V.5 Vapor Monitoring - Results and Interpretation	67
V.6 Assessment of the Experimental Plan and Implementation Test with Recommended Modifications	71
VI. SUMMARY AND CONCLUSIONS	75
VI.1 Summary	75
VI.2 Conclusions	76
REFERENCES	81
APPENDIX A: Categorized Bibliography	
APPENDIX B: Interpretation of Occupational Exposure Data	
APPENDIX C: Summary of Regulations	
APPENDIX D: Property Data for Chemical Cargos	
APPENDIX E: Background Voyage Report - Manned Barge - Gasoline	
APPENDIX F: Background Voyage Report - Parcel Chemical Tanker	
APPENDIX G: Experimental Test Plan	
APPENDIX H: Task IV Voyage Report	

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
III.1	Tankerman Open Gauging Product Ullage at Tank Top-off. Gauging Tube Terminates at Weatherdeck.	20
III.2	Tankerman Observing Cargo Level and Pump Inlet During Heel Stripping	26
III.3	A Difficult Monitoring Situation - The Shirtless Work Environment	27
III.4	Tankerman Gauging Cargo Ullage Through a Restricted Gauging System (Sounding Tube) that Penetrates the Liquid Surface	42
V.1	Tankerman Gauging Product Ullage from On Top of Expansion Trunk Hatch	66

LIST OF TABLES

<u>Table</u>	<u>Page</u>
II.1 Computer Search Strategy	6
II.2 Productivity of Composite Search	6
II.3 Categorization and Minimum Requirements of Commonly Carried Chemicals	10
III.1 Voyage-Related Activities	14
III.2 Summary of Environmental Area Monitoring Data for Asbestos and Oil Mist - Engine Room	16
III.3 Summary of Environmental Monitoring Data for Benzene in Gasoline - Deck Department (At Sea and In Port)	17
III.4 Voyage-Related Activities	30
III.5 Summary of Charcoal Tube Sampling Information for Chemical Cargos	32
III.6 Summary of Environmental Monitoring Data from Parcel Chemical Tanker Operations - Deck Department (At Sea and In Port)	33
III.7 Summary of Environmental Area Monitoring Data for Asbestos and Oil Mist on Parcel Chemical Carrier - Engine Room (At Sea)	35
III.8 Calculated Fractions of Mixture Threshold Limits for Multiple Vapor Exposures	37
IV.1 Voyage Identification and Vessel Characteristics	53
V.1 Venting/Gauging Requirements Vs Operational Practice for Subchapter O Commodities	63
V.2 Summary of Short-Loadings	67

GLOSSARY OF TERMS

A/B	- Able-Bodied Seaman
ACGIH	- American Conference of Governmental Industrial Hygienists
AIHA	- American Industrial Hygiene Association
B/3	- Ship's Beam/3
CHRIS	- Chemical Hazards Response Information System
LEL	- Lower Explosive Limit
MAC	- Maximum Allowable Concentration
NIOSH	- National Institute for Occupational Safety and Health
O ₂ /CGI	- Oxygen/Combustible Gas Indicator
O/S	- Ordinary Seaman
OSHA	- Occupational Safety and Health Administration
OVA	- Organic Vapor Analyzer
PEL	- Permissible Exposure Limit
SwRI	- Southwest Research Institute
TLV-C	- Threshold Limit Value - Ceiling
TLV-STEL	- Threshold Limit Value - Short-Term Exposure Limit
TLV-TWA	- Threshold Limit Value - Time Weighted Average
UEL	- Upper Explosive Limit
USCG	- United States Coast Guard

GLOSSARY OF CHRIS ABBREVIATIONS FOR VOYAGE CHEMICALS

BAN	- n-Butyl alcohol
BNZ	- Benzene
BTC	- n-Butyl acrylate
CBT	- Carbon tetrachloride
CRF	- Chloroform
DBO,P	- o-Dichlorobenzene, p-Dichlorobenzene
DCM	- Methylene chloride
DEA	- Diethanolamine
EAC	- Ethyl acrylate
EAL(200),(190)	- Ethyl alcohol
EGL	- Ethylene glycol
EPC	- Epichlorohydrin
MEK	- Methyl ethyl ketone
MMM	- Methyl methacrylate
PAT	- n-Propyl acetate
POX	- Propylene oxide
SHD	- Sodium hydroxide
TCE	- 1,1,1-Trichloroethane
TDI	- Toluene 2,4-diisocyanate
TOL	- Toluene
VAM	- Vinyl acetate
XLM,O,P	- m-Xylene, o-Xylene, p-Xylene

I. INTRODUCTION

This final report presents the results of Phase I of a Crew Exposure Study that was performed by Southwest Research Institute for the U. S. Coast Guard, Office of Research and Development, Marine Safety Technology Division. The purpose of this study is to characterize the occupational exposure profiles of crew members to chemical substances in the work environment on bulk liquid tankers and barges at sea and on offshore drilling and production facilities. These chemical substances include the liquids, vapors, dusts, mists, and gases that are associated with various operations. Occupational exposures include the inhalation, dermal, and ingestion routes of entry into the body. Because the nature of the potential exposures and the work routines on product tankers and barges differ greatly from those on offshore facilities, the results of the Crew Exposure Study are published in two separate volumes. Volume I reports the results for offshore oil and gas drilling and production operations. Volume II reports the results for bulk liquid carrier operations at sea.

I.1 Background

The U. S. Coast Guard is responsible for the health and safety of marine transportation workers. This responsibility is derived, in part, through the Ports and Waterways Safety Act as amended in 1978. Additional responsibility is derived from a Memorandum of Agreement between the U. S. Coast Guard and the Occupational Safety and Health Administration. This agreement was published in the Federal Register on March 6, 1980, and defines the responsibilities and cooperational guidelines for each agency. The Coast Guard is aware that there are potential health and safety issues associated with bulk liquid carrier operations. These issues need to be clarified so that the Coast Guard can discharge its responsibility. At the same time, it is recognized that the existing data base on work place concentrations and occupational exposures needs to be expanded to include the full scope of vessel operations. In addition, the impact of the unusual and extended work schedules of merchant marine tankermen requires investigation. To this end, the Coast Guard contracted with Southwest Research Institute to perform a research project that would characterize occupational exposures to the various contaminant forms that may exist aboard ocean-going vessels that transport bulk liquids.

I.2 Objectives

The main objective of this study was to characterize the exposure profiles of licensed and unlicensed merchant marine tankermen to the various forms of potentially hazardous contaminants that may be encountered during their work and rest periods. To accomplish this objective, four separate tasks were identified, and each task had a subset of specific objectives.

Task 1 - Background Study and Definition of Problem

- o Overall Objective - Conduct a background study to define potentially hazardous sources associated with various operations that may bring the tankermen into contact with toxic and flammable substances.
- o Specific Objectives
 - Review the reports of previous investigations that relate to this project and which are identified by literature searches and written inquiries.
 - Review the existing set of regulations that pertain to cargo transfer and transport.
 - Compile and tabulate property data for potentially hazardous substances that are encountered in tanker operations.
 - Perform on-site observations aboard tankers at sea to identify contaminant sources and to document work activities that pose a potential for exposure to these contaminants.

Task 2 - Analytical Modeling

- o Overall Objective - Develop analytical models, if appropriate, to simulate the effect of contaminant sources on exposure to hazardous substances during the operations observed in Task 1.
- o Specific Objectives
 - Determine whether the contaminant sources that were observed in Task 1 are amenable to analytical modeling.
 - Incorporate knowledge of model predictions as a guide to the design of full-scale at-sea tests.

Task 3 - Experimental Test Plan

- o Overall Objective - Identify the experimental measurement techniques and develop an experimental test plan for acquiring the data needed to assess worker exposure.
- o Specific Objectives
 - Identify appropriate sampling and analytical methods for determining work place concentrations and personal exposures for dusts, mists, gases, liquids, and vapors.

- Design a test plan for acquiring exposure profiles for a representative cross-section of vessel configurations, operational procedures, and products during at-sea voyages.

Task 4 - Testing of Experimental Procedures

- o Overall Objective - Implement the experimental plan on one vessel.
- o Specific Objectives
 - Implement the plan for one of the vessels that was identified in the experimental plan.
 - Perform occupational exposure monitoring and work documentation on two crew members for the duration of the voyage.
 - Analyze and interpret the results relative to established exposure limits for chemical substances.
 - Based on the overall experiences of the voyage, modify the test plan, if necessary.

I.3 Perspective

The trial execution of the experimental plan represents the culmination of "A Crew Exposure Study - Phase I." The refined test plan will then be fully implemented in a dedicated data collection effort, "A Crew Exposure Study - Phase II," aboard the remainder of the vessels in the experimental plan.

II. BACKGROUND STUDY

II.1 Literature Search

The initial effort on this project was to conduct a computerized and manual search of the open literature. The purpose of the search was to uncover either abstracts or bibliographic citations that relate directly or indirectly to ongoing or past research. Specific areas of interest included flammable and toxic hazards of chemical vapors, current laws and regulations governing vapor emissions and exposures, vapor emissions, and plume dispersion as related to tanker operations. Key words or phrases were first defined and then arranged into the group files shown in Table II.1. These files were combined on a computer and applied sequentially to various data banks. The productivity of the composite searches is summarized in Table II.2.

A categorized bibliography of the literature items that have been ordered, received, and reviewed is presented in Appendix A. Much of this literature was helpful to specific areas of this project; however, none of the papers dealt directly with occupational exposures during tanker/barge operations.

A manual search for literature on interpretation of exposure data in unusual work routines was also conducted. The results of this search are discussed in Appendix B.

II.2 Related Occupational Health Investigations

A search was conducted to identify domestic and international governmental agencies, research laboratories, and industry associations that have a continuing concern for safety and health aboard chemical tankers at sea. Each of the following organizations was then contacted by letter requesting information on past or current research efforts to characterize the occupational exposures of crewmen to all forms of contaminants, i.e., gases, liquids, vapors, dusts, and mists, in the work environment.

- o Marine Technology Directorate
Science Research Council
London, England
- o Norwegian Petroleum Directorate
Stavanger, Norway
- o National Petroleum Council
Washington, D. C.
- o Det norske Veritas
Oslo, Norway
- o International Chamber of Shipping
London, England

TABLE II.1. COMPUTER SEARCH STRATEGY

<u>GROUP I</u>	<u>GROUP II</u>
Gas ? *	Toxic ?
Vapor ?	Hazard ?
Mist ?	Flam ?
Dust ?	
Aerosol ?	<u>GROUP IV</u>
Particulat ?	Hygiene
	Health
<u>GROUP III</u>	Occupational (w) Safety
Drill ?	Occupational (w) Disease
Transport ?	Industrial (w) Safety
Deliver ?	Industrial (w) Disease
Distribut ?	
Convey ?	<u>GROUP V</u>
Transfer ?	Model ?
Rout ?	Micromeritic ?
Stor ?	Disper ?
	-

* ? - denotes a root word code or truncator. All words in the title or abstract that contain the truncator will respond.

TABLE II.2. PRODUCTIVITY OF COMPOSITE SEARCH

File Name	No. of Citations	No. of Finds
APILIT	405	35
LABORDOC	126	2
COMPENDEX	125	22
APTIC	173	4
NTIS	65	9
ENVIROLINE	34	8
POLLUTION ABSTRACTS	18	5
MRIS	14	10
ENVIRONMENTAL REPORTS BIBLIOGRAPHY	254	30
CONFERENCE PAPERS INDEX	613	18
OCEANIC ABSTRACTS	261	26
SSIE (CURRENT RESEARCH)	151	8
TOTALS	2239	177

- o American Petroleum Institute
Washington, D. C.
- o Intergovernmental Maritime Consultative Organization
London, England
- o Oil Companies International Marine Forum
London, England
- o Organisation for Economic Co-Operation and Development
Paris, France
- o Chemical Carriers Association
New York, New York
- o Chalmers University of Technology
Goteborg, Sweden
- o International Labour Organization
Geneva, Switzerland
- o Norges Skipsforskninginstitutt (NSFI)
Oslo, Norway
- o Institute of Occupational Health
Oslo, Norway
- o National Defense Research Institute
Stockholm, Sweden
- o Arbetarskyddsfonden
Stockholm, Sweden
- o World Health Organization
Geneva, Switzerland
- o System for a Safe Ship (SOLAS Program)
Oslo, Norway

Responses were received from 16 of these organizations. A majority of these responses suggest that very little research has been conducted or is being planned to characterize the exposures of crewmen aboard chemical tankers. The Norwegian Petroleum Directorate indicated that they have several related programs under evaluation, but none that have been awarded. The National Defense Research Institute indicated that they are currently collecting data for a study of the effects of acute exposures to vapors of gasoline and other petrochemical products on human performance during product loading. Reports are not yet available for review.

Another organization that referenced past research was NSFI. In 1974, the Institute for Occupational Health in Norway conducted a program

to monitor the environment of crew members on 19 Norwegian chemical tankers. Copies of the project reports were requested, but were not received.

The World Health Organization (WHO) has collaborated with the following two occupational health centers that specialize in health problems of seafarers.

- o Bernard-Nocht-Institute für Schiffs und Tropenkrankheiten
Department for Nautical Medicine
Hamburg, Federal Republic of Germany
- o Institute for Maritime and Tropical Medicine
Gdynia, Poland

WHO contacted these two institutes on behalf of SwRI to obtain any research information that may be relevant to the current product. The Bernard-Nocht-Institut responded and indicated that their primary capability was in literature searching as opposed to conducting research.

Based on these responses, there does not appear to be any duplication of effort between the Crew Exposure project and projects of other national and international organizations. In addition, there is no technical information available on cargo-related occupational exposures or exposure profiles for crew members on chemical tankers and barges.

II.3 Pertinent Regulations

This section contains a review of the current and proposed USCG and OSHA regulations relative to the marine portion of this project. These regulations are briefly discussed below and are summarized in Appendix C.

OSHA Regulations

OSHA regulations of particular interest are in 29 CFR, Parts 1910, 1915, 1918, and 1918a. Excluding ship's personnel, jurisdiction appears to apply to all other workers who are involved in ship repair and cargo handling. Part 1918a is a newly proposed regulation entitled "Marine Terminals" and discusses operations specifically at marine terminals.

In 1980, the USCG and OSHA formally agreed to jointly address the topic of safety and health aboard inspected tank vessels. These agreements, known as Memorandums of Agreement, were published in The Federal Register, i.e., Volume 45, Nos. 46 and 47. The purpose of these agreements is to establish guidelines for interagency cooperation leading to the development of health standards that are not covered by existing regulations and which apply specifically to the marine transportation industry. These MOA's were published in March 1980. A joint Memorandum of Understanding (MOU) is to be published to define procedures for cooperation and detailed plans for development of health standards.

U. S. Coast Guard Regulations

Titles 33 and 46 in the Code of Federal Regulations (CFR) address the Coast Guard's authority over the subject matter. In Title 33, Part 126, shore-side transfer or loading of hazardous materials is discussed. Vessel-side regulations are contained in Title 46, Subchapter D, Parts 30 through 40, and Subchapter O, Parts 150 through 154.

Included as part of Title 46, Subchapters D and O, are lists of chemicals governed by each of the subchapters. Only Subchapter O chemicals have complete gauging, venting, and tanker vent height requirements. Table II.3 presents the Subchapter O and D cargos that have been observed during this project and companion projects (References 1 and 2). For those that are Subchapter O chemicals, the minimum requirements mentioned above are included for both tankers and unmanned barges. These regulations provided a perspective of actual operations relative to operational requirements.

II.4 Chemical Cargo Property Data

This project and the projects in References 1 and 2 required cargo property data for prediction or interpretation purposes. These data include selected physical properties and occupational exposure limits. Appendix D contains a tabulation of such data for a group of products that are frequently transported by water; many of these cargos have been monitored during these projects. This listing is not meant to be all-inclusive, and Reference 3 and the other references in Appendix D should be consulted for property data on other cargos.

TABLE II.3. CATEGORIZATION AND MINIMUM REQUIREMENTS
OF COMMONLY CARRIED CHEMICALS *

Chemical	Sub- chapter	Gauging		Vent		Tanker Vent Height During Loading and Transit
		Tankers	Unmanned Barges	Tankers	Unmanned Barges	
Acetone	D					
Benzene	O	R	O	PV	PV	B/3
Butanol	D					
Butyl acrylate (n-)	O	R	O	PV	PV	4m
Carbon tetrachloride	O	C	O	PV	PV	B/3
Caustic soda (solution)	O	O	O	O	O	NR
Chloroform	O	R	O	PV	O	B/3
Diethanolamine	O	O	O	O	O	NR
Diethylene glycol	D					
Epichlorohydrin	O	C	C	PV	PV	B/3
Ethylene dichloride	O	R	R	PV	PV	4m
Ethyl acrylate	O	R	R	PV	PV	4m
Ethyl alcohol	D					
Hexane	D					
Methyl isobutyl ketone	D					
Methyl ethyl ketone	D					
Methanol	D					
Methyl methacrylate	O	R	R	PV	PV	4m
n-Butyl alcohol	D					
n-Propyl acetate	D					
Propylene oxide	O	C	R	PV	SR	4m
Styrene	O	O	O	PV	O	4m
Toluene	D					
Vinyl acetate	O	O	O	PV	PV	4m
Xylene	D					

Gauging

C - closed
O - open
R - restricted

Vent

O - open
PV - pressure vacuum valve
SR - safety relief

Tanker Vent Height

NR - no requirements
4m - four meters
B/3 - ship's beam/3

* 46 CFR Parts 151 and 153

III. PRELIMINARY VOYAGE OBSERVATIONS

Two at-sea voyages were conducted during the background phase of this study. One of the vessels was a parcel chemical tanker, and the other vessel was a manned barge carrying gasoline. The duration of each round-trip voyage was nominally 14 days. With respect to Deck Department operations, a gasoline carrier was selected because (1) the volume of this product ranks high on the list of bulk liquid products that are annually shipped by water between domestic ports, (2) this product contains a benzene fraction, and (3) because of the advent of an ACGIH-recommended exposure guideline for total gasoline vapor (Reference 4). The chemical tanker was selected because the wide variety of cargos that are carried simultaneously presents the potential for multiple exposures to different chemicals. The vessel selection was also guided by the fact that one vessel was diesel driven, while the other was steam driven, and the work environment in the Engine Departments should reflect this difference in propulsion systems. Lastly, the chemical tanker contained a pumproom that discharged selected products.

III.1 Observation Objectives

Both of these voyages were conducted for the overall purpose of becoming familiar with the operational activities and work environments aboard the vessels during the four main segments of a voyage: product loading, laden voyage, product discharge, and the ballast voyage.

Specific objectives included:

- o Identification of sources that generate or release chemical substances in the work/living environment and which may pose a potential concern for occupational health. In this context, the work environment includes the Deck and Engine Departments, and chemical substances include vapors, gases, dusts, mists, and bulk liquids. Cargo or noncargo-related substances were included in this definition.
- o Documentation of work activities, the duration of these activities, and the worker's proximity to the sources of these various chemical substances.
- o Conducting environmental monitoring for airborne contaminants during selected work scenarios.

These objectives and the results obtained from the background voyages support the basic project objective, which is to design and implement an experimental plan for fully characterizing the occupational exposures of personnel aboard bulk liquid carriers.

These voyages resulted in the observation reports that are presented in detail in Appendices E and F. The next two sections of this

report summarize and highlight the more important aspects and results of these voyages.

III.2 Manned Barge - Gasoline

This voyage was the first of the two preliminary voyage observations. Prior to vessel selection and negotiations with shipowners, it was recognized by the U. S. Coast Guard and SwRI that the bulk liquids of interest could be transported aboard conventional parcel chemical tankers or vessel configurations known as manned, ocean-going barges. It was postulated that differences in carrier configuration could result in operational procedures and equipment that may be unique to each class of vessel and which could accentuate or minimize the potential for occupational exposures. With the class of vessel having been identified, a gasoline cargo was selected because it is a high-volume product, cargo transfer rates are considerably in excess of those that are used for pure chemicals, it is an extremely high vapor pressure product that contains a benzene fraction, and there is now a recommended guideline for total gasoline vapor exposures.

The details of this voyage are presented in Appendix E, and the remainder of this section highlights the important features of the observation.

III.2.1 Voyage Overview and Observation Plan

This 14-day round-trip voyage began and ended at the same terminal. Three grades of motor gasoline were open-loaded into 18 cargo tanks. Cargo ullage was open-gauged. Those products were subsequently discharged at three separate terminals. Empty tanks were not backfilled, but remained either empty or were ballasted. Nine of the product tanks were washed and gas freed on the ballast leg in preparation for docking at a fourth terminal where hot work was performed on the hull exterior. The duration of this voyage appears to be representative of cargo transport operations between domestic ports (Canal Zone passages excluded).

For planning purposes, each leg of the voyage or major operation was considered separately. That is, the voyage was broken down into a

- o loading operation,
- o laden leg,
- o discharge operation, and
- o ballast leg.

On each leg of the voyage or major operation, the plan was to observe and document work activities in both the Deck and Engine Departments. With respect to documentation of work activities, emphasis was placed upon the duration of the activity, the worker's proximity to observed sources of airborne contaminants, and those situations that resulted in extended work shifts. The underlying assumption was that the

potential for occupational exposures in each department is a function of the phase of the voyage. In keeping with this assumption, the environment in the deckhouse was monitored during major operations to assess the potential for contaminant infiltration into the crew's living quarters.

The plan also included provision for personal and area monitoring of contaminant levels in each department. This sampling effort was exploratory in nature and was not intended to produce complete exposure profiles on individual crew members. In the Deck Department, active and passive vapor monitoring was conducted for the benzene fraction in gasoline. Active dosimetry consists of a pump that draws vapor-laden air through a sorbent bed such as activated charcoal. Vapors are retained in the bed by the mechanism of adsorption. Passive dosimeters do not use the pump; the vapors are collected and retained on a sorptive element by diffusion and adsorption. The same analytical chemistry technique is used for both collection elements to determine the amount of trapped analyte. Asbestos and oil mist levels were monitored in the engine room.

Other objectives included in the plan were

- o Assessment of the frequency and duration of intermittent venting of cargo vapors from sealed tanks during the laden voyage. In this regard, the potential for exposure to cargo vapors during deck day work was of interest.
- o Monitoring of air velocities in the living accommodations to determine the feasibility of using passive dosimetry in these areas during characterization of exposure profiles.
- o Documentation of dermal exposures to cargo and non-cargo-related materials.

III.2.2 Summary of Project Activities

The voyage objectives, as outlined above, were met during this 14-day period. This voyage also offered an opportunity to collect additional information that complements the observation plan. Table III.1 summarizes the shipboard activities that were conducted.

III.2.3 Environmental Monitoring - Methods and Results

Environmental monitoring was conducted in the Deck Department for the benzene fraction in gasoline. Conventional pump/charcoal tube methods and, to a limited degree, passive dosimeters, were employed for this purpose. Both occupational exposure and area samples were collected on deck. In the Engine Room, only area samples were collected for airborne asbestos and oil mist.

Sampling and analysis for benzene on charcoal tubes followed the NIOSH-recommended procedure in Method No. S311 (Reference 5).

TABLE III.1. VOYAGE-RELATED ACTIVITIES

ON-DECK

1. Document work scenarios that result in work periods greater than 8 hours (both licensed and unlicensed crew members).
2. Document composition of work units during operations in port and at sea.
3. Document responsibilities of members of Deck Department.
4. Document work activities (not observed) based on discussions with the Chief Mate and review of the Deck Work Book.
5. Document observed work activities of members of work units.
6. Document frequency and duration in proximity to contaminant sources.
7. Document noncargo-related exposures (painting, sandblasting, and use of phosphoric acid rust neutralizer).
8. Parallel active and passive personal sampling on crew as well as parallel area sampling at drip tray which was a common or frequent site to congregate.
9. Exposures considered = inhalation, dermal contact, and ingestion.
10. Source sampling (tank vapor emissions) during loading, discharging, ballasting, and tank cleaning.
11. Conduct tank cleaning tests.
12. Test rise in vapor concentration in a sealed tank.
Tank washed and then sealed for approximately 2 days.
13. Enter gas freed product tanks with crew and vessel owner.
Document work activities (sweep solid debris on tank bottoms and inspect tank coatings), vapor levels, and crew safety procedures.
14. Observe in-transit pop-off of tank pressure relief valves.

ENGINE ROOM

1. Stand watches with 3rd Assistant Engineer to document work activities.
2. Walk through surveys to identify potential contaminant sources.
3. Area samples for asbestos and oil mist.
4. Document major equipment components.
5. Document fluids (degreasers) used for equipment cleaning.
6. Document work responsibilities of each officer (4) in Engineering Department.
7. Document typical repair, maintenance, and housekeeping activities that are performed in port and at sea.
8. Document method of ventilating engine room.

DECKHOUSE

1. Surveys of vapor concentration in Deckhouse (main deck and boat deck levels) during loading, ballasting, discharge, and tank cleaning operations.
2. Monitor air velocities in crew quarters next to beds to determine feasibility of passive dosimetry during nonwatch rest hours.

The majority of these samples were collected on small tubes, i.e., 100 mg/50 mg. On two samples (EX-11 and SB-20), large tubes (400 mg/200 mg) were used for sampling over an extended time period. In both cases, pumps were precalibrated to the recommended flow rate using a bubble meter with the appropriate load in-line. As a part of the analysis procedure, the desorption efficiency for benzene on charcoal was determined for both tube sizes.

<u>Tube Size*</u>	<u>Desorption Efficiency, %</u>
100/50	86.7
400/200	98.7

Du Pont's Pro-Tek® G-BB passive dosimeters were used on all of the project voyages. The manufacturer's sampling and analysis procedures were followed. A desorption efficiency of 94.7 percent was determined analytically for benzene on the charcoal strips in this device.

In the Engine Room, sampling and analysis for airborne asbestos was conducted in accordance with NIOSH Method No. 239. The apparatus and filter media that are recommended in NIOSH Method S272 were used for oil mist sampling. However, the recommended method of analysis was not used because, based on experience, many types of oils do not fluoresce. The method of choice consisted of extracting the oil deposits from the filters with carbon tetrachloride followed by a scan of the infrared absorption spectra between reciprocal wavelengths of 3200 to 2400 cm^{-1} . The weights of the unknown deposits were quantified at a reciprocal wavelength of 2935 cm^{-1} because it most closely matched the dominant absorption wave-number (2930 cm^{-1}) of U.S.P. heavy mineral oil that was used for standards development. Concentrations were subsequently calculated as mg/m^3 expressed as equivalent mineral oil. A desorption efficiency of 100 percent was assumed for the extraction procedure. This assumption is justified for survey type sampling, where the concentrations may be low and where precise constituents are not as easily identifiable, as is benzene in gasoline. More detailed analytical determinations would be indicated if the resulting equivalent concentrations were excessive or suspect.

The results of the sampling and analyses are presented in Tables III.2 and III.3. The equations that were used in calculating concentrations for charcoal tubes and dosimeters are shown in Appendix H and are not repeated here. All concentrations reflect the temperature at the time of sampling and are referenced to 25°C. Concentrations are uncorrected for barometric pressure. Charcoal tube samples in Table III.3 have alphanumeric designators, while passive dosimeters have five-digit sample numbers. The alphanumeric sample numbers in Table III.2 refer to filters.

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*Numbers indicate weight of adsorbent (mg) in the primary and backup sections of the sampling tube.

TABLE III.2. SUMMARY OF ENVIRONMENTAL AREA MONITORING DATA
FOR ASBESTOS AND OIL MIST - ENGINE ROOM

Sample No.	Location	Sample Duration (Min.)	Sampling Rate (LPM)	Temperature (°C)	Unknown	Weight of Analyte (µg) or Number of Fibers	Concentration
D-20	Adjacent to Main Engine Exhaust Stack Header	254	1.488	39.5	Asbestos	ND	ND
D-15	Adjacent to Fuel Injector Rack	250	1.062	37	Oil Mist	56	0.2 mg/m ³ *
D-11	Adjacent to Generator Exhaust Stack	360	1.475	28	{ Asbestos Oil Mist	ND 31	ND 0.06 mg/m ³ *

NOTES:

1. Weight of analyte corrected for blank.
2. Number of fibers > 5µ.
3. ND - not detectable.
4. * - concentration as equivalent mineral oil.

TABLE III.3. SUMMARY OF ENVIRONMENTAL MONITORING DATA FOR BENZENE
IN GASOLINE - DECK DEPARTMENT (AT SEA AND IN PORT)

Operation	Sample No.	TLV-TMA* (ppm)	TLV-STEL* (ppm)	Benzene Concentration (ppm)	Sample Duration (min.)	Temperature (°C)	Relative Humidity (%)	Sampling Rate (LPM)	Weight of Analyte Corrected for Blank (µg)
Tank Loading - Periodic Gauging	SB-1	10	25	5.2	194	18.7	83	0.202	576
Tank Loading - Periodic Gauging	SB-2			2.4	165	19.5	70	0.188	207
Tank Loading and Top-off of Four Tanks	SB-3			7.8	254	25.6	52	0.171	940
Tank Loading - Periodic Gauging	SB-4	10	25	5.1	232	27.0	49	0.172	557
Tank Loading and Top-off of Three Tanks	SB-5 47740			6.3	201	22.8	65	0.190	670
Tank Loading and Top-off of Three Tanks	SB-5 47740			1.5	196	22.8	65	41.4**	36
Tank Gauging - Discharge and Stripping	SB-12 47759	10	25	0.86	81	17.8	72	0.186	37
Tank Gauging - Discharge and Stripping	SB-12 47759			ND	74	17.8	72	41.4**	ND
Tank Gauging - Discharge and Stripping	SB-12 47759			0.17	225	17.3	77	0.208	23
Area Sample at Drip Pan	SB-13 47758	10	25	ND	222	17.3	77	41.4**	ND
Area Sample at Drip Pan	EX-11 47757			2.1	338	28.1	60	0.198	502
Area Sample at Drip Pan	EX-11 47757			2.7	357	28.1	60	41.4**	120
Tank Washing	SB-14 SB-20	10	25	3.6	89	19.6	80	0.187	189
Tank Washing	SB-14 SB-20			1.6	387	23.8	80	0.196	348
Tank Washing	SB-14 SB-20			ND	6	27.0	61	0.186	ND
Open Ullage Ports and Gauging Tubes (18 Tanks) after Docking	SB-10 SB-11	10	25	ND	9	19.2	63	0.186	ND
Open Ullage Ports and Gauging Tubes (18 Tanks) after Docking	SB-10 SB-11			ND	9	19.2	63	0.186	ND
Open Ullage Ports and Gauging Tubes (18 Tanks) after Docking	SB-10 SB-11			ND	9	19.2	63	0.186	ND
Tank Entry Four Tanks Inspect Coatings	SB-30	10	25	3.8	82	32.5	NM	0.203	173

* 1981 ACGIH values

** Benzene sampling rate for passive dosimeters, cm³/min.

† Parallel active and passive samples

ND - not detectable

NM - not measured

It should be noted that the sampling rate for Sample No. D-15 is less than the 1.5 LPM rate that is recommended by NIOSH for oil mist. In fact, the pretest calibration rate was 1.5 LPM, but this rate deteriorated to a posttest calibration rate of 0.623 LPM. The rate that is indicated is the numerical average of these two values. All pumps were calibrated before and after each use. Only in the above case was there a marked difference in the flow rate.

III.2.4 Data Interpretation

This subsection is concerned with the environmental concentration levels that are presented in Tables III.2 and III.3. The Engine Room data will be discussed first, followed by the Deck Department data.

Engine Room

The original asbestos insulation was in the process of being replaced with a nonasbestos material as a part of the vessel's long-range maintenance plan. However, the original material, including lagging, was still in place on the main engine exhaust stack header and the exhaust stack on the diesel electric generator. Accordingly, these sites were selected for area monitoring for asbestos fibers. The sampling was conducted while the vessel was underway because it was assumed that the increased vibration levels would promote release of airborne fibers. The filters were analyzed by phase contrast microscopy at 500X magnification; 100 fields were counted, and each field had an area of $3.9 \times 10^{-3} \text{ mm}^2$. No detectable fibers greater than 5μ were observed on either filter. Therefore, the basic assumption was refuted, and airborne concentrations of asbestos fibers were not found in the Engine Room.

Sampling for oil mist was also conducted while the vessel was underway at sea. Both sampling locations represented areas of work activity during Engine Room inspection rounds, and oil deposits were present on the surfaces of surrounding structures. The sampling results indicate that measured concentrations, expressed as equivalent mineral oil, are roughly one to two orders of magnitude below the ACGIH TWA-TLV of 5 mg/m^3 for mineral oil mist, and if a time-weighted average mist concentration were calculated for an eight-hour period, assuming zero concentration for the remainder of the 480 minutes, the difference would be even greater. Had the measured concentrations been significantly higher, then a more detailed chemical analysis for mist composition would have been indicated.

During this voyage, the ship did not take on bunker fuel, and routine maintenance of the bunker systems in the Engine Room was not observed. This is one aspect of Engine Room operations that could be included in future voyages during Phase II of this study.

Deck Department

Motor gasoline is a complex blend of hydrocarbons. Phillips and Jones (Reference 6) have identified 142 compounds in gasoline vapor.

McDermott and Killiany (Reference 7) found that, during gasoline transfer operations, 92 percent of the vapors were represented by 21 light-end compounds in the alkane, alkene, and aromatic categories. Several of these 21 compounds have established sampling and analysis procedures and occupational exposure limits. Benzene, which is present in gasoline vapor at approximately 0.7 percent by volume (air excluded), was selected as the compound of choice for the sampling effort.

Benzene has an established occupational exposure limit. The ACGIH recommends a TLV-TWA of 10 ppm and a TLV-STEL of 25 ppm. In addition, a TLV-TWA and TLV-STEL of 300 ppm and 500 ppm, respectively, is recommended for exposures to total gasoline vapor. The documentation for total gasoline exposure limits (Reference 8) is based, in part, on the work of McDermott and Killiany.

Any of the 21 compounds that make up 92 percent of gasoline vapor and which have an established sampling and analysis method could be used as a tracer to infer total gasoline vapor concentration in air. In this case, benzene served as the tracer. The atmospheric concentration of total gasoline vapor can be estimated from the benzene concentration in air using the following expression, which can be easily derived.

$$C_{\text{Benzene}} \text{ (ppm)} = 0.007 C_{\text{Gasoline}} \text{ (ppm)}$$

The constant is the fractional representation of benzene in the 21 dominant vapor components.

Several observations can now be made regarding the environmental concentrations in Table III.3 that resulted from the charcoal tube samples.

1. The benzene concentrations reflect the total accumulated dose of the chemical over the duration of the sampling period. As such, none of the benzene concentrations exceeded the TLV-TWA of 10 ppm. Because of the averaging effect, shorter duration (15-minute) samples would be needed to determine if the TLV-STEL was exceeded. If it is assumed that the exposure to benzene was zero for the remainder of an eight-hour period, then the time-weighted exposure would be proportionately less.
2. There is a trend in the data that has been observed by SwRI on previous exposure monitoring tests aboard chemical tankers. The operations of open tank gauging (periodic and top-off), as shown in Figure III.1, tank cleaning, and tank entry result in the highest occupational exposure levels.
3. The lower exposure levels during product discharge and tank stripping reflect the fact that air is being ingested into the tank.
4. The area sample at the drip pan beneath the loading/discharging manifold indicates that accumulations of raw

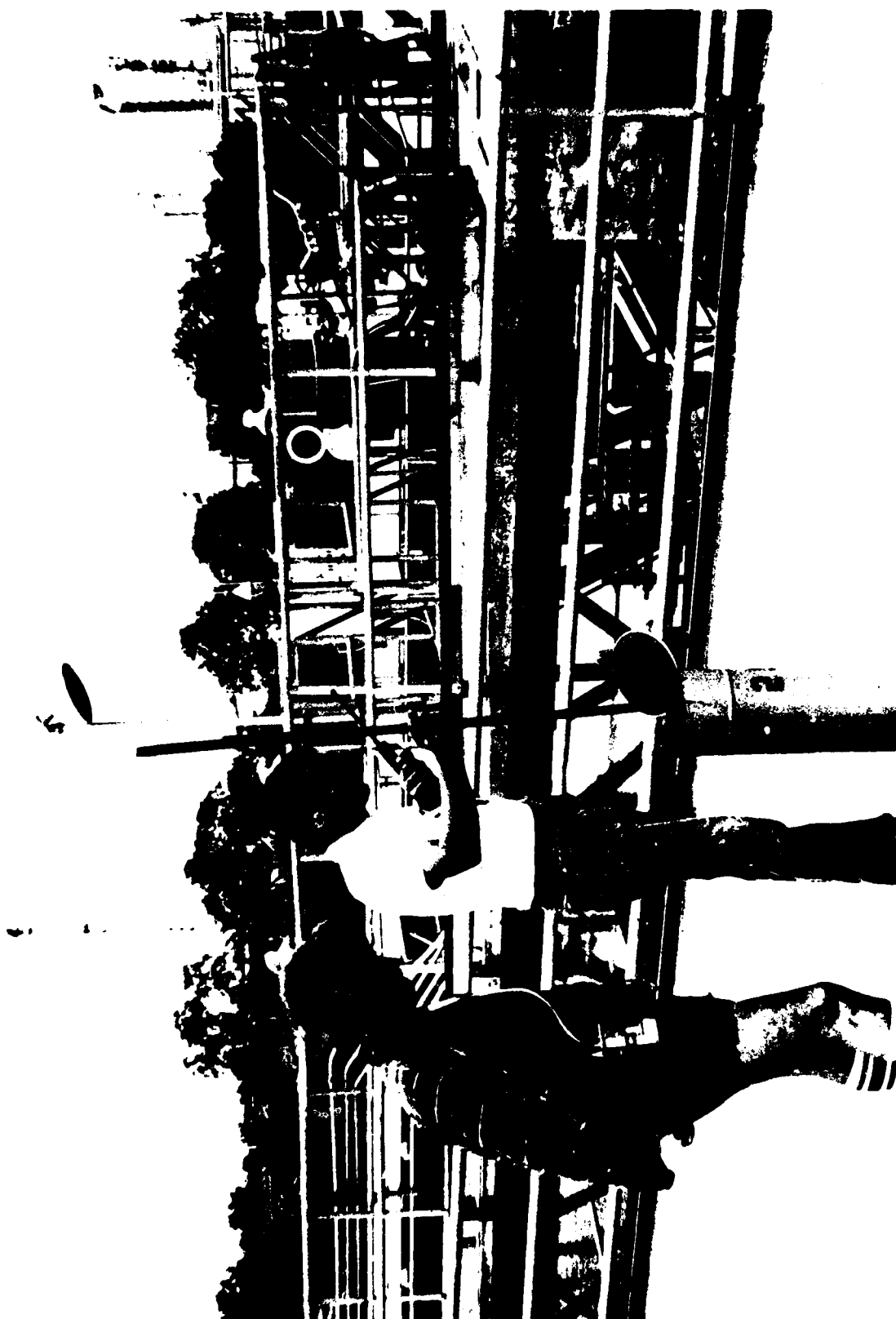


FIGURE III.1.1. TANKERMAN OPEN GAUGING PRODUCT ULLAGE AT TANK TOP-OFF.
GAUGING TUBE TERMINATES AT WEATHERDECK.

product in the tray vaporize and contribute to the total exposure because this is a site where personnel congregate during slack work times.

5. The operation of opening ullage ports and gauging tubes on empty and fully loaded tanks prior to product discharge did not result in a measurable exposure. This activity was originally of interest because of the potential for pressure buildup in the tank that would result in an instantaneous release of vapor when access ports were opened.
6. Benzene concentrations were converted to equivalent total gasoline vapor concentration by the method presented earlier. The time-weighted average exposure to total gasoline vapor was then calculated, assuming that exposure concentrations were zero for the remainder of an eight-hour period of time following the exposure. That is,

$$C \text{ (TWA-Gas)} = \frac{C_{\text{Benzene}}}{0.007} \times \frac{t_{\text{Exp}} \text{ (Min.)}}{480}$$

These calculations indicated that the total gasoline vapor concentration was equal to or greater than the ACGIH TLV-TWA for four of the samples.

<u>Sample No.</u>	<u>Equivalent TWA Total Gasoline Vapor Exposure, ppm</u>
SB-1	300
SB-3	590
SB-4	352
SB-5	377

This approach demonstrates the utility of the tracer or component approach to infer the total exposure to a vapor mixture when certain basic information about the mixture is known. Gasoline composition varies with the season and the manufacturer. The accuracy of the approach may be improved if vapor composition data such as that which was generated by McDermott and Killiany were known for each manufacturer and season.

7. Passive dosimeters were employed in parallel with charcoal tubes on four occasions. The measured concentrations at the drip pan agree quite well. It is difficult to draw any comparison for the samples that were collected during discharge and stripping except to observe that all concentrations were minimal.
8. Section III.4 discusses maritime work schedules. These schedules may be termed unusual or novel in the sense that

they do not approximate the 8-hour day, 5-day week that forms one of the criteria for the time-weighted average exposure guidelines of the ACGIH. An example of an unusual work schedule is the repetitive 4-on, 8-off routine. Up to this point, the interpretation has been based upon an exposure of finite duration followed by no exposure for the remainder of the 8-hour period without considering the exposure scenario during succeeding time periods. Since the maritime work schedules depart from conventional schedules, there is some question as to the suitability of the TLV-TWA in interpreting exposures during the unusual work routine. In response to this concern, research is being conducted to generate numerical correction or adjustment factors that can be applied to the TLV-TWA. These adjustment factors reflect the work schedule, the exposure environment, and body burden of vapor in question. One of these adjustment factor models has been derived by Hickey and Reist (Reference 9), and for illustrative purposes it was applied to the exposures (Sample Nos. SB-1 and SB-4) of the Second Mate during consecutive 4-hour watch periods that were separated by an 8-hour rest period. For this example, the exposure concentrations were assumed to exist for a full 4 hours; that is, the exposure durations of 194 and 232 minutes were extended to 240 minutes. In applying this model, the following criteria and/or assumptions were used.

- o The Mate works a repetitive 4-on, 8-off schedule for 30 days, followed by a 30-day shore leave.
- c The exposure concentration to benzene is constant during each work period. This assumption is correct for the two work periods that were monitored, but it is unlikely that the assumption is valid for all work periods because the exposure potential is variable and is a function of operational state of the vessel. For example, 5-ppm exposures to benzene would not be expected each work shift when the vessel is at sea on the laden voyage. To date, there are no adjustment factor models that totally reflect a time-dependent exposure environment. This limitation is recognized, but for this example, a 5.15-ppm (numerical average of Sample Nos. SB-1 and SB-4) concentration was assumed.

The inputs that are required by the Hickey and Reist model are:

$$\begin{array}{rcl}
 t_{1n} & = & 8 \text{ hours} \\
 t_{2n} & = & 16 \text{ hours} \\
 T_n & = & 168 \text{ hours} \\
 n & = & 5 \text{ days}
 \end{array}
 \left. \vphantom{\begin{array}{rcl} t_{1n} \\ t_{2n} \\ T_n \\ n \end{array}} \right\} \text{normal work week}$$

$$\left. \begin{array}{l} t_{1s} = 4 \text{ hours} \\ t_{2s} = 8 \text{ hours} \\ T_s = 1440 \text{ hours (60 days)} \\ m = 60 \text{ days} \end{array} \right\} \text{unusual work schedule}$$

Substitution of these work schedule inputs into the model yields an expression for the adjustment factor, F_p .

$$F_p = \frac{(1 - e^{-8k})(1 - e^{-120k})(1 - e^{-1440k})(1 - e^{-12k})}{(1 - e^{-4k})(1 - e^{-720k})(1 - e^{-168k})(1 - e^{-24k})}$$

The adjustment factor becomes chemical specific through the variable, k , which is related to the biological half-life of the chemical, $T_{1/2}$.

$$k = \frac{\ln 2}{T_{1/2}}$$

Mason and Dershin (Reference 10) indicate a half-life for benzene of 7.7 hours. For this model, the result is

$$F_p (\text{benzene}) = 1.27$$

This model concludes that the exposure limit, TLV-TWA, of 10 ppm could be increased by a factor of 1.27 to nearly 13 ppm for this special work schedule and assumed exposure environment. It must be emphasized, however, that this result is a prediction, and adjustments to the existing exposure limits would be warranted only after the models have been fully validated.

A similar exercise could have been performed on Sample Nos. SB-3 and SB-5, which were collected on the Third Mate during consecutive watch periods.

The experimental plan in Section IV defines a number of voyages for for the purpose of fully characterizing exposure profiles. These voyages should provide a sizeable body of data that can be used to explore the relative merits of TLV adjustment factor models.

9. A benzene exposure of 3.8 ppm was obtained from the charcoal tube sample that was collected during entry in Tanks 3C, 2C, and 2S. According to the conversion criterion, this translates into an exposure level of 543 ppm total gasoline vapor. The sampling pump was turned off between egress and entry into successive tanks. Recall from Appendix E that the entry

times for Tanks 3C, 2C, and 2S were 45, 22, and 15 minutes, respectively. During tank entry, the total gasoline vapor concentration was measured with the Organic Vapor Analyzer (OVA) at three levels—top to bottom. The average concentration in these three tanks was 380 (3C), 325 (2C), and 149 (2S) ppm. The time-weighted average concentration from these instrumental readings is

$$\bar{C} = \frac{380 \times 45 + 325 \times 22 + 149 \times 15}{82} = 323 \text{ ppm}$$

This average concentration of 323 ppm gasoline vapor that was obtained by a direct reading instrument represents a lower bound as to the concentration that would be anticipated from the personal dosimeter because many of the instrumental readings approached or exceeded 1000 ppm. The instrument and dosimeter were worn by the same individual. If the time structure of the OVA instrument readings were known in greater detail, then the calculated value of $\bar{C}$ would approach 543 ppm. Until more detailed time resolutions are documented, there is no obvious inconsistency or discrepancy between these data points.

III.2.5 Summary of Important Results

1. Engine Room vapor concentrations (as methane) ranged from 7-27 ppm in port and 6-15 ppm while underway at sea. The higher concentrations in port suggest that vapors infiltrate from the deck through the Engine Room ventilation system.
2. Airborne asbestos could not be detected in the Engine Room.
3. Deckhouse vapor concentrations (as methane) were consistently higher during product loading and tank cleaning than during product discharge or the laden voyage. Infiltration through forward and aft access hatches is the probable mechanism because the air conditioning system was closed and did not communicate with the environment exterior to the deckhouse.
4. Air velocity measurements in crew quarters indicated that passive dosimetry is inappropriate for personal sampling during rest periods because velocities are less than manufacturer-recommended minimums.
5. The extended work schedule was observed in the Deck Department. With an average of 4 hours overtime per day, work durations of 30, 20, 16, and 13 hours were observed.
6. Noncargo-related exposures should be examined when they occur. These exposures include sandblasting, spray painting,

spraying of rust deactivators, and skin contact with general purpose cleaning solvents.

7. Crew members (licensed and unlicensed deck department) were monitored for exposure to the benzene content in gasoline. All measured concentrations were less than 8 ppm for sampling periods ranging from 6 to 387 minutes.
8. Dermal contact with raw product occurs primarily during manifold preparation, hose hookup, and disconnect. The hands are the primary site of contact, and exposure time was approximately five minutes.
9. Accidental eye contact with gasoline occurred once.
10. Total gasoline vapor concentrations approach 40 percent v/v at the end of tank loading and full tank ballasting.
11. Soft drinks and other refreshments in open containers were consumed on deck during product transfer operations and tank cleaning.
12. During heel stripping of product and wash slops from the tank, the worker's breathing zone is fully exposed to tank atmosphere because of the need to view the liquid level on the tank bottom, as shown in Figure III.2. In this position, monitoring devices are shielded from the actual tank atmosphere, which presents a monitoring and interpretation problem.
13. During tank entry, blower operation, availability of respiratory protection for the crew, and deck safety watches were not consistently employed as safety procedures.
14. In-tank vapor concentrations during man entry were quite variable from roughly 25 to 395 ppm (total gasoline vapor). When debris was disturbed, vapor concentrations above the debris on the tank floor were substantially higher than the general tank atmosphere, often exceeding 4200 ppm.
15. Oil mist concentrations in the engine room were acceptable relative to an exposure standard which is based on mineral oil.
16. Tank gauging and tank top-off during loading produced estimated time-weighted average exposures to total gasoline vapor that equalled or exceeded the recommended TLV-TWA of 300 ppm.
17. As shown in Figure III.3, tankermen who do not wear shirts pose an obstacle to exposure monitoring.

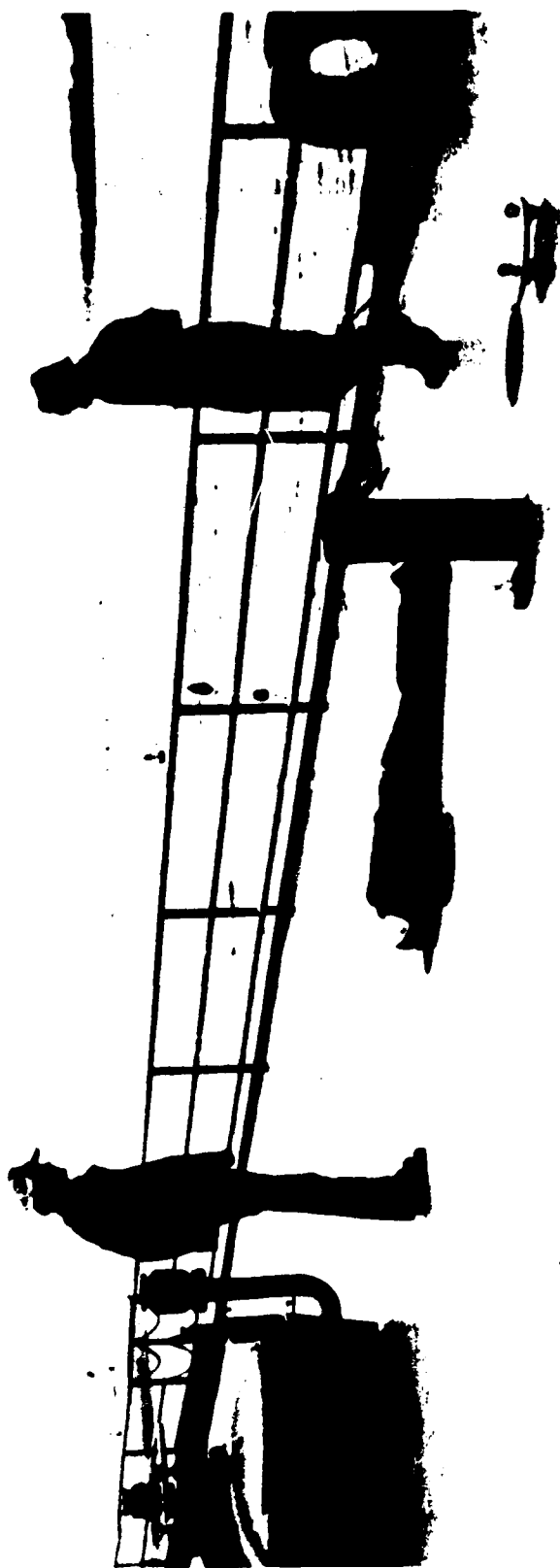


FIGURE III.2. TANKERMAN OBSERVING CARGO LEVEL AND PUMP INLET DURING HEEL STRIPPING

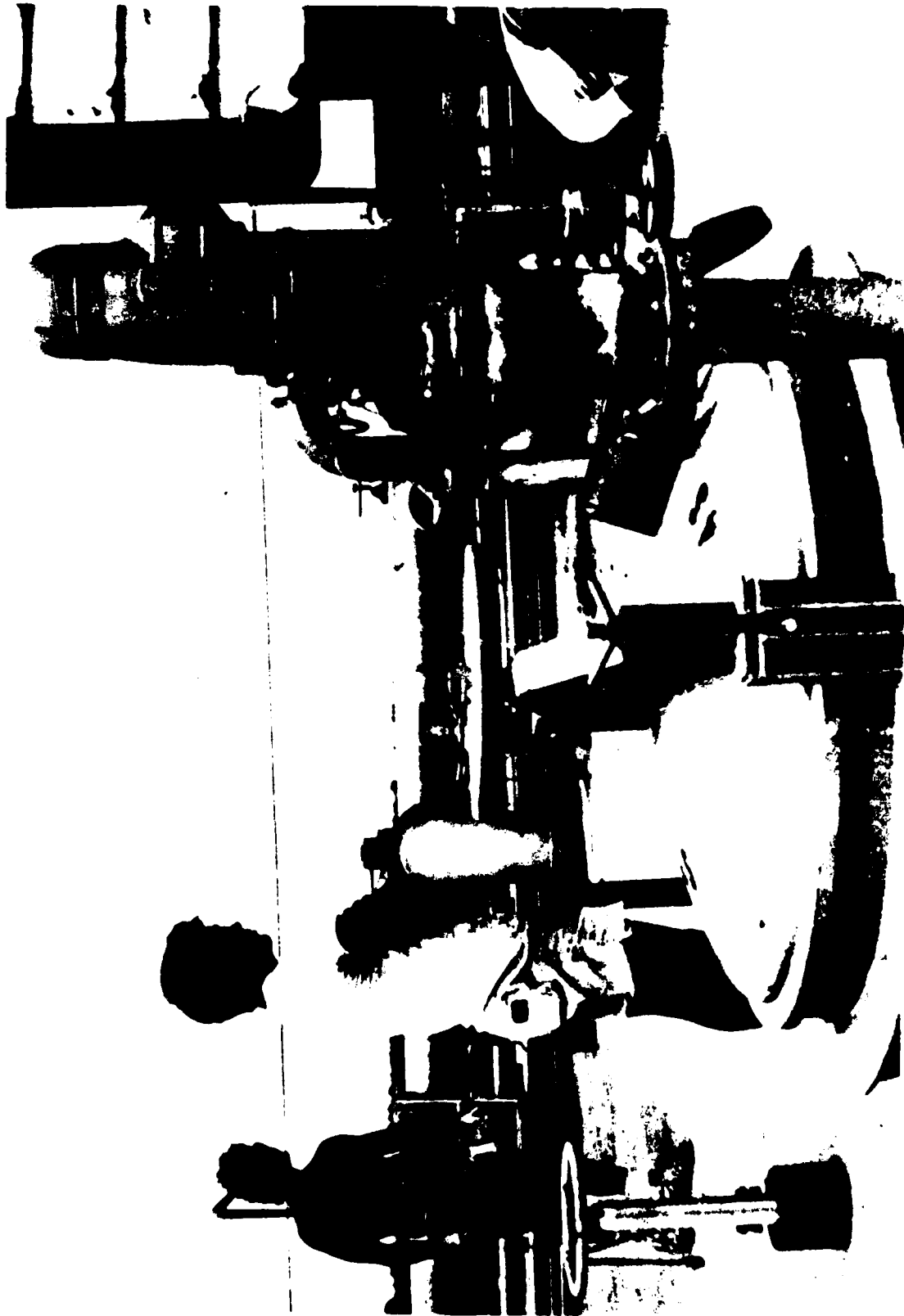


FIGURE III.3. A DIFFICULT MONITORING SITUATION - THE SHIRTLESS WORK ENVIRONMENT

III.3 Parcel Chemical Carrier

The second preliminary voyage observation was conducted on a parcel chemical carrier. While many of the operations and activities paralleled those on the manned ocean-going barge, there were distinct differences that are noteworthy. The cargos that were transported consisted of a variety of chemicals and petroleum products rather than one single commodity. As such, observation of occupational exposures to more than one product was possible. The ship contained a pumproom that housed large centrifugal pumps which were used to off-load the large volume cargos such as aviation and motor gasoline. The pumps were located at an elevation slightly higher than the cargo tank bottoms. Periodic entry in the pumproom was necessary to ensure the pumps' safe operation. As a result, exposure to product vapors from leakage around pump shaft seals was observed. The chemical carrier was an older ship, and its crew size was approximately twice that of the ocean-going barge.

A summary of the activities on this second voyage is presented in this section. A detailed account of the voyage is contained in Appendix E.

III.3.1 Voyage Overview and Observation Plan

A total of 14 days was spent on the parcel chemical tanker by the SwRI observation team. Prior to their boarding, the ship had already loaded aviation and motor gasoline at two previous terminals. The initial observation made by SwRI personnel was the off-loading of a portion of this cargo at this final loading port. A total of 16 different products was eventually loaded at this port. These products consisted of a variety of specialty lube oils, petroleum solvents, and five pure chemicals. The chemicals included methyl ethyl ketone (MEK), xylenes (XLO, XLP, XLM), ethanol (EAL), epichlorohydrin (EPC), and n-butyl alcohol (BAN). The ship's entire cargo was subsequently discharged at two different terminals. On the ballast leg, extensive tank cleaning of all cargo tanks was performed in preparation for Coast Guard biennial inspection.

An observation plan, similar to that utilized on the manned ocean-going barge, was followed on the chemical carrier. The voyage was divided into four major segments: loading, laden voyage, discharge, and ballast voyage. With respect to these voyage segments, the plan was to document the number and type of crewmen that comprised the watch complements for both Engine Room and Deck Department and observe their duties and work activities. Of primary interest was the documentation of potential sources of exposure to various airborne contaminants and the worker's proximity and duration near these sources. Extended work periods exceeding 8 hours in a 24-hour period were noted, and deckhouse living quarters were monitored for contaminant infiltration to assess potential exposures during off-hours.

Both personal and area environmental sampling methods were included in the observation plan. Deck department personnel were monitored for vapor exposure from the liquid cargos of interest by using both active and passive dosimetry techniques. Engine Room areas were monitored for oil mist and asbestos particulates. The intent of these samples was exploratory in nature and was designed primarily to collect a limited data base prior to developing a full experimental plan.

Other activities in the observation plan included documentation of dermal exposure to cargo and noncargo-related products, measurement of air velocities within living quarters to determine feasibility of passive dosimetry, documentation of activities involving pumproom operation, observation of tank cleaning procedures, and man-entry practices into gas-freed cargo tanks.

III.3.2 Summary of Chemical Tanker Activities

The previously cited tasks were accomplished on the voyage. In addition, other observations pertaining to work practices and exposure potentials were performed. Table III.4 lists the composite of the activities that were conducted during this voyage.

III.3.3 Environmental Monitoring - Methods and Results

Personal and area monitoring of cargo vapors were conducted in the Deck Department using primarily active (pump/tube) dosimeter methods. During selected sampling situations, passive dosimeters were used in parallel with the active dosimeters. Only area monitoring was conducted in the Engine Room, where the contaminants of interest were airborne asbestos and oil mist.

Adsorbent tube sampling and analysis procedures for cargo vapors were based on the methods recommended by NIOSH. These methods are summarized in Table III.5 for the chemicals that were monitored. Chemical abbreviations correspond to the Coast Guard's CHRIS system. Passive dosimeters were of the same type as were used on the gasoline carrier voyage. The manufacturer's recommended analysis procedures were followed.

The results of the sampling activities in the Deck Department are presented in Table III.6. Alphanumeric sample numbers apply to charcoal tubes, while passive dosimeters have five-digit sample numbers. Five of these samples (VF5, VF12, VF14, VF18, and VF20) were collected while several chemicals were being either loaded or discharged simultaneously. Consequently, these samples were analyzed for multiple analytes, and they reflect multiple vapor exposures. During sample collection, all of the vapors that could contribute to the crew member's exposure were noted. The tankerman's work activities and other concurrent deck operations guided the identification of these vapors. However, not all of the analyte levels could be quantified on every sample because certain analyte combinations had different desorption requirements. When this situation occurred, documented work activities and operations were

TABLE III.4. VOYAGE-RELATED ACTIVITIES

Deck Department

1. Document work scenarios that result in work periods greater than eight hours (both licensed and unlicensed crew members).
2. Document composition of work units during operations in port and at sea.
3. Document responsibilities of members of Deck Department.
4. Document work activities (not observed) based on discussions with the Chief Mate and other members of Deck Department.
5. Document observed work activities of members of work units.
6. Document frequency and duration of worker proximity to contaminant sources.
7. Document noncargo-related exposures (painting).
8. Parallel active and passive personal sampling on crew during loading and discharge operations and man-entry into cargo and ballast tanks and pumproom.
9. Parallel active and passive area sampling associated with pumproom operations and closed loading of Epichlorohydrin (EPC).
10. Measurement of chemical vapor emissions during loading, discharging, ballasting, and tank cleaning.
11. Observed tank cleaning of all cargo tanks in preparation for Coast Guard inspection.
12. Conduct tank cleaning tests.
13. Enter gas-freed product and ballast tanks with crew.
 - o Document work activities (sweep solid debris on tank bottoms and mop up residual cargo), vapor levels, and crew safety procedures.
14. Observe mucking of two ballast tanks that had leakage of gasoline product from adjacent cargo tank through oil-tight bulkhead.
15. Document vapor exposures during cargo discharge due to leaky product line drain valves.
16. Observe and document dermal exposure to cargo liquids during tank sampling and manifold valve blind removal prior to discharge.

TABLE III.4. VOYAGE-RELATED ACTIVITIES
(Concl'd)

Engine Room

1. Walk-through surveys to identify potential contaminant sources.
2. OVA measurement of vapor concentrations in Engine Room (six levels) during operations in port and at sea.
3. Document major equipment components.
4. Area sampling for asbestos and oil mist.
5. Document fluids (degreasers) used for equipment cleaning.
6. Document work responsibilities of Engine Room crew.
7. Document typical repair, maintenance, and housekeeping activities that are performed in port and at sea.
8. Document method of ventilating Engine Room.
9. Discussions with Engine Room personnel regarding chemical vapor infiltration in the Engine Room during tank cleaning on the ballast voyage.

Deckhouse

1. OVA measurement of vapor concentration in Deckhouse (all levels) during loading, ballasting, discharge, and tank cleaning operations.
2. Monitor air velocities in crew quarters next to beds to determine feasibility of passive dosimetry during nonwatch rest hours.
3. Document method of ventilating Deckhouse.

TABLE III.5. SUMMARY OF CHARCOAL TUBE SAMPLING
INFORMATION FOR CHEMICAL CARGOS

Chemical	NIOSH Method No.	Adsorbent Material	Sampling ⁽³⁾ Rate (LPM)	Sampling ⁽³⁾ Time (min.)	Desorption Solution
Methyl ethyl ketone (MEK)	S3	Charcoal	0.20	50	Carbon disulfide
Epichlorohydrin (EPC)	S118	Charcoal	0.20	100	Carbon disulfide
Ethyl alcohol (EAL)	S56	Charcoal	0.05	20	Carbon ⁽¹⁾ disulfide
Mixed xylenes (XLO,XLM,XLP)	S318	Charcoal	0.20	60	Carbon disulfide
n-Butyl alcohol (BAN)	S66	Charcoal	0.20	50	Carbon ⁽²⁾ disulfide
Benzene ⁽⁴⁾ (BNZ)	S311	Charcoal	0.20	60	Carbon disulfide

- (1) Containing 1% 2-butanol
(2) Containing 1% 2-propanol
(3) TLV-TWA sampling
(4) Benzene in gasoline

reviewed, and the chemicals that were selected for analysis were those that were judged to be present in the highest concentrations. The remaining analytes were sacrificed. For example, BAN was sacrificed on the above five samples, but it was retained on Sample No. VF18 at the expense of other analytes.

Engine Room area samples were analyzed for airborne asbestos and oil mist according to the procedures that were outlined in Section II. A summary of the sampling results is shown in Table III.7. Fiber counts and oil weights have been corrected for blanks. For the asbestos samples, 100 fields were counted, the microscope field area was 0.00397 mm², and the effective collection area was 855 mm² for the 37-mm-diameter filters.

III.3.4 Data Interpretation

Engine Room

Five of the eight environmental samples that were collected in the Engine Room were analyzed for asbestos. The resulting asbestos concentrations were either not detectable or were well below ACGIH and OSHA exposure limits. The specific asbestos form was not identified. Those samples that did not contain detectable fiber counts were collected at

TABLE III.6. SUMMARY OF ENVIRONMENTAL MONITORING DATA FROM PARCEL CHEMICAL TANKER OPERATIONS - DECK DEPARTMENT (AT SEA AND IN PORT)

Activity	Sample No.	Chemical(s) Adsorbed	TLV-TWA (ppm)	TLV-STEL (1) (ppm)	Exposure Concentration (ppm)	Exposure Duration (min.)	Temp. (°C)	Relative Humidity (%)	Sampling Rate (LPM)	Analyte Weight (µg)
Restricted tank gauging - loading	VF5	HEX EPC(2) EAL	200 2 1000	300 5 -	0.92 0.47 0.16	172 172 172	28.8 28.8 28.8	72 72 72	0.201 0.201 0.201	74.8 41 7
	VF6 47754	Xylenes (2) Xylenes	100 100	150 150	0.28 0.47	106 106	25.6 25.6	83 83	0.197 30.9 (4)	25 2
	VF14	HEX EPC EAL Xylenes	200 2 1000 100	300 5 - 150	0.09 0.10 0.41 0.25	202 202 202 202	18.3 18.3 18.3 18.3	90 90 90 90	0.204 0.204 0.204 0.204	9 11 22 46
Restricted tank gauging - discharge	VF12	HEX EPC EAL Xylenes	200 2 1000 100	300 5 - 150	0.78 0.38 2.76 0.21	110 110 110 110	19.2 19.2 19.2 19.2	85 85 85 85	0.194 0.194 0.194 0.194	40 21 7 20
	VF18	BAN	50	-	4.44	176	19.7	67	0.208	423
	VF20	HEX EPC EAL Xylenes	200 2 1000 100	300 5 - 150	ND (5) 0.12 0.80 ND	93 93 93 93	20.6 20.6 20.6 20.6	85 85 85 85	0.208 0.208 0.208 0.208	ND 6 20 ND
Restricted tank gauging - ballasting into cargo tank	VF15	BNZ (6)	10	25	0.14	141	28.6	59	0.194	12
Product sampling of loaded tanks through ullage ports	VF10	HEX Xylenes	200 100	300 150	1.21 0.09	13 13	16.7 16.7	90 90	0.204 0.204	7.8 1
	VF7	BNZ	10	25	0.51	22	31.1	76	0.205	7
Man-entry into pumproom - mucking bilge	VF8	BNZ	10	25	0.84	22	31.1	76	0.198	11
Man-entry into forward ballast tank to check on suspected AvGas leak from adjacent product tank	VF11	BNZ	10	25	ND	144	27.9	87	0.196	ND
	VF13	BNZ	10	25	ND	165	26.9	85	0.209	ND
	47753	BNZ	10	25	ND	165	26.9	85	41.4 (4)	ND
Man-entry into fresh water ballast tank to check on suspected motor gas leak from adjacent product tank	VF100	BNZ	10	25	ND	17	30.0	70	0.204	ND

TABLE III.6. SUMMARY OF ENVIRONMENTAL MONITORING DATA FROM PARCEL CHEMICAL
TANKER OPERATIONS - DECK DEPARTMENT (AT SEA AND IN PORT)
(Concl'd)

Activity	Sample No.	Chemical(s) Adsorbed	TLV-TWA ⁽¹⁾ (ppm)	TLV-STEL ⁽¹⁾ (ppm)	Exposure Concentration (ppm)	Exposure Duration (min.)	Temp. (°C)	Relative Humidity (%)	Sampling Rate (LPM)	Analyte Weight (µg)
Man-entry into Cargo Tank 3S to position stripping hose and to remove cover plate that provides access into double-bottom of adjacent EPC tank	VF102	EPC	2	5	0.40	84	31.1	74	0.204	17
		EAL	1000	-	66.65	84	31.1	74	0.204	1434
Man-entry into Cargo Tank 3P to remove residual cargo from tank	VF103	EAL	1000	-	239.29	30	29.4	77	0.203	1840
Area sample - loading; downwind of EPC tank at man-breathing height	VF4	EPC	2	5	0.22	188	28.8	72	0.199	21
Area sample - discharging; near pump-room exhaust fan discharge (area frequently passed by Mate on watch)	VF1 } 47756 } (3)	BNZ	10	25	5.23	208	30.4	69	0.207	711
		BNZ	10	25	10.50	208	30.4	69	41.4(4)	261
Area sample - discharging; bottom of pumproom	VF2 } 47741 } (3)	BNZ	10	25	4.07	193	30.6	69	0.199	492
		BNZ	10	25	2.00	193	30.6	69	41.4(4)	48.9
Area sample - laden voyage; same as VF2 except after mucking and cleaning of bilge	VF16	BNZ	10	25	0.02	566	21.9	79	0.192	7

NOTES: (1) 1981 ACGIH values

(2) Primary route of entry by skin; all other chemicals by inhalation

(3) Parallel active and passive samples

(4) Sampling rate for passive dosimeters (cm³/min.)

(5) ND = not detectable

(6) All benzene levels reflect that component in gasoline.

TABLE III.7. SUMMARY OF ENVIRONMENTAL AREA MONITORING DATA FOR ASBESTOS
AND OIL MIST ON PARCEL CHEMICAL CARRIER - ENGINE ROOM (AT SEA)

Sample No.	Location	Sample Duration (min.)	Sampling Rate (LPN)	Temp. (°C)		Number of Fibers (2) or Weight of Oil Analyte (mg)	Concentration Fibers (2) / cm ³ or mg/m ³ *
D1	Control Panel Desk 1600-2000 Watch	225	1.475	33.3	Unknown	0.5	0.003
					Asbestos		
					Oil Mist	140	0.43
D2	Walkway Near Boiler Uptake	218	1.475	45	Asbestos	ND	ND
					Oil Mist	174	0.58
D3	Lube Oil Purifier and Main Reduction Gear	213	1.475	33.3	Oil Mist	222	0.73
D5	Control Panel Desk 1200-1600 Watch	226	1.475	38.9	Asbestos	ND	ND
					Oil Mist	201	0.63
D9	Lube Oil Vent for Main Reduction Gear	180	1.475	41.7	Oil Mist	1028	4.1
D10	Control Panel Desk (Overlap of 1200-1600 and 1600-2000 Watches)	271	1.475	36.7	Asbestos	2	0.01
					Oil Mist	237	0.63
D16	Lube Oil Vent for Main Reduction Gear (Same as D9)	256	1.445	36.7	Oil Mist	570	1.62
D19	Insulated Piping of Low Pressure Steam Turbine	222	1.550	36.7	Asbestos	ND	ND

(1) Weight of analyte corrected for blank

(2) Fibers > 5µ, corrected for blank

* Concentration as equivalent mineral oil

sites where insulation had deteriorated, and airborne fibers were expected.

Sample Nos. D1 and D10, which showed fiber counts, were collected at the control panel desk, some distance from the deteriorated insulation. The desk was located in proximity to a discharge duct that provided fresh air to this portion of the Engine Room. The main exhaust duct for the Engine Room was located topside in the vicinity of the fresh air intakes. As the boiler tubes were blown during the sampling period, it is possible that the resulting equipment vibrations generated airborne fibers that were (1) captured by the exhaust system, (2) discharged to the ambient atmosphere, and (3) entrained into the fresh air supply.

With the exception of Sample Nos. D9 and D16, all measured oil mist concentrations were well below the ACGIH TLV-TWA of 5 mg/m³. These are replicate samples that were collected near the lube oil vent for the main reduction gear, but at different times. As concentration increased with Engine Room temperature, it is possible that the mist was, in part, thermally induced.

All of the area samples produced measurable oil mist concentrations. While these data do not reflect personal exposures, they do aid in characterizing and understanding the exposure environment. The samples collected at the control panel desk ranged from roughly 0.4 to 0.6 mg/m³ with sample durations that approximated a 4-hour watch period. Engine Room personnel spend nearly three-fourths of a watch at the console desk. Higher mist concentrations would be anticipated during maintenance and repair activities in the vicinity of the main reduction gear.

Deck Department

Environmental monitoring was conducted for the vapors of the pure chemical cargos that were identified in Section III.3.1, as well as the benzene fraction in gasoline. Personal exposures were monitored during the following work scenario.

- o Restricted gauging during loading, discharging, and ballasting operations,
- o Collection of quality control samples from loaded product tanks,
- o Confined space entry.

Area samples were also collected and included pumproom concentrations before and after bilge cleaning. Passive dosimeters were used in parallel with charcoal tubes on selected occasions.

Restricted gauging during loading, discharging, and ballasting operations produced occupational exposures to individual chemical vapors that were nominally less than 4 ppm with the majority being less than

1 ppm. None of the individual concentrations exceeded the TLV-TWA during a sampling interval. Assuming a zero level exposure for the remainder of an 8-hour period, the time-weighted average exposure to individual chemicals was substantially less than the appropriate TLV-TWAs. In addition to assessing the exposures to individual chemicals, simultaneous exposure to multiple chemical vapors was also assessed by applying the ACGIH mixture criterion

$$\sum \frac{C_i}{T_i} > 1$$

where C_i is the concentration of the i -th mixture component, and T_i is its TLV-TWA. On the basis of additive effects, the results in Table III.8 indicate that all mixtures were below the allowable Threshold Limit, the highest being 24 percent of the mixture limit. It should be noted that EPC was the only product on the ship that was close-loaded and close-gauged with vapors vented at a distance of B/3 above the deck. Thus, measured concentrations of EPC represent the descent of diluted vapor back to deck level. In fact, the major contribution to the mixture summation for Sample Nos. VF5 and VF12 is due to EPC.

TABLE III.8. CALCULATED FRACTIONS OF MIXTURE THRESHOLD LIMITS FOR MULTIPLE VAPOR EXPOSURES

Sample No.	Chemicals	$\sum \frac{C_i}{T_i}$
VF5	MEK, EPC, EAL	0.24
VF12	MEK, EPC, EAL, Xylenes	0.20
VF14	MEK, EPC, EAL, Xylenes	0.05
VF20	EPC, EAL	0.06

Ethyl alcohol (EAL) vapor was present during loading (Sample No. VF5) and discharging (Sample No. VF12). The higher concentration on VF12 reflects the higher line pressures during discharge that result in product leakage past drain valves and into the work area. The BAN concentration on VF18 most likely resulted from the same cause.

A product sample is normally collected from each tank for quality control purposes. The exposure samples that were collected during this operation met all of the assessment criteria that were applied to the gauging operations.

Five confined space entries were documented and monitored:

- o Two entries were made into separate EAL tanks. One entry was for removal of residual product from the pump sump. The resulting EAL concentration, as measured on Sample No. VF103, was approximately 20% of the TLV-TWA for a 30-minute exposure. The second entry involved a potential for exposure to EPC in addition to EAL. During this 84-minute entry, EPC and EAL exposures were below their respective TLV-TWAs. Exposure to the mixture represented 27% of the mixture Threshold Limit with EPC providing the major contribution.
- o Two entries were made into noncargo tanks. Both entries involved segregated ballast tanks, and each entry was made because leakage of gasoline from adjacent cargo tanks had been suspected. Benzene exposures were monitored during these entries, but concentrations were not detectable.
- o Two crew members entered the pumproom to clean the bilge. This activity is not routine on each voyage, but was necessary on this voyage because the ship was scheduled into the yard for biennial inspection. During this operation, products, namely gasoline, were not flowing through the pumproom. The exposures to the benzene fraction of any gasolines in the bilge were monitored over a 22-minute work period. Both samples produced benzene concentrations that were less than 1 ppm; thus, TWA and STEL limits were not exceeded.

The pumproom is used primarily during product discharge, ballasting, and tank cleaning. The large centrifugal pumps in this room may develop cargo leaks that accumulate in the bilge. Bilge cleaning is generally performed when the leaks are substantial or the ship is scheduled for inspection. The pumpman's responsibilities require that he enter this confined space during product discharge, and the bilge accumulations and leaks can generate a work atmosphere that is a potential source of exposure. Area Sample No. VF2 was collected to characterize the benzene vapor environment in the pumproom. This sample was collected during gasoline discharge and at a location where the pumpman would work. Although the pumpman spends a small portion of his time in this space, the measured benzene level of 4 ppm is meaningful because it is of the same order of magnitude as the exposure levels that were monitored during open gauging of gasoline tanks on the ocean-going barge (see Section III.2 of this report). While the 4-ppm level is below ACGIH TWA and STEL limits, it would represent a contribution to the pumpman's total occupational exposure.

Sample No. VF2 represents conditions when products are flowing through the pumproom. The pumproom has its own mechanical exhaust ventilation systems. The discharge was located on deck adjacent to the deckhouse superstructure and near the walkway that provided access to the second level of the deckhouse. Crew members, specifically the Mate on watch,

frequently walked past this discharge. Sample No. VF1 was collected in the vicinity of the pumproom exhaust and walkway. The measured area concentration of 5 ppm benzene with gasoline flowing through the pumproom is consistent with the benzene level of 4 ppm (Sample No. VF2) in the pumproom during this same operation.

After products have been discharged through the pumproom and the pumps have been turned off, the ventilation system is operated to purge this space of the vapor environment prior to man-entry. Sample Nos. VF7 and VF8 indicate that the ventilation was effective in controlling exposures during bilge cleaning. Area Sample No. VF16 was collected in the pumproom after bilge cleaning and indicates that the mucking operation and mechanical ventilation combined to produce a postmucking benzene concentration that was essentially not detectable.

Recall that the EPC vapors were discharged at a height of B/3 above the deck during loading. Area Sample No. VF4 was collected at breathing-zone height above the deck and downwind of the vapor discharge point. The measured EPC concentration confirms the levels that were obtained with personal monitors. This venting method is required by Subchapter O of the USCG regulations. It effectively separates the vapor discharge point from the work area and allows the high vapor concentrations that exist at the end of loading to be diluted and dispersed by the ambient atmosphere.

Several of the charcoal tube samples that were collected during this voyage indicated the presence of vapor mixtures in the work environment, particularly during loading and discharging. None of the multiple vapor exposures exceeded the ACGIH mixture Threshold Limit when additive effects were assumed because component levels were individually quite low. While these exposures meet recognized criteria for assessing vapor mixtures, there is no convenient mathematical method for assessing work place exposures to multiple vapors at very low levels. The National Academy of Sciences (Reference 11) acknowledges that there is a need to define the potential risks or hazards for this class of exposure, but the tools to accomplish this are beyond the state-of-the-art.

During four sampling intervals, passive dosimeters were used in parallel with charcoal tubes. Only two sets of samples produced results that were detectable at levels greater than 1 ppm, and these pairs of samples were for benzene in gasoline. For both sets, the active and passive dosimeters agreed within a factor of two at nominally the 5-ppm level. Neither method exhibited a consistent bias.

The measured benzene concentrations were converted to total gasoline vapor concentration using the method outlined in Section III.2.4. These concentrations were then adjusted to time-weighted averages over an 8-hour period, assuming that gasoline vapor was absent for times greater than the sampling durations. Only the area samples that were collected in the pumproom and near the pumproom ventilation exhaust during product discharge produced results that can meaningfully be compared to gasoline

vapor exposure limits. The calculations are summarized below. The remaining samples resulted in TWA gasoline vapor concentrations that were less than 10 ppm.

Sample No.	C _{BNZ} , ppm	Sample Duration, min.	Equivalent Gasoline Vapor Concentration, ppm	TWA Gasoline Concentration, ppm
VF1	5.23	208	747	324
47756	10.50	208	1500	650
VF2	4.07	193	581	234
47741	2.0	193	286	115

These calculations indicate that the proposed ACGIH TLV-TWA of 300 ppm for total gasoline vapor was exceeded for the samples that were collected at the pumproom exhaust (VF1 and 47756). As these levels are indicative of the concentrations that existed in a work traffic lane, they would make an important contribution to an exposure profile. If it was known that the sampling environment were constant during the 208-minute period, then the proposed TLV-STEL of 500 ppm would also have been exceeded by a wide margin.

The estimated pumproom concentrations of total gasoline vapor did not exceed the TLV-TWA when they were adjusted to an 8-hour period. Again, assuming constancy of vapor environment, the TLV-STEL was exceeded by Sample No. VF2, but not by Sample No. 47741.

III.3.5 Summary of Important Results

1. Deckhouse hydrocarbon vapor concentrations were typically low (< 7 ppm) at sea and in port except during ballasting operations (14-40 ppm). Deckhouse infiltration of cargo vapors can occur through port, starboard, and aft access hatches, and through the galley ventilation system. Infiltration cannot occur through the primary deckhouse ventilation system because it operates in a closed, recirculation mode.
2. Air velocity measurements in crew quarters indicated that passive dosimetry is inappropriate for personal sampling during rest periods because velocities are less than manufacturer-recommended minimums.
3. Tank cleaning was identified by the crew as the operation that would most likely result in infiltration of cargo vapors into the deckhouse.
4. Unexpectedly high concentrations of gasoline vapor were detected in the deckhouse on the first day of the voyage. The emission source proved to be a loose flange connection

on the filling line for the fresh water ballast tank; this flange was located inside the deckhouse. Apparently, gasoline had leaked from the adjacent cargo tank, past an oil-tight bulkhead, and into the fresh water ballast tank.

5. Engine Room hydrocarbon vapor concentrations were less than 10 ppm at sea and in port.
6. During at-sea operations, asbestos and oil mist concentrations were below recognized exposure limits in the Engine Room.
7. Cargo vapors can infiltrate into the Engine Room because the inlet to the ventilation system draws from the ambient air.
8. Crew members did work an extended work schedule (beyond the routine 4-hour watch), particularly during the operations of tank cleaning, cargo loading, and cargo discharge. A few instances were noted where crewman were on duty for 16 to 24 hours continuously. Other crew members worked a standard 8-hour work day.
9. Crew members were monitored for exposure to ethyl alcohol, methyl ethyl ketone, epichlorohydrin, xylene, and benzene (from gasoline). Occupational exposure levels were generally higher for tank entry operations than for other work activities. Restricted gauging (through a sounding tube), as shown in Figure III.4, and closed gauging reduced exposure levels for tankermen during cargo loading as compared to open gauging.
10. On-deck chemical vapor concentration during cargo discharge was unexpectedly high due to emissions from leaking drain valves in the cargo transfer lines. Hydrostatic pressure at these locations in the lines is higher during cargo discharge than during cargo loading.
11. Area samples inside and on the outside of the pumproom during product discharge indicated that concentrations approached or exceeded the recommended TLV-TWA for total gasoline vapor.

Dermal contact with chemical products was observed during removal of blind flanges from the cargo transfer manifold. Discussions with crewmen revealed that skin contact also occurs when the ship's product cargo transfer lines are drained. The drain valves are located in a tightly confined region between the transfer piping and the deck. When the valves are opened, the crewmen cannot move away quickly enough to avoid splash contact with the product.



FIGURE III.4. TANKERMAN GAUGING CARGO ULLAGE THROUGH A RESTRICTED GAUGING SYSTEM (SOUNDING TUBE) THAT PENETRATES THE LIQUID SURFACE

III.4 Work Schedules

The work schedules of land-based industries consist predominately of the eight-hour work day and the five-day work week. Perturbations on this schedule do occur, such as a short-term requirement for daily or weekend overtime. After these short-term requirements are satisfied, the conventional schedule is then resumed. If the work environment includes occupational exposures to air contaminants, then the land-based work schedule permits a 14- to 16-hour biological purge period between exposures on consecutive days, as well as a 48-hour weekend purge period. The Time-weighted average Threshold Limit Values (TLV-TWA) that are used in assessing these occupational exposures are based on this work-rest cycle.

The work schedules aboard marine bulk chemical tankers are quite different from land-based schedules. Depending upon the policies of the organization that provides the crew for a ship, the overall annual work cycle or tour may include, but not be limited to,

- o 30-day work tours separated by 30-day periods of shore leave,
- o 4-month tours on the ship separated by two months of shore leave, or
- o eight months on the ship followed by four months of shore leave.

These work tours may be extended if the ship is at sea on the last day of a tour or if a replacement is not available to relieve a crew member at the end of his regular tour. During a tour, the crew members work and live on the ship. Opportunities for shore time while in port do occur, but these opportunities are rather infrequent.

Based on the voyages of this project, three formal work schedules were identified:

- o Schedule 1 - This schedule represents the traditional repetitive work schedule of four hours on watch followed by eight hours off watch. For example, a crew member may work the 0800-1200 and 2000-2400 hour watches every day. His total work time would be eight hours out of every 24-hour period, but the maximum biological purge period would be eight hours.
- o Schedule 2 - This schedule consists of alternating 6-hour periods on watch followed by six hours off watch, e.g., watches from 0600-1200 and 1800-2400 hours each day. With 12 hours of work in each 24-hour period, the maximum biological purge period on this schedule is six hours.

- o Schedule 3 - This schedule consists of eight consecutive hours of work each day and exists between 0800 and 1700 hours.

The Engine Department personnel followed Schedule 1 or a combination of Schedules 1 and 3. Deck Department operations require more flexibility in work scheduling. The Chief Mate may switch the Deck Department personnel from Schedule 1 to Schedule 2 on a single voyage in order to accommodate an increased work load. Also, all three schedules and combinations of schedules may coexist in the Deck Department. Schedules 1 and 3 were observed within the Deck Department on one background voyage. On the other background voyage and the Task IV voyage, all three schedules were observed, and for one period of time, all three schedules were in effect (simultaneously) for various Deck Department personnel.

Work Schedules 1 and 2 may be termed "Unusual Work Schedules" in the context of both the daily work routine and the annual work cycle. Although Schedule 3 is conventional in terms of the duration of the daily work period, it is also unusual because

- o the employee lives in his work environment,
- o there is no weekend break, and
- o the annual work cycle differs from the conventional work year.

The personnel in each of the ship's departments operate under a formalized or basic work schedule. However, because of the Deck Department's operational requirements for cargo transfer, ballasting, navigation, tank cleaning, docking and undocking, and some maintenance activities, the duration of a continuous work period may be extended on through one or more rest periods. These situations result in what is termed an "Extended Work Schedule." These extended schedules arise because of responsibility, overtime, or other unique factors. On most vessels, the Chief Mate has overall responsibility for tank cleaning; his continued supervision of this activity results in an extended work period. Overtime, which can be either mandatory or voluntary, may minimize or nullify a formal rest period. An example of mandatory overtime would be for docking or undocking if it occurs while the individual is off-watch. Voluntary overtime is performed off-watch and may average four to five hours per day. This extra work time may be spent in the Engine Room on maintenance and housekeeping activities or on-deck as part of a long-term repair program. Unique factors which do not occur on a routine basis can also contribute to an extended work schedule. An example of such a factor is shift swapping for free time ashore. Examples of documented extended work schedules are given below.

Chief Mate

<u>Time (Hours)</u>	<u>Activity</u>
1400-2000	Regular deck watch plus "all hands" for undocking
2000-0400	Tank washing and ventilating at sea
0400-0800	Regular navigation watch
0800-1600	Continue tank washing, stripping, and ventilating
1600-2000	Regular navigation watch

30 consecutive work hours

Able-bodied Seaman (A/B)

<u>Time (Hours)</u>	<u>Activity</u>
0800-1600	Day deck work shift
1600-2000	"All hands" preparation for docking
2000-2400	Work a trade-off shift in port to repay a previous shift exchange
0000-0400	Navigation watch

20 consecutive work hours

Ordinary Seaman (O/S)

<u>Time (Hours)</u>	<u>Activity</u>
0800-1600	Deck work shift cleaning debris from tank bottoms
1800-2300	Assist in heel washing of tanks

13-hour day

Ordinary Seaman (O/S)

<u>Time (Hours)</u>	<u>Activity</u>
0000-0400	Regular cargo transfer deck watch
0400-0800	"All hands" for undocking
0800-1600	Deck day work shift at sea

16 consecutive hours

Other examples of extended work schedules, up to 24 consecutive hours, are given in the Background Voyage Reports in the appendices.

The "Unusual Work Schedule" and the "Extended Work Schedule" represent an important departure from the conventional concept of a work schedule. The methods that are used to assess occupational exposures must reflect these work schedules, which are unique to the maritime industry.

III.5 Work Practices

The subject of work practices deals with the manner in which tasks are performed, and it reflects the worker's level of awareness of the potential hazards of the chemical substances in his work environment. From an industrial hygiene viewpoint, the following work practices are noteworthy.

- o During loading, discharging, ballasting, and tank cleaning, crew members frequently brought open containers of soft drinks and coffee onto the deck. These containers were set on expansion trunks and other locations in the vicinity of a work station. The extent to which cargo vapors are absorbed in these liquids and subsequently ingested is unknown.
- o Product vapors are discharged from a tank during loading. The direction of vapor plume travel is governed generally by the local wind direction. All voyages considered, there was no uniform attempt to stand upwind or crosswind of the vapor discharge during open gauging of tanks.
- o Multi-component marine epoxy paints are stored in bulk and are manually mixed in either the forecastle or a midship storage room. These paints and their thinners contain xylene, naptha, butanol, and methyl ethyl ketone. Manufacturers recommend in their Material Safety Data Sheets that these paint materials be handled in the presence of adequate ventilation so as to avoid symptoms of vapor exposure such as headache, drowsiness, dizziness, and irritation. During the background voyages, it was judged that the storage and mixing spaces did not have adequate natural or mechanical ventilation for vapor removal. One of the spaces had an access door, and a mechanical exhaust fan was in place on one wall of the enclosure. The exhauster was not used during mixing operations because the crew did not know if the electric drive motor was intrinsically safe. Another enclosure had a single access door, but no provision for crossdraft natural ventilation. Comments of the deck crew indicated that the lack of ventilation had produced the above exposure symptoms.

- o Observed on-deck dress codes varied from long-sleeved shirts and pants to shorts and no shirts. The latter form of dress provides little protection against dermal contact with product liquids, product vapors, or nonproduct liquids such as acid-based derusting solutions that are applied with a spray applicator. The use of rubber gloves and safety goggles was seldom observed during activities in which a high probability of contact with chemical liquids occurred. Such activities included obtaining tank and line samples of the loaded cargo and removal of manifold product valve blinds prior to discharge.
- o On the gasoline carrier, tank entries in port were preceded by a Marine Chemist's certification. At sea, the Chief Mate tested the tank atmosphere with an O₂/CGI. On the chemical tanker, all tank atmospheres were not routinely tested by a crew member before entry; these tests were dismissed, presumably because prior experience had indicated that the cleaning procedure produced an acceptable work environment. Exceptions included tanks where EPC or gasoline contamination was suspected. Overall, none of the tanks' atmospheres were tested with devices that are chemical specific such as colorimetric indicator tubes.

IV. DEVELOPMENT OF AN EXPERIMENTAL PLAN

IV.1 Approach to Plan Development

The primary objective of the U. S. Coast Guard's Crew Exposure Study is to fully characterize the occupational exposure profiles of crew members aboard vessels that transport bulk liquids by water. In this context, exposures include inhalation and dermal contact with cargo- and noncargo-related materials in the form of liquids, vapors, dusts, mists, and gases. It is recognized that the direct ingestion route of exposure is rare, but where there is a potential for indirect ingestion as a result of personal habits with food and drink, this form of exposure is also of interest. The products that were chosen for evaluation were those that have established exposure standards and developed sampling and analysis methodologies; products meeting this criteria include a wide range of pure chemicals, gasolines, and crude oil. This definition excludes a small portion of the products that may be proprietary compounds or blends for which this type of information may not be available. However, the work documentation associated with these latter compounds will provide additional insight into the total exposure potential.

The purpose of the preliminary voyage observations was to observe and document cargo- and noncargo-related operations and work practices to the extent that an experimental plan could be developed that would be responsive to the primary project objective. These voyages provided the necessary input with respect to

1. Deck Department operations associated with cargo loading and discharging, maintenance on the laden voyage, cargo tank ballasting, and tank cleaning/entry on the ballast leg of the voyage;
2. Engine Room/Pumproom operations during the various phases of a round-trip voyage; and
3. The effect of cargo handling operations on the environment in the crew's living quarters.

This information was then supplemented by extensive industrial hygiene and engineering test data that have been collected by SwRI during vessel operations in marine terminals in support of past and ongoing U. S. Coast Guard research projects (Contract Nos. DOT-CG-904571-A and DOT-CG-70363-A). The resulting experimental plan identifies the number of voyages that would be needed to achieve the stated objective for a representative cross-section of the industry and an environmental sampling plan for a composite work scenario that reflects the observed activities. The plan includes both the Deck and Engineering Departments; the observations and environmental monitoring that have been conducted to date indicate that the emphasis of the plan should be placed upon Deck Department operations because of the intimate involvement with the cargos.

Three methods of approach to plan development were considered:

- o Statistical Approach - This approach would attempt to identify the number of voyages that are needed to ensure that the results are significant at a prescribed level of confidence, given a specific range of physical inputs. Based on prior experience, this approach was rejected because, in all likelihood, the number of voyages would be prohibitive from the standpoint of time and cost schedules.
- o Chemical Specific Approach - This approach would first attempt to identify key or high-interest chemicals based on specific criteria such as toxicity, shipping volumes, etc. Then a search would be required to identify vessels that transport a multiplicity of these products. This approach was also rejected for several reasons, which include
 - o uncertainties in identifying vessels whose loading plans include a majority of these high-interest chemicals;
 - o potential biases that could result from a restricted chemical list which excludes other products whose vapors contribute to the overall exposure environment (profile).

Therefore, it was judged that the experimental plan should not be restrictive as to cargos, but should be responsive to the products of interest as defined at the beginning of this section. Finally, it should be noted that the chemical transport industry is flexible and responds to market demands. Changing economic situations could essentially void a chemical-specific plan and introduce inefficiencies and time delays in executing such a plan.

- o Operational/Configurational Approach - This approach formed the basis for the experimental plan, which is presented in detail in Appendix G. The plan focuses on the end-product of this research effort, namely, an assessment of the occupational environment that is representative of the industry. Specific details of the plan are presented in Section IV.2.

IV.2 Elements of the Experimental Test Plan

IV.2.1 Vessel and Voyage Selection Criteria

The test plan consists of the following numbers of recommended voyages:

- o seven voyages to characterize the exposure profiles of Deck Department personnel to various forms of chemical substances in the work environment;

- o two voyages to perform similar characterization for Engine Room/Pumproom personnel;
- o an optional voyage that would be directed at the Deck Department personnel aboard a crude oil tanker operation.

The crude oil tanker test represents the only product-specific voyage. It was included because large volumes of crude oil are transported in U. S. waters. In addition, there are difficulties that exist in cleaning residual crude from empty tanks which can pose a rather unique exposure scenario. Also, the use of inert gas and crude washing systems on these ships could pose additional crew exposure potentials beyond those encountered on chemical or gasoline tankers.

The remaining nine voyages were defined in two steps.

Step 1. Based on the preliminary voyage observations of this project and prior testing experience on several bulk liquid carriers, a set of quantitative factors or variables were defined which have been shown to affect, or have the potential of affecting, occupational exposures. These factors relate generally to the configurational features of a ship, but they also reflect operational procedures. Therefore, the following factors can be considered to be controllable for experimental design purposes as opposed to uncontrolled variables such as atmospheric conditions:

- o Crew Size
- o Integral vs Double-Bottom Tanks
- o Deckhouse Configuration
- o Gauging System
- o Venting System
- o Cargo Discharge System
- o Propulsion System

As shown in Appendix G, a range of configurational variations was then defined for each major variables.

Step 2. Specific vessels were then correlated with individual variable subclasses. These vessels exhibit either a specified configurational feature or operational procedure that has been observed to preempt minimum USCG requirements. An example of a variance in operational procedure would be open gauging and open venting of a Subchapter O chemical whose minimum requirements are restricted gauging and venting through a 4m pressure/vacuum vent. Finally, vessel identity was cross-indexed by variable subcategory. Seven vessels and nine voyages were defined. The vessel names have been coded for anonymity

purposes. The vessel/voyage matrix is presented in Table IV.1.

Before proceeding to a discussion of the sampling plan for occupational exposure monitoring, it is appropriate to mention that the experimental plan was implemented on one voyage during this Phase I study. According to the experimental plan, the remaining voyages are assigned to a Phase II study. Voyage No. 7 aboard Vessel No. 4 was selected for this purpose. In retrospect, this voyage identified two additional operational variables that were not anticipated during the initial design of the plan. These variables are short-loading and shore-stop, both of which act in a direction to reduce exposure potential for deck personnel during cargo loading. In a short-loading, the tank is not filled to its operating capacity; the tank is slack. As such, there is insufficient time for a substantial vapor-rich blanket to develop and be discharged before the loading is halted. In a shore-stop, termination of product delivery is controlled by the tank farm as opposed to a ship-stop where termination is controlled by the ship via transceiver communication with the dock and tank farm. Since delivery is controlled from the shore, there is little necessity for continuous open gauging at tank top-off.

IV.2.2 Sampling Plan

The vessel and voyage selection criteria identified ten voyages to characterize the occupational exposures of personnel in the Deck Department and the Engine Department/Pumproom. Because of the difference in work activities, shift schedules and environments, separate sampling plans are necessary for each of these two departments. The majority of the voyages would be directed to the Deck Department because the environmental monitoring data that have been collected to date during the background voyages and the marine terminal study indicate that the potential for exposure is greater in this department. The sampling plan in Appendix G reflects this Deck Department priority; development of an analogous sampling plan for the Engine Department/Pumproom would be deferred until Phase II of the study.

The approach to the experimental design is not chemical-specific, and, in addition, work schedules are apt to be different on each of the seven Deck Department voyages. Therefore, at this stage, the sampling plan cannot be completely specific, but must contain a degree of generality; the plan can then be made more specific when exact product loading plans and work schedules become known. To this end, the plan is based upon a postulated voyage scenario and a number of assumed, but unspecified, cargos. Within this framework, it was possible to estimate the numbers and types of exposure samples (based on experience and NIOSH sampling protocols), as well as equipment requirements. The key elements of this plan are summarized below.

- o Voyage scenario - 14-day round trip that includes loading, discharge, laden leg, and the ballast leg during which tanks are cleaned and entered.

TABLE IV.1. VOYAGE IDENTIFICATION AND VESSEL CHARACTERISTICS

<u>Voyage No.</u>	<u>Vessel No.</u>	<u>Vessel Characteristics</u>	<u>Vessel Department</u>
1	1	1a, 2a, 3a, 4a, 5b	Deck
2	2	1a, 2b, 3a, 4a, 5b	
3	3	1b, 2a, 3b, 4a, 5b	
4	5	1b, 2a, 3a, 4b, 5ab	
5	6	1b, 2b, 3b, 4b, 5bc	
6	7	1b, 2b, 3a, 4a, 5ab	
7	4	1b, 2b, 3a, 4c, 5ac	Engine/Pumproom
8	3	6b, 7b	
9	4	6b, 7a	

Code of Vessel Characteristics

1. Crew Size	5. Vent Systems (Loading)
a. Minimum Crew	a. b/3 or 4m (or high velocity)
b. Maximum Crew	b. Reasonable Height
2. Tank/Hull Type	c. Vapor Return
a. Tank Walls Integral with Hull	6. Cargo Discharge System
b. Double-Bottom Tanks	a. Dedicated Deepwell
3. Deckhouse Configuration	b. Pumproom
a. Single Aft Deckhouse	7. Propulsion System
b. Aft and Midship Deckhouse	a. Diesel
4. Gauging Systems	b. Steam
a. Open	
b. Restricted	
c. Closed	

- o Loading plan - Seven chemicals of interest in 12 tanks.
- o Two crew members would be monitored on each voyage. In the aggregate, all levels of licensed and unlicensed seaman would be represented.
- o Monitoring would include normal and extended work periods. A choice of instrumentation methods is suggested for monitoring the living environment in the crew's quarters during off-watch periods. In this latter case, the concern is for vapor infiltration into accommodation areas.
- o The plan includes cargo-related exposures as well as those that are not cargo related, such as sandblasting and spray painting activities.
- o With respect to cargo vapor monitoring, the plan emphasizes the use of traditional solid sorbent methods (pumps and tubes). Passive dosimeters may be used in parallel with the tubes if logistics and costs permit. Some chemical vapors require the use of impingers for sampling. These devices are not really compatible with personal monitoring aboard ship, and they are best utilized as area monitors.
- o Sampling and analysis would be conducted in accordance with NIOSH-recommended procedures.
- o The plan includes short-term samples for high-probability exposure situations such as tank top-off with open gauging and tank entry for cleanup.
- o For other than the short-term cargo vapor exposures, the plan is based on product vapor samples of one hour in duration. This basis is consistent with the sampling duration for many chemicals as recommended by NIOSH. The plan, however, must be flexible so that durations can be extended in situations where it is known that the potential for exposure is low. In the final analysis, the plan must be fine tuned based upon the actual products that are involved, and it must respond to shipboard conditions that may differ from those in the plan.
- o In addition to inhalation exposures, dermal exposures are also of interest. As these latter exposures cannot be measured directly, Appendix G outlines seven elements that would be documented for a dermal exposure to assist in its interpretation.

- o Work activities of the selected crew members would be documented in conjunction with the personal monitoring tasks. Items of interest from an interpretation standpoint include the nature of the work activity and its duration and proximity to sources of airborne contaminants and the use of any protective equipment.
- o Where multiple chemical exposures are likely, these would be duly noted and would be reflected in the sample analyses. Many chemical vapors require the same sampling medium, but different sampling rates, and it may not be feasible to instrument a worker for all multiple vapor combinations that may exist during a work shift. When a multiple vapor component environment exists, those components that have identical medium and rate requirements would be designated as primary analytes. Those that have the same media requirements, but different rate requirements, would be designated as secondary compounds. Concentrations would be calculated based on actual sampling conditions.
- o With respect to multiple vapor sampling, the key is noninterference with the work activity. A crew member can accommodate up to two sets of pumps/tubes and a passive dosimeter without reducing his work efficiency.

IV.2.3 Data Interpretation

The objective of the monitoring effort is to characterize an individual's exposure profile during a voyage. To this end, the monitoring results may be displayed on a concentration-time histogram to provide a visual indication of the exposure levels, their durations, and the presence of multiple contaminants in the work/living environment. This display may have some disadvantages if concentrations are at or below the detection limit of the analytical chemistry instrumentation.

Interpretation of the data from the industrial hygiene viewpoint is a separate issue. Judgments as to the acceptability or unacceptability of individual exposures or sequences of exposures require a set of valid assessment criteria. The American Conference of Governmental Industrial Hygienists (ACGIH) criterion for assessing a time-weighted average exposure (TLV-TWA) to a single contaminant is based upon an 8-hour work day and a 14- to 16-hour biological purge period between exposure to the same chemical on consecutive work days. Given the unusual and extended work schedules that exist in the marine industry, the absence of a weekend, the varying potential for exposure during a voyage, and the fact that the crew members essentially live in their work environment, there is reason to question the immediate applicability of the TLV-TWA to these situations. On the other hand, due to the nature of certain chemicals, the not-to-exceed or ceiling concentration criterion, as given by the

TLV-C, may be used in interpreting specific marine exposures, as can the short-term limit, TLV-STEL, if it is interpreted as a maximum allowable concentration or MAC.

The ACGIH criterion for exposures to multiple vapor mixtures assumes that the effect of each component is independent and additive and that a single organ system is involved. However, a recent study (Reference 11) by the National Academy of Sciences (NAS) indicates that for small doses the same numerical mixture criterion can be derived in a probabilistic sense when the mixture components affect different organ systems.

The components of a vapor mixture may react biochemically to produce potentiation, i.e., an effect that is greater than (synergism) or less than (antagonism) the result produced by each component acting individually. However, the toxicology of interactions is an embryonic discipline, and guidelines or criteria for interpreting interactive effects of multiple vapor exposures are not available. The NAS study concluded and recommended that the ACGIH additive procedure be applied when assessing the Threshold Limit Value for vapor mixtures.

Apart from the subject of interactive effects, the unusual or extended work schedule is a major factor that inhibits interpretation of the exposure data. One possible solution that is being actively pursued by industrial hygienists is to generate numerical adjustment factors that can be applied to the ACGIH-TLVs and the OSHA-PELs and which reflect the work schedule, the biological half-life of a contaminant, and the exposure environment. These adjustment factors have not been validated and do not, as yet, totally reflect the marine work environment.

The above discussion is warranted because it establishes a perspective on the subject of interpretation, and it identifies areas where information and data are needed. Given this state-of-the-art, the experimental plan outlines a combination approach to exposure assessment.

- o For a single chemical exposure during an extended work period, apply the OSHA compliance criteria based on calculated upper and lower confidence limits.
- o Apply the ACGIH methodology for time-weighted average exposures during selected 8-hour periods.
- o Apply the ACGIH additivity criterion for vapor mixtures.
- o Assess ceiling exposures in the usual fashion and interpret the TLV-STEL as an MAC.

IV.3 Impact of Analytical Modeling on the Experimental Plan

This project contained a task entitled Analytical Modeling. The purpose of this task was to identify vapor release scenarios that could potentially contribute to occupational exposures, determine if they are amenable to mathematical modeling, identify existing models that adequately describe the phenomena, and develop additional models if they are needed. Based on the results of the background voyages, several vapor release scenarios were identified.

- o Dispersion and dilution of the vapor plume that is discharged from a tank during loading. The vapor release point may be an open ullage port near deck level, or it may be at a greater distance above the deck as in the case of a B/3 vent.
- o Uptake, dispersion, and dilution of the vapors that are generated during gas-freeing of product tanks both with respect to the fate of the vapors that are discharged on deck as well as the in-tank environment that may be encountered during man-entry following ventilation.

All of these vapor release phenomena are amenable to mathematical modeling, and functional models are available. Product vapors are also released through P/V valves as a result of breathing of loaded tanks. While this release could be modeled, it is doubtful that a modeling effort is required because, based on past experience, the releases occur at sea, they have not been observed frequently, and when they have occurred there was minimal deck activity and, thus, minimal exposure potential.

The models that do exist have been developed or refined by SwRI in conjunction with References 2 and 12. Each model requires a set of specific inputs that reflect the chemical, operational, and configurational variables, which will vary with the ship and its crew. For this reason, the predictive capability of these models can only provide qualitative rather than quantitative guidance for the development of the experimental plan as illustrated below.

- o During B/3 venting, the models predict that at a given distance downwind of the vent, concentrations at man-breathing height are less than would exist during open venting through an ullage port. With B/3 venting, a correspondingly smaller portion of the deck contains concentrations that have health significance. It follows then that sample durations may be extended in the low concentration environment that would occur during B/3 venting. During open venting at deck level, the sample durations may have to be reduced to reflect the higher breathing zone concentrations that would be encountered.
- o The vapor concentration levels that are discharged from a restricted gauging system are substantially less than the concentrations that are discharged during open gauging through an

ullage port. Consequently, dispersed vapor levels will be correspondingly lower from restricted systems, and STEL or short-term, high-concentration monitoring would not be indicated.

- o During ventilation of a product tank, evaporation of pure chemical or chemical from a water solution increases the time required to gas-free to a sub-TLV concentration. The presence of tank internal structure has the same effect. Therefore, higher concentrations should be anticipated from a monitoring standpoint for man-entries immediately following the initial tank cleaning operation. That same tank may be subsequently entered on a number of occasions, and if each entry is preceded by a gas-freeing period, lower exposure concentrations should be anticipated.

In summary, the above considerations influenced the approach that was taken in developing the experimental plan. A different approach would have been indicated if model validation were the plan objective. The operational and configurational approach is consistent with the industrial hygiene objectives of this project.

V. IMPLEMENTATION OF EXPERIMENTAL PLAN

V.1 Vessel Selection

The experimental plan in Appendix G identifies several voyages to characterize crew exposure profiles in the Deck Department. Each voyage represents a vessel that has certain combinations of operational and configurational variables that could influence the potential for occupational exposures. According to the objective for Phase I, the experimental plan is to be implemented on one of these voyages in Phase I. Based on the results of this voyage, the test plan would be modified, if needed, with the remainder of the voyages being conducted in Phase II.

To this end, Voyage No. 7 aboard Vessel No. 4 was selected for the initial implementation of the test plan. The selection criteria that apply to this vessel are as follows:

- o Maximum Crew Size - The Deck Department consisted of 14 licensed and unlicensed crew members compared to the 9-man Deck Department on one of the background voyages.
- o Double-Bottom Tanks - All product tanks had double bottoms, were free of internal structure, and did not serve as ballast tanks.
- o Single Aft Deckhouse - Theoretically, the absence of a mid-ship deckhouse eliminates one air stagnation zone that would exist on the windward side of the house and one wake region of recirculating flow on the lee side of the house when the wind is directed generally along the ship's longitudinal axis. For quartering winds, the two regions of separated, recirculating flows do not exist. The main point is that there are fewer opportunities for cargo vapors to be retained in the work place because they are subject to the dispersion and dilution mechanisms of the ambient wind.
- o Gauging System - This vessel has a closed, tape gauging system on all product tanks. This system meets or exceeds the minimum requirements for Subchapter O chemicals. However, in practice, open gauging preempted the minimum requirements.
- o Venting System - This vessel has a dedicated B/3 vent with P/V valve for each product tank. This arrangement meets or exceeds the minimum venting requirements for Subchapter O chemicals; these requirements apply to venting during loading as well as in transit. Operational procedures preempted B/3 venting with venting through open ullage ports. This vessel is also configured to accept vapor return systems as required by the loading terminal. These systems would appear to achieve a level of vapor control during loading that exceeds the most stringent venting requirement for any Subchapter O chemical.

At the time that the experimental plan was developed, there were two variables or operational factors that had not been encountered during the numerous cargo transfer observations and tests that had formed the experience base for development of the plan.

- o The first variable was "shore-stop" loading. In this loading method, the tank farm has responsibility for terminating product delivery when the scheduled quantity of a cargo has been taken aboard. This mode of operation apparently relieves the crew from the necessity of continuously gauging a tank to its final ullage, as is the procedure for "ship-stop" loading where the crew assumes the responsibility for terminating delivery. This scenario would apply to either a tank that is loaded to capacity or a tank that is "short-loaded."
- o The second variable is "short-loading." This term indicates that the volume of product that is loaded into the tank is intentionally less than the rated capacity of the tank, which is usually 95 to 98 percent full. The majority of the chemicals on this vessel were short-loaded. As such, the loading is terminated before the high concentration vapor blanket above the liquid surface is vented from the tank.

Both of these variables, shore-stop and short-loading, act to reduce the potential for occupational exposure to cargo vapors. From an economic standpoint, short-loading is not a desirable operating procedure. On this voyage, short-loading reflected the prevailing demand for several of the products.

V.2 Voyage Summary

A detailed report of the activities and results that were obtained from this voyage is contained in Appendix H. Therefore, only the highlights of the voyage will be presented here.

The voyage consisted of docking at eight terminals in seven days for the purpose of loading 19 separate products and discharging one product. Of these 20 products, 13 were included in the sampling plan. The objective of the voyage was to perform a trial implementation of the experimental test plan with the goal of characterizing exposure profiles. The plan was implemented in the Deck Department.

According to plan, two crew members who worked cargo transfer watches were identified. Both crew members were A/Bs. During the succeeding seven days, their activities were documented and exposures monitored to the maximum extent possible by two project team members. Documentation included a definition of the task, its duration, and proximity to sources of vapor. Monitoring utilized both adsorbent tube/pump methods and passive dosimeters. In the former case, NIOSH-recommended flow rates and sampling durations were followed for primary (defined later) chemicals. Sampling durations were selectively extended when the work environment obviously contained low level concentrations. Ceiling and STEL

exposure samples were also attempted. All samples were refrigerated from the time of sampling until they were analyzed by an AIHA Accredited Laboratory using either NIOSH-recommended analytical procedures or those recommended by the dosimeter manufacturer. The test plan also included dermal exposures as well as noncargo-related exposures. Dermal exposures were documented when they occurred, but there were no activities conducted that would promote noncargo exposures, e.g., spray painting, sandblasting, etc. The deckhouse environment was also monitored for potential vapor infiltration through accessways or from air conditioning and ventilation systems.

There were also opportunities to observe and/or monitor other events that were unrelated to the deck watches of the two A/Bs, but which contributed to the overall understanding of chemical tanker operations. These included

- o tank inspection by cargo surveyors prior to loading,
- o one tank cleaning experiment,
- o tank entry following cleaning, and
- o surveys of fugitive vapor emissions from loaded, closed tanks.

Work schedules were quite regular. For the majority of the voyage, cargo transfer watches consisted of six hours on and six hours off. The schedule was then changed back to the traditional 4-on, 8-off routine. Extended work periods (more than eight to ten consecutive hours per day) did not occur.

This voyage took place in mid-December 1981. During that 7-day period, climatic conditions ranged from near freezing temperatures with high wind chill factor to rain over a broad temperature band to periods of more acceptable weather. The weather contributed to some aborted sampling efforts.

The reader may wish to review the voyage report in Appendix H before proceeding to the remaining sections.

V.3 Assessment of Operations

This voyage afforded an excellent opportunity to observe during seven days all of the principal cargo-related operations that would normally occur on longer 14-day round-trip voyages. These operations included cargo loading and discharging, tank cleaning, and tank entry. In addition, there were opportunities to observe the effectiveness of various procedures. A retrospective commentary on vessel operations is given below.

Tank Gauging and Venting

Of the 19 individual products that were loaded onto the ship, eight are classified as Subchapter O chemicals and are subject to the minimum gauging and venting requirements of USCG. Table V.1 summarizes the minimum venting and gauging requirements for these eight chemicals, the equipment that met these requirements, and actual methods that were used. This table indicates that for five of these chemicals (CBT, EAC, MMM, BTC, and VAM), the venting and gauging methods that were used did not coincide with the minimum requirements.

The case of VAM represents a paradox. Open gauging is acceptable, but product vapors are to be vented at a height of at least 4 m. To accomplish this, it would be necessary to dog down the ullage port between gaugings. A minimum requirement of R gauging would appear to be more consistent with the 4m/PV venting requirement.

The practice of open gauging when closed systems are available is not uncommon and is quite independent of whether or not the commodity is subject to Subchapter O or D. It is a commentary on the reliability of closed gauging systems and the emphasis on preventing deck spills. During one VAM loading, the closed system was used even though open gauging would have been acceptable. Low ambient temperatures increased the viscosity of the tape lubricant, which resulted in a sluggish response and questionable readings. During entry in Tank 5C, it was noted that one of the two wire guides for the float was missing--the system was inoperative.

Tank Cleaning Procedures

A written, step-by-step tank cleaning procedure is based on a number of criteria:

- o The degree of cleanliness that is required by the next product that is to be loaded into the tank with due regard for wall and coating materials.
- o The time required to turn the tank around.
- o The vapor environment in the tank if it is to be entered for manual cleaning or inspection.
- o The vapor levels that are discharged from the tank during ventilation.

A written procedure for cleaning the CRF tank in preparation for xylene loading was available, but, as has been observed on other vessels, the actual procedure that was used was based on the Chief Mate's experience in similar situations and the time frame in which the tank must be turned around. The experience factor is important because it may be a more practical approach to achieving the same end result.

TABLE V.1. VENTING/GAUGING REQUIREMENTS VS OPERATIONAL
PRACTICE FOR SUBCHAPTER O COMMODITIES

<u>Chemical</u>	<u>Minimum Requirements</u>			<u>Method Used</u>	
	<u>Gauging</u>	<u>Venting</u>	<u>Vent Height</u>	<u>Gauging</u>	<u>Venting</u>
CBT	C	PV	B/3	O	O
EAC	R	PV	4m	C(O)	VR(O)
DEA	O	O	NR	O	O
POX	C	PV	4m	NO	VR
MMM	R	PV	4m	O	O
BTC	R	PV	4m	O	O
VAM	O	PV	4m	O(C)	O(VR)
SHD	O	O	NR	O	O

NOTES:

1. O = open, R = restricted, C = closed
2. PV = pressure/vacuum release valve
3. B/3 = ship's beam/3, 4m = 4 meter, NR = no requirement
4. Ship's equipment included B/3 vents with PV and C gauging systems on all tanks.
5. VR = vapor return
6. NO = not observed
7. Entries in parentheses represent methods used during loading of same product at a second terminal.

The actual washing with cold water was preceded by a 90-minute ventilation period, which was not included in the written procedure. Presumably, the purpose of the prewash ventilation was to evaporate a majority of pure product residue in the tank. Shortly after washing began, concentrations at the expansion trunk rose to nearly the same level as existed before ventilation was started. Past experience with tank cleaning experiments has indicated that vented concentrations are relatively constant during washing (without simultaneous blower operation) at roughly the level that exists before washing is initiated. Therefore, the prewash ventilation may have been unnecessary in terms of minimizing the overall tank cleaning time. On this premise, the 90-minute forced discharge of vapors into the work environment may also have been unnecessary, and it would have eliminated a potential exposure condition.

The tank was ventilated during washing. Given the above behavior of vented concentrations during washing without ventilation, the benefit of ventilating while washing is unknown. Because vapor concentrations at the tank opening are relatively constant regardless of whether blowers are used or not, it would follow that elimination of the blower during washing would also eliminate a potential exposure situation that results from forced discharge of product vapors.

Tank Entry

Tanks were entered frequently by crew members during this 7-day observation. A given tank may be entered several times over a period of days beginning with the initial entry after cleaning and followed by additional entries to wipe up water that has condensed. Entries were not preceded by tests of the tank atmosphere for oxygen concentration, combustible gas (CG) level, or toxicity level. Equipment such as O₂/CG detectors and colorimetric indicators was available on board. Deck standby and blower operation during entry are safety precautions that were not applied consistently.

Protective Equipment

Various levels of protective equipment were used by the crew.

- o The clothing and respiratory protection that were used by personnel involved in the TDI loading reflects the toxic potential of this chemical. That other crew members were on deck without this equipment while TDI operations were in progress is inconsistent.
- o Chemical goggles and rubber gloves and boots were used by all crew members who were involved with the SHD loading.
- o Full-face, air-purifying respirators were available and were used selectively by individuals involved in tank entry and gauging.

V.4 Potential for Occupational Exposure

Work practices, equipment, and operational procedures can combine to produce an enhanced or reduced potential for exposure. During this voyage, varying exposure potentials were observed:

- o Shore-stop loading reduces the potential for exposure. The mechanics of this loading procedure and the reason for the reduced potential were discussed earlier.
- o Short-loading also reduces exposure potential as described in Section V.1. Table V.2 summarizes the extent of short-loading.
- o Potential exposures are reduced when vapor return systems are used during loading. Three products, EAC in 9S, POX in 5P,S and VAM in 9P, were loaded to 83, 95, and 96 percent full, respectively; each of these products had a vapor return system on the tanks.
- o Carbon tetrachloride was loaded into Tank 9CP. The tank was 92 percent full, and vapor return was not used. As will be seen later, this resulted in an enhanced exposure potential.
- o The majority of the tank gauging was performed manually through open ullage ports with the crew member standing on the expansion trunk hatch, as shown in Figure V.1. This method of gauging increases the separation distance of the breathing zone from the ullage port and should reduce the exposure potential.
- o Tank entry without prior testing of the tank atmosphere enhances the exposure potential.
- o Tank ventilation before and during washing would appear to increase the potential for exposure.
- o Product sampling at the slipstream valve on the loading manifold increases the potential for dermal contact with the hands and for product to splash up from the drip pan onto clothing. Narrow-neck collection bottles cannot accommodate the product flow, which is under pressure from the manifold line.
- o The work scenarios indicated that crew members that were involved with cargo transfer tended to remain on the elevated catwalk when they were not gauging tanks. This work practice would appear to reduce the potential for exposure to high concentrations of cargo vapors because the tankerman is physically removed from proximity to many sources.



FIGURE V.1. TANKERMAN GAUGING PRODUCT ULLAGE FROM ON TOP
OF EXPANSION TRUNK HATCH

TABLE V.2. SUMMARY OF SHORT-LOADINGS

<u>Tank No.</u>	<u>Chemical</u>	<u>Tank Capacity (Metric Tons)*</u>	<u>Amount Loaded (Metric Tons)</u>	<u>Percent Full</u>
11P	TCE	920	300	33
9CS	DCM	361	250	69
7S	DEA	787	400	51
8CF	PAT	255	200	78
13S	DBO,P	1102	500	45
10S	MMM	886	450	51
7P	BTC	648	450	69
8P	EAC	560	275	49
1P	TOL	528	350	66
5C	XLO,M,P	1643	500	30

* Tank capacity at 100 percent full and specific gravity of product.

V.5 Vapor Monitoring - Results and Interpretation

The vast majority of the vapor concentrations that were obtained from the occupational exposure and area samples were, in general, significantly less than have been measured on any previous vessel where open gauging and open venting were used (Reference 1). More specifically, concentrations tended to be nondetectable, but were quantified at the detection limit of the analytical instrumentation that was used for the analysis. The reasons for this behavior have been suggested earlier and are reiterated here--the combined effects of shore-stop, short-loading, and the gauging method that involved standing on the expansion trunk hatch cover. The only other loading scenario that has produced comparable results was obtained aboard vessels that were fitted with restricted gauging systems, e.g., Reference 2 and the tanker voyage that was discussed in Section III.3.

According to the interpretation plan (Appendix G), the measured exposure data were first to be graphed in histogram form for each watch period so that profiles of environmental concentration levels could be observed for individual chemicals as well as vapor mixtures. However, the large number of concentration data points that are below instrument detection limits (Tables III.C and IV.B of Appendix H) precluded this approach.

Vapor Mixtures

During each watch period, the sampling plan reflected the potential presence of multiple chemical vapors in the work environment. The environmental concentration data that were collected using tube methods were analyzed to determine if the mixture exposure limits were exceeded during any sampling interval, assuming additive effects. That is

$$\sum_{i=1}^n C_i/T_i \stackrel{?}{>} 1$$

where

C_i = measured concentration of i-th component during sampling interval

T_i = applicable time-weighted average exposure limit for the i-th component in the mixture

As would be expected, the mixture limits were not exceeded with one possible exception. Sample Nos. 100 and 101 were collected simultaneously on AB2 in Terminal No. 1. The sampling durations were nearly identical. Sample No. 100 was set up for DCM as the primary analyte with CBT and TCE as secondary chemicals. Sample No. 101 had CBT and TCE as primary chemicals with DCM being designated as the secondary analyte. Excluding DCM, which was essentially nondetectable, the measured CBT and TCE concentrations are shown below with the addition of an entry for the summation indicated above.

<u>Sample No.</u>	<u>C_{CBT} (ppm)</u>	<u>C_{TCE} (ppm)</u>	<u>$\sum C_i/T_i$</u>
100	10.4	2.1	1.05
101	9.2	2.3	0.93

The TCE concentration has a very small contribution to this summation. Note that CBT is the dominant mixture component in each case and that the CBT concentrations agree well despite the difference in sampling rates. This is the only instance in which the mixture limit was approached or possibly exceeded during a sampling interval. In retrospect, of the loadings that were monitored, only the CBT tank was filled nearly to capacity (92 percent full) without the aid of a vapor return system. Thus, the rich vapor blanket that had developed above the liquid surface was open vented to the work environment. The results for CBT represent the integrated effect over the sampling duration, but the majority of AB2's exposure to CBT may have been received during a 6.5-minute period when he collected a product sample from the tank just prior to the end of loading. Assuming that this was the case and that no further CBT exposure was received during the remainder of the 117-minute sampling period for Sample No. 101, a uniform, peak CBT concentration can be estimated.

$$C_{\text{Peak}} = \frac{9.2 \text{ ppm} \times 117 \text{ min.}}{6.5 \text{ min.}} = 166 \text{ ppm}$$

Under this assumption, mixture considerations are no longer appropriate, and the important fact is that the OSHA ceiling of 25 ppm and the ACGIH STEL of 20 ppm would have been exceeded by a wide margin. This assumption could only have been verified by collecting a short-term sample. As this crew member was already wearing three sampling devices and there was no prior indication that the tank would not be short-loaded (low levels anticipated), the sampling approach was justified.

Tank Entry

Following cleaning of the CRF tank, occupational exposures were monitored on two crew members that entered the tank to clean up solid debris and liquid residues. Three samples of 15-, 15-, and 10-minute durations were collected on each individual. The results are summarized below. For each individual, the samples are sequential, beginning with entry through egress.

<u>Crew Member</u>	<u>C_{CRF} (ppm)</u>
A	31.7
	22.4
	14.0
B	26.9
	17.1
	10.6

The decline in concentration with time reflects continued ventilation of the tank over the 40-minute period. Crew member A wiped residual liquids from the pump sump using rags, and his exposures are correspondingly higher than those of crew member B, who swept solid debris from the tank floor. The implication is that the liquid residues still contained CRF in solution and that it volatilized during the mucking operation. None of these exposures, however, exceeded either the ACGIH STEL or the OSHA ceiling of 50 ppm. The time-weighted average exposure was then calculated assuming that there was no further CRF exposure for the remainder of an 8-hour period. That is,

$$\bar{C} = \frac{\sum_{i=1}^3 C_i t_i}{480}$$

where C_i is the CRF concentration during sampling interval t_i . On this basis, neither of the exposure scenarios produced an average concentration that exceeded the ACGIH TLV-TWA of 10 ppm. It is fortunate that neither of these limits was exceeded because the tank atmosphere was not tested prior to entry. Perhaps to compensate for this fact, both crew members

wore full-face, air-purifying respirators with the correct adsorption filters. This tank was entered on a subsequent occasion, and measured concentrations were roughly 30 ppm.

Passive Dosimeters

Passive dosimeters were selectively used in parallel with charcoal tube/pump devices. They were used most extensively during the last deck watch period when EAC, TOL, and BTC were loaded. During this watch period, three sets of parallel samples were collected on each of two crew members who were involved in cargo transfer. The results are discussed below.

For AB3, the parallel results confirm one another in that the adsorbed analyte weights were for the most part below instrument detection limits. The indicated limit concentrations for a given chemical differ because of the difference in the equation forms that are used to calculate concentration; the analyte weights that represent detection limits are the same, however. AB3's activities were confined primarily to the central and starboard deck where MMM was loaded. EAC, TOL, and BTC were being loaded into port tanks and were included in the analysis because these vapors could be transported by the wind to the starboard deck. The conclusion is that the parallel results are not in conflict and that exposures to these three product vapors as monitored by either procedure would have been very low if they could have been quantified.

The parallel results for AB4 on the port deck present a slightly different situation. For discussion purposes, these data sets are repeated below.

<u>Sample No.</u>	<u>Vapor Concentration, ppm</u>		
	<u>EAC</u>	<u>TOL</u>	<u>BTC</u>
114	2.4	15.4	2.6
62026	7.0	30.6	5.5
116	<0.1	3.2	1.5
62027	1.5	3.1	5.1
120	1.1	5.7	0.3
62029	2.9	14.1	<0.9

Three-digit sample numbers correspond to charcoal tubes and five-digit numbers signify passive dosimeters. With two exceptions, both sampling methods produced measurable concentrations. The passive dosimeter data are consistently higher than the tube data. The differences, expressed as ratios, are of the same magnitude as was obtained during the gasoline carrier voyage. These differences are higher than would be expected and cannot be explained on the basis of sampling and analytical errors. A valid explanation is that both samplers did not "see" the same exposure

environment. Both sampling devices were attached to opposite lapels. The data suggest that AB4's normal gauging procedure resulted in the passive dosimeters being closer spatially to the source (open ullage port) than were the charcoal tubes (farthest from the source). The vapor environment near an ullage port is not spatially uniform because the vapors are discharged as a plume that has a trajectory and which subsequently becomes diluted and dispersed. The TOL concentrations in the second data set suggest that a more uniform vapor field was encountered during gauging of that product tank.

Similar situations are anticipated on future characterization voyages. In these cases, the following additional information requirements or procedural changes should be considered.

1. Include in the documentation the location of the sampler on the crew member and his preferred bodily position in relationship to sources.
2. Alternate sampler locations when sequential samples are collected.
3. A second dosimeter on the same lapel as the charcoal tube would aid in determining the degree of agreement between tubes and badges.

Closure

The results that were obtained from this voyage indicate that very low-level exposures to multiple chemical vapors were encountered most frequently, and these levels were probably influenced more by the loading method than any variable in the vessel selection criteria. Mixture exposure limits may have been exceeded on one occasion as a result of a slightly different loading procedure, although it can be argued that the forcing function was a short-term exposure. Potential concentration biases that result from sampler location are also recognized, and corrective measures have been recommended. Exposures during tank entry were acceptable relative to TWA and ceiling limits on this voyage.

V.6 Assessment of the Experimental Plan and Implementation Test with Recommended Modifications

A retrospective evaluation of the experimental plan is in order so that recommended modifications can be incorporated into the Phase II program. Our assessment of the original plan is as follows:

- o The basic experimental test plan (Appendix G) was quite adequate, and its implementation demonstrated the feasibility of exposure profile monitoring.
- o Even though the plan was not chemical-specific, the estimated quantities and types of sampling equipment, based on

an assumed work scenario and number of chemicals, was conservative. Therefore, monitoring opportunities were not lost because of the lack of backup equipment and supplies.

- o Implementation of the plan on any voyage begins when the ship's loading plan becomes known a few days before docking. Changes to this loading plan can and will occur, e.g., substitution of DEA for diethylamine. However, it is not possible to be prepared for all contingencies. In the case cited, the adsorptive sampling medium appeared to be appropriate for both commodities, and the analytical chemistry analysis of these samples was successfully accomplished without the aid of a NIOSH method. In other cases, a monitoring opportunity may be lost or samples may be sacrificed because the sampling medium is either not appropriate for the substituted chemical or an analysis procedure cannot be identified. Such a situation has not been encountered to date, but its potential is acknowledged.
- o A crew member can be conveniently instrumented with up to two pump/tube combinations and a passive dosimeter without interfering with his work. The adsorptive medium and sampling rate for one pump/tube combination may be appropriate for several cargo vapors that are present in the work place, but the procedures for desorbing the analytes may be different. In these cases, a decision must be made as to the analytes that will be retained and those that will be sacrificed with due regard for toxicity and maximizing data output. This situation was encountered during the background voyage aboard the parcel chemical tanker. To avoid such situations, it would be necessary to use an additional pump/tube combination, which may interfere with the crew member's ability to work efficiently.
- o A similar situation exists when the sample collection medium and desorptive methods are appropriate for a subset of the vapors that coexist in the work environment, but the recommended sampling rates are different. The crew member may already be wearing a full complement of sampling equipment, and it would be prohibitive to add another device. In these cases, a primary compound that had a consistent set of sampling requirements was identified. Other vapors that had the same collection medium and desorption method were sampled at the primary rate, but were identified as secondary analytes for chemical and computational analysis purposes.
- o The two previous points acknowledge the potential loss of sampling data that may result from differences in desorption and/or sampling rate requirements and the constraint on the amount of monitoring equipment that is worn by a crew member. When these situations occur, the potential for data loss may

be minimized if monitoring equipment is worn by the project observer who is responsible for documenting work activities and performing the sampling on a given crew member. This approach requires that the observer duplicate, as closely as possible, the crew member's work task, the duration of the task, and the tankerman's proximity to vapor sources. The observer's sampling device can then be analyzed for the concentration data that would otherwise have been lost. This alternative should produce a valid addition to the tankerman's exposure profile.

- o Continuous sampling of the crew members' quarters during off-watch periods was a line item in the original plan. Based on the experiences to date, it is doubtful that it need be rigidly included in future voyages. Rather, a more flexible approach is recommended in which the deckhouse atmosphere would continue to be surveyed using portable, direct-reading instrumentation (OVA) until such time as instrumental readings warrant active dosimetry. Based on velocity surveys of crew accommodations during the background voyage, passive dosimetry methods are not appropriate for monitoring the deckhouse environment.
- o Several chemicals require impinger techniques for personal exposure monitoring. These methods are not practical in the marine work environment. Likewise, the "waltzing impinger" method is not realistic. As an alternative, we recommend increased use of impingers as area monitors that are located in high traffic patterns or where crew members congregate.
- o The experimental plan called for documenting work activities and monitoring occupational exposures on two crew members per voyage. Implicitly, it was assumed that two members of the project team would perform these functions, i.e., one-on-one. The experiences on the implementation voyage clearly indicate that additional staffing would be desirable on selected voyages in Phase II, subject to the availability of accommodation space on the ship and a pre-voyage assessment of the cargo-related operations. One additional project member would have greatly facilitated sample handling, labeling, and storage. Other functions such as instrument calibration and collection of written information (tank cleaning procedures, ullage-volume equivalents, loading time profiles, etc.), which were performed off-watch, could be conveniently accomplished by a third individual.
- o Solid sorbent tubes and pumps should continue to be used as the primary sampling equipment for occupational exposures. Passive dosimeters may be used as backup monitors to acquire a parallel data base.
- o The use of higher-than-recommended sampling rates should be investigated for short-duration, relatively low-level concentration environments such as were encountered during surveyor

inspection of the xylene tanks. The objective would be to bring tube concentrations closer to the OVA measurements by processing more analyte vapor through the sorptive bed.

- o During the latter stages of this research project, it became known that on some vessels the interior walls of the passage ways and accommodation spaces in the deckhouse may consist of a three-layer composite material that contains an asbestos-bearing core. It is recommended that the potential for generation of airborne asbestos fibers be assessed in Phase II. This effort could consist of (1) a determination of the extent to which this wall material is in current use on chemical transport vessels, (2) a review of the construction and fiber bonding techniques, and (3) environmental monitoring for asbestos fibers in the living spaces if necessary.

VI. SUMMARY AND CONCLUSIONS

VI. Summary

The objectives that were defined for the at-sea portion of this study have been achieved.

A rather complete perspective of Deck and Engineering Department operations was obtained on two round-trip background voyages that lasted approximately 14 days and included cargo loading, cargo discharging, tank cleaning, tank entry, and ballasting operations. The vessels differed with respect to the cargos that were carried, loading rates, venting and gauging systems, and propulsion systems. On each voyage, potential sources of occupational exposure to cargo and noncargo-related materials were documented in each department. Crew members' work activities on-watch were also documented, as was their duration in proximity to these contaminant sources. A limited amount of personal and area monitoring was conducted to support these observations.

The information that was obtained during these background voyages was combined with experimental data that had been generated in marine terminals during cargo loading operations. This body of information, knowledge, and experience formed the basis for developing an experimental plan to fully characterize the exposure profiles of tankermen throughout the course of a voyage. The plan identified ten voyages; the emphasis is on Deck Department operations, with fewer voyages being specifically directed toward Engine/Pumproom operations. The basic objective of that plan is to ensure that the results reflect a representative cross-section of the bulk liquid transportation industry. To that end, vessel selection was based on combinations of operational and configurational variables that were either known or were assumed to influence the potential for occupational exposures. In addition, specific voyages are associated with definite classes of cargos, including pure chemicals, gasolines, and crude oils. Round-trip voyage work schedules were then constructed for both licensed and unlicensed seamen. These schedules represent composites of the schedules that had been observed, and they were used to estimate the sampling and equipment requirements.

The experimental plan was then implemented on a seven-day voyage that included operations in eight terminals. This was a highly condensed voyage. With the exception of tank ballasting, all of the cargo-related operations that are normally conducted in the Deck Department were observed without the need for an extended ballast leg. Occupational exposures and work documentation were collected on two individuals during their cargo transfer watches. In addition to these primary activities, experimental data were also collected during tank cleaning and tank entry. The vapor environment in the living accommodations was surveyed to assess the extent of vapor infiltration into the deckhouse. Fugitive emissions from loaded, closed tanks were also monitored.

Before presenting the major conclusions that have resulted from this study, it is appropriate to acknowledge that the success of this project is due in large part to the excellent cooperation of the ship owners, ship charterers, and terminal operators who participated in the study. We greatly appreciate their continued interest and involvement in the project.

VI.2 Conclusions

The conclusions presented below pertain solely to the scope of this project and the documentation and experimentation activities that were conducted aboard three vessels. No attempt has been or should be made to generalize the results outside of this context. Conclusions have not been made regarding the typical or atypical nature of operations or procedures over a long period of time.

1. Occupational exposure profile monitoring in the marine environment is feasible. With sufficient prevoyage information and planning, monitoring of exposures to single and multiple chemical vapors can be accomplished. The logistics of monitoring aboard a tanker are, however, somewhat more complex than would be required for monitoring in a land-based industry. In general, the maritime work place is larger and the tankerman's mobility requirements are greater than would be encountered for manufacturing equipment operators who remain relatively stationary while performing repetitive work. During a watch, the tankerman has a defined set of responsibilities that are not highly repetitive and are not, as a rule, confined to a small, specific area of the deck. Over and above his basic duties, he must be flexible so that he can respond to the changing operational requirements of the vessel. The exposure environment varies with space and time, and it may change unexpectedly with the occurrence of an unanticipated event. The environment can potentially include more vapor components simultaneously than are encountered in many other industries. With planning, flexibility, and experience, these factors can be handled by the industrial hygiene field monitoring team, with the realization that the tankerman is the final judge as to the amount of monitoring equipment that he can wear before it interferes with his work.
2. This study does not duplicate any other known work that is being conducted in this country or abroad. Literature searches and direct contacts support this conclusion.
3. Exposure levels are difficult to quantify when
 - o dress codes permit shorts and no shirts, and
 - o the nose and head are fully immersed in an opening such as an open expansion trunk, ullage port, or open

Butterworth hole. In these cases, the monitoring apparatus is shielded and will not reflect the true exposure.

4. Tank entry is an operation that poses a potential for exposure because, if the tank atmosphere is tested before entry, the instruments are usually not sufficiently sensitive to concentrations that have health significance. Conversely, the tank atmosphere may not be tested before entry.
5. In the Engine Rooms, ambient levels of asbestos were significantly less than either existing or proposed exposure limits. The use of asbestos as an insulation material is being phased out, and it is being replaced by a nonasbestos form of material. Ambient oil mist concentrations were also acceptable relative to an exposure limit that is based on mineral oil. These observations reflect operations while the ships were underway at sea. It is recommended that monitoring for coal tar pitch volatiles during bunker system operations and a comprehensive definition of dermal exposures to concentrated cleaning solvents be included in Phase II voyages.
6. It is not feasible to use stationary passive dosimeters to characterize exposures in crew quarters during off-watch periods. Measured air current velocities were below minimum levels recommended by the dosimeter manufacturer. An alternative is to survey the quarters with direct reading instruments. Active area dosimetry could then be considered if it is justified by the survey measurements, and then, only if it is acceptable to the crew member.
7. Deckhouse concentrations appeared to be more dependent on the loading method and the location of access doors from the deck into the house than on direct infiltration of vapors through house ventilation systems. Measured concentrations were highest with forward facing access doors when product tanks were loaded to capacity and were open vented. Similar results were obtained during tank cleaning. The combination of short-loading, vapor return, and port/starboard access doors tends to reduce the potential for vapor infiltration. As would be expected, low levels were measured during cargo discharge and the laden voyage.
8. The background and implementation voyages aboard two parcel chemical tankers indicated that
 - o restricted gauging under full-loading and open venting conditions reduces the exposure potential, and
 - o short-loading, shore-stop, vapor return, and manual gauging from on top of the expansion trunk cover combine to reduce the exposure potential.

In either case, the potential for multiple vapor exposures exists, but measured levels were quite low and were frequently nondetectable. These situations predominated over high concentration exposures.

This conclusion pertains strictly to operations aboard these two vessels.

9. The voyage aboard the gasoline carrier indicated the open gauging under full-loading conditions accentuates the exposure potential. Monitoring was conducted for the benzene fraction in gasoline vapor. The measured benzene concentrations did not exceed the prevailing time-weighted average exposure limits. However, calculation estimates of the corresponding exposures to total gasoline vapor suggest that the ACGIH time-weighted average exposure limit of 300 ppm was exceeded.
10. Dermal and ocular exposures to bulk cargos were observed, as were dermal exposures to noncargo-related materials. The data base on incidence rates or frequency of occurrence is not yet sufficiently complete to permit more than this statement of observation.
11. Ingestion as a route of exposure is less likely to occur. However, the potential does exist when open refreshment containers are present on deck while cargo-related operations are underway.
12. Work schedules in the Deck Department included the traditional 4-on, 8-off maritime schedule, a 6-on, 6-off routine, and the more familiar 8-hour work day. On one vessel, all three schedules coexisted simultaneously. On another vessel, the first two schedules were in effect during different portions of the voyage. On the third vessel, the first and last schedules were in effect.
13. Operational responsibilities or overtime (mandatory or voluntary) can result in a crew member working into or through a scheduled off-watch period. This scenario describes the "extended work schedule"; documented examples of such schedules include up to 30 consecutive hours of work.
14. Established time-weighted average exposure limits are based on the five-day work week and the conventional eight-hour work day. As these limits do not reflect the traditional maritime schedules, variations in these schedules, or the extended work schedule, there are limitations on the extent to which exposure data can be interpreted at present. One important limitation results from the fact that maritime schedules do not include a 16-hour biological purge period, even when a crew member works eight hours per day on a 4-on, 8-off schedule. Proposed methods of adjusting TLV-TWA's or

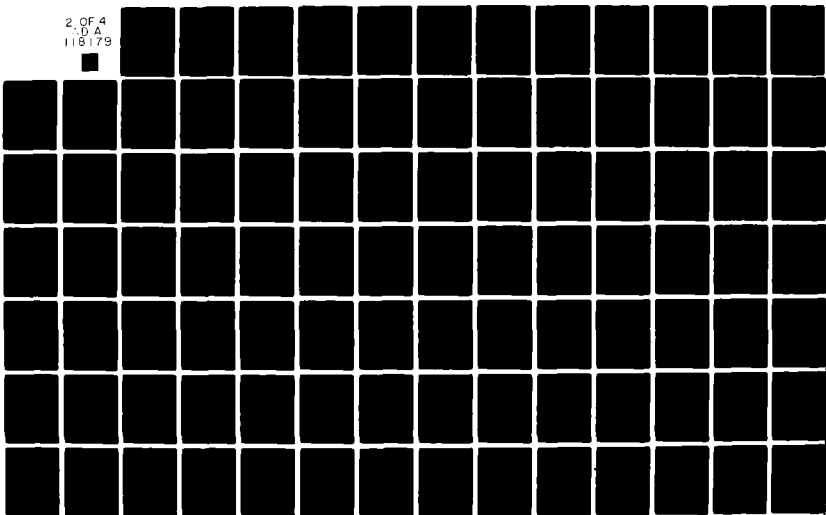
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CG-D-22-82 A CREW EXPOSURE STUDY PHASE I. VOLUME II
/ W.J. ASTLEFORD, ET AL SOUTHWEST RESEARCH INST., SAN ANTONIO, T

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PELs for these unusual or novel work schedules by accounting for the biological half-life of a chemical were cited earlier in this report. These methods need to be refined in order to reflect that, while the work schedule may persist, the exposure environment is not constant during each shift and the composition of the environment varies. Interpretation of exposures that exceed ceiling limits or maximum acceptable concentrations is more well defined.

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APPENDIX A

CATEGORIZED BIBLIOGRAPHY

A-1

CATEGORIZED BIBLIOGRAPHY

"A CREW EXPOSURE STUDY--PHASE I"

- A - TOXICITY, TOXICOLOGY
- B - PLUME AND PLUME MODELS
- C - REGULATIONS
- D - SAMPLING PROCEDURES AND EQUIPMENT
- E - MARINE TERMINAL EMISSIONS STUDY
- F - BUILDING MATERIALS AND SHIP CONSTRUCTION
- G - EXPLOSION MODELS
- H - CONTROL OF HYDROCARBON EMISSIONS, DUSTS
- I - HAZARD ASSESSMENT MODELS AND CLASSIFICATION
- J - SHIPTANK GAS ATMOSPHERE CONTROL
- K - SAFETY ASPECTS OF TRANSPORTING HAZARDOUS CARGOS
- L - DISCHARGING OF HAZARDOUS WASTES FROM SHIPS
- M - TANKER CLEANING OPERATIONS
- N - ANALYSIS OF MAJOR HAZARDOUS ACCIDENTS
- O - AEROSOL
- P - URINE/BLOOD SAMPLING

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APPENDIX B

INTERPRETATION OF OCCUPATIONAL
EXPOSURE DATA

B.

INTERPRETATION OF OCCUPATIONAL EXPOSURE DATA

The tankerman represents a subset of a larger group of workers known as Marine Hazardous Chemical Workers (MHCW). If the MHCW's followed a conventional work schedule (8 hours/day, 5 days/week), then interpretation of environmental exposure data would be greatly simplified because the existing health standards, OSHA and ACGIH, References B.1 and B.2, respectively, could be applied with a high degree of confidence. For the conventional work schedule, these standards represent airborne concentration levels above which continued exposure constitutes a known biological hazard (factors of safety in the standards are acknowledged). Thus, it would be possible to assess simultaneous multiple exposures on an additive basis.

$$E_M = \sum_{i=1}^n C_i / TLV_i$$

where

C_i = exposure concentration of i-th contaminant

TLV_i = time-weighted average TLV for i-th contaminant

If E_M is greater than unity, the mixture TLV has been exceeded. Unfortunately, the antagonistic and protagonistic effects of multiple vapor exposures cannot be easily assessed even for conventional work schedules. If an exposure profile to a single chemical were available for an 8-hour work day, then an assessment of compliance with the TWA-TLV could be made

$$\bar{C} = \frac{\sum_{i=1}^n C_i t_i}{8}$$

where

C_i = measured exposure concentration during
time period t_i

If $\bar{C}$ is less than the TWA-TLV, the daily exposure is acceptable. Ceiling, MAC, and STEL exposures could also be assessed, i.e., paragraphs b and c, pages 2 and 3 of Reference B.2.

Unfortunately, the work schedules for many MHCW's depart drastically from the conventional routine upon which the exposure standards are based. Examples include the following:

- o Extended work shift hours of Mates and Seamen during loading of a chemical tankship. By virtue of responsibility or a desire for overtime pay, shift length may extend to 24 to 36 hours without substantial rest or biological purge period. Even during minimal rest times, workers remain in their work environment.
- o The USCG Marine Inspector that may work well beyond 8 hours per day on successive days to complete a battery of tank inspections. In discussions with USCG Marine Inspectors, SwRI has been advised that the 8-hour work day does not exist during periods when the number of tanks to be entered is large. Entry and inspection generally represent 10-30% of an inspector's work load.
- o The Marine Chemist, who certifies tanks safe for man-entry prior to the arrival of the USCG Marine Inspector, may work for extended periods of time to ensure the continued validity of a certificate, may enter a tank several times to measure concentrations and may be involved with the same number of different chemical tanks in a given work duration as the Marine Inspector.

Research efforts to cope with the problem of interpreting exposures during extended or unusual work schedules have been based primarily on calculated numerical reductions in the TWA-TLV. The industrial hygiene literature was manually searched for recent literature on TLV modifications. The results of that search are summarized below.

Current TWA-TLV's are based on an 8-hour work day and a 5-day work week. These TLV's are not applicable to novel or unusual work schedules that may extend significantly beyond the 8-hour work day and, hence, produce a decreased recovery or purge period between successive exposures. Brief and Scala (Reference B.3) suggest a numerical reduction in the TWA-TLV and the corresponding excursion factor. The reduction factor is

$$RF = \frac{8}{h} \left(\frac{24 - h}{16} \right)$$

The first term accounts for increased exposure time, while the second term accounts for a decreased purge period. The applicable or new TLV is then

$$TLV_{New} = RF (TLV_{Old})$$

Obviously, this expression is not valid for marine operations where a worker is on duty for more than 24 hours.

The ACGIH TLV's (based on an 8-hour work day) permit excursions in exposure concentrations above the TLV provided there is a compensating exposure period below the TLV such that the TWA exposure is less than the TWA-TLV. The authors postulate a modified excursion factor (EF) to account for these unusual work schedules

$$EF_{New} = [(EF_{ACGIH} - 1) RF + 1]$$

Thus, the permitted excursion in ppm for the modified work schedule is

$$\text{Excursion (new-ppm)} = EF_{New} TLV_{New}$$

The authors recommend cautious use of this adjustment scheme. They also indicate that this procedure can be applied to TLV's that have a "C" or ceiling designation that is not based on sensory irritation.

Calabrese (Reference B.4) acknowledges the work of Brief and Scala (Reference B.3), but takes exception to their general formula approach (GFA) because

- o it does not take into account or define high risk individuals, i.e., individuals that have differential susceptibility to specific pollutants;
- o it does not take into account possible enhancement of susceptibility or risk due to modification of Circadian rhythms attendant with novel work schedules;
- o it cannot account for the unknown effect of modified schedules on toxicological response to carcinogens;
- o the GFA treats the purge period for all chemicals equally. Calabrese indicates that the purge period correction should be chemical specific and related to its metabolism, site of action, etc. (i.e., the chemical's biological half-life).
- o the TLV's have inconsistent, highly-variable factors of safety already built in.

Hickey and Reist (Reference B.5) derived analytical expressions that may be used to predict the allowable exposure threshold during unusual work schedules. These analytical expressions are derived using a one-compartment model of the human body subject to the criterion that the peak body burden, based on biological uptake rates, for the unusual work schedule should be equal to the peak burden during normal schedules.

For continuous chemical vapor exposure, as may occur over prolonged periods on a tankship, the adjustment factor for the TLV is

$$F_P = \frac{(1 - e^{-8k})(1 - e^{-120k})(e^{-64k})}{(1 - e^{-168k})(1 - e^{-24k})(1 - e^{-kt})}$$

where

t = exposure time

k = composite uptake/excretion rate by respiration (k_1) and metabolism (k_2); $k = k_1 + k_2$

The uptake/excretion rates, k_1 and k_2 , may or may not be available in the literature. If they are not, then equivalent biological half-life data may be used to calculate $k_1 + k_2$ since

$$T_{1/2} = \frac{\ln 2}{k_1 + k_2} = \frac{\ln 2}{k}$$

where

$T_{1/2}$ = biological half-life

The equivalent exposure thresholds can then be calculated

$$TLV_{New} = F_P (TLV_{Old})$$

where

TLV_{Old} = prevailing OSHA or NIOSH TWA-TLV

Roach (Reference B.6) proposed a method of modifying existing TLV's for unusual work schedules that may include extended work cycles (multi-week) and extended work shifts (greater than 8 hours). The criterion for TLV adjustment is based upon limiting body burden during any part of an unusual work shift or cycle to the body burden under normal working conditions (8 hours per day, 5 days per week). The model presented apparently applies to a constant level of exposure. The approximate adjustment factor is obtained by applying the following equation for each work shift and then selecting the minimum value of R.

$$R = \frac{(1 - e^{-8a})(1 - e^{-120a})(1 - e^{-64a})}{(1 - e^{-24a})(1 - e^{-168a})(1 - e^{-ma})(\int e^{-ma})}$$

where

- l = number of hours in a work cycle
- m = length of a particular work shift
- n = elapsed time from end of previous shift to end of a particular work shift
- a = factor related to biological half life

Alternately, the minimum value of R corresponds to the maximum shift body burden and can be identified as the shift for which n is a minimum. The new TLV is equal to $R_{\min}$ multiplied by the conventional TWA-TLV.

As in Hickey's previous work (Reference B.5), special TLV's are generated from normal TLV's by applying an adjustment factor, F_p , which represents an equality of peak body burden under special and normal work schedule exposure situations. Hickey (Reference B.7) suggests that if an individual works W weeks in an exposure environment, with $52 - W$ weeks of seasonal nonexposure, then the TLV adjustment factor is

$$F_p = \frac{(1 - e^{-8k})(1 - e^{-120k})(1 - e^{-8400k})}{(1 - e^{-kH})(1 - e^{-24kD})(1 - e^{-168kW})}$$

where

- k = excretion rate of chemical substance which is derivable from its biological half-life
- H = hours/day worked (extended work day)
- D = days/week worked on extended schedule

If this seasonal adjustment were shown to be valid, it may be adaptable as an administrative control to modify work schedules or work/nonwork cycles.

All of these TLV adjustment methods are purely theoretical at this time since none of the approaches has been verified. Epidemiological studies or biological monitoring may provide a future framework for assessment of the TLV adjustment factors.

Exposure to sensory irritants may result in a decreased respiratory rate. Kane (Reference B.8) measured the decrease in respiratory rate as a function of airborne concentrations of sensory irritants. Using the concentration that produced a 50% reduction in respiratory rate as the criterion for sensory irritation, Kane proposed a method for establishing TLV's, STEL's, etc. The scheme is as shown on the next page.

In an extension of earlier work, Kane (Reference B.9) demonstrated that the 1978 TWA-TLV for ethyl acetate is too high and that for methanol

is too low using a criterion that the TWA-TLV should lie between $0.1 C_{RD50}$ and $0.01 C_{RD50}$, where C_{RD50} is the vapor concentration that causes a 50% reduction in respiratory rate. C_{RD50} is an indicator of sensory irritation. The TWA-TLV's for other chemicals, e.g., ethanol, IPA, NBA, DMK, etc., were within the accepted range.

<u>Concentration</u>	<u>Designation</u>	<u>Proposed Standard</u>
$10 C_{RD50}$	Lethal	--
C_{RD50}	Toxic	--
$0.1 C_{RD50}$	Effective	Highest acceptable TLV; $0.2 C_{RD50} = \text{STEL}$
$0.01 C_{RD50}$	Ineffective	Lowest acceptable TLV
$0.001 C_{RD50}$	Acceptable	--

where C_{RD50} is the contaminant concentration that results in a 50% reduction of respiratory rate.

Kane's method of establishing exposure limits based on the C_{RD50} is independent of work schedules and biological half-lives. As such, it may represent an alternative approach to TLV adjustment in the marine environment. However, as with the modeling approach, the C_{RD50} method would require additional data and in situ verification.

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APPENDIX C

SUMMARY OF REGULATIONS

SUMMARY OF REGULATIONS - TANK VESSELS

Agency	Regulation Code No./Title	Applicable Contents	Remarks
USCG	33CFR, Part 126, "Handling of Explosives or Other Dangerous Cargos Within or Contiguous to Waterfront Facilities"	Shoreside regulations for handling cargoes listed in 46CFR, Table 30.25-1 and 33CFR Subpart 124.14.	Facility must have proper surveillance, prohibition of smoking, control of hotwork and operation of motor vehicles during cargo transfer, good housekeeping, proper lighting, and fire protection equipment. Prior to transfer of cargo, the person in charge must have warning signs displayed, pans or buckets placed under cargo hose connections, cargo information cards for the specific cargo to be transferred, and a "Declaration of Inspection" from the vessel which is to transfer or receive cargo.
	46CFR, Subchapter D, Parts 30-40, "Tank Vessels"	Requirements for materials, design, construction, inspection, manning and cargo handling for tankships and barges.	Applicable parts of this subchapter are Parts 30, 32, and 35.
	46CFR, Part 30, "General Provisions"	Definition of applicable terms in Subchapter D.	Reid Vapor Pressure (RVP)-Vapor pressure of liquid in pounds per square inch @ 100°F flammable liquid - any liquid whose flash point is less than 80°F (open cup) combustible liquid - any liquid whose flash point is greater than 80°F Grade A Cargo - flammable liquid that has a RVP greater than 14 psi Grade B Cargo - flammable liquid that has a RVP greater than 8.5 psi but less than 14 psi Grade C Cargo - flammable liquid that has a RVP less than 8.5 psi Grade D Cargo - combustible liquid with flash point between 150°F and 80°F Grade E Cargo - combustible liquid whose flash point is greater than 150°F
		Cargoes regulated by Subchapter D.	Listed in Table 30.25-1 of Part 30.
	46CFR, Part 32 "Special Equipment, Machinery, and Hull Requirements"	Liquid level gauging for tankships constructed after July 1, 1951.	Gauging of cargo tanks carrying Grade A liquids shall be done without opening ullage hatches, cargo hatches, or Butterworth, such as with a sounding tube.

SUMMARY OF REGULATIONS - TANK VESSELS (Cont'd)

Agency	Regulation Code No./Title	Applicable Contents	Remarks
USCG	46CFR, Part 32 "Special Equipment, Machinery, and Hull Requirements"	Pumps, piping and hose for cargo handling on tankships constructed after July 1, 1951.	Fixed piping systems are required for all Grade A through E cargoes, and they shall not run through spaces where ignition sources are present.
		Inert gas systems.	Required on all tankships of 100,000 DWT after January 1, 1975, except for liquified gas cargo and Grade E cargo that is transported at a temperature of 9°F below its flash point. Oxygen level of inert gas must be less than 5% by volume.
		Venting requirements for cargo tanks on tankships constructed after July 1, 1951.	All cargo tanks on tankships carrying: Grade A liquid must be fitted with a vent system consisting of branch vent lines connected to vent header terminating at a height of 4 meters above the weather deck and an equal distance away from any living or working space or sources of ignition. The branch vent lines must have either no valves or pressure/vacuum (P/V) valves that allow pressure relief of the cargo tank. A flame arrester or P/V valve must be fitted on the vent header. Grade B and C liquids must be fitted with individual P/V valves and vent lines extending to a reasonable height above the weather deck or a venting system as noted for Grade A liquids. Grade D and E liquids must be fitted with a goose-neck vent and flame screen.
	46CFR, Part 35, "Operations"	Venting requirements for cargo tanks on barges constructed after July 1, 1951	All cargo tanks of barges carrying: Grade A, B, and C liquids must be fitted with a vent system as noted for Grade B and C liquids on tankships. Grade D and E liquids must be fitted with a vent system as noted for Grade D and E liquids on the tankships.
		Inspection and testing required for repairs or alterations in and around cargo tanks that have carried bulk flammable or combustible liquids.	Inspection will be carried out in accordance with the "Standard for the Control of Gas Hazards on Vessels to be Repaired, NFPA Code No. 306" by a marine chemist or a person authorized by the Officer in Charge. When neither are reasonably available, the senior officer of the vessel will inspect the tank.

SUMMARY OF REGULATIONS - TANK VESSELS (Cont'd)

Agency	Regulation Code No./Title	Applicable Contents	Remarks
USCG	46CFR, Part 35, "Operations"	Cargo handling, personnel and procedures	A sufficient number of crew members shall be on duty to perform cargo transfer operations. For an unmanned barge, a person holding a valid license as Master, Mate, Engineer, or Certified Tankerman shall be present. Prior to transfer of cargo, the tank vessel shall be electrically bonded to the shore, sea valve and scupper shall be closed, and pans or buckets shall be placed under cargo hose connections. A "Declaration of Inspection" check list shall be completed to assure readiness for cargo transfer and protection against fire hazards.
	46CFR, Subchapter O, Parts 150-154, "Certain Bulk Dangerous Cargos"	Uniform minimum requirements for unmanned barges and self-propelled vessels as per bulk liquid cargo carried.	Applicable parts of this subchapter are Parts 151, 153, and 154.
	46CFR, Part 151, "Unmanned Barges Carrying Certain Bulk Dangerous Cargos"	Cargo tank venting requirements for unmanned barges are listed in Table 151.05 on a per chemical basis.	Type of cargo venting includes open, pressure/vacuum (P/V), and safety relief (SR) venting. - Open venting of cargo tanks allows no restriction on movement of vapor or liquid to or from the tank through the vent line. The outlet should terminate in a goose-neck bend at a reasonable height above the weather deck. - Pressure/vacuum venting requires that a pressure/vacuum valve be placed in the vent piping to automatically limit the pressure or vacuum in a cargo tank. - Safety relief venting requires that a safety relief valve be placed in the vent line to automatically limit the pressure in the cargo tank.
		Cargo tank gaging requirements for unmanned barges are listed in Table 151.05 on a per chemical basis.	Types of cargo gaging include open, restricted, and closed gaging. - Open gaging allows determination of cargo liquid level through any opening in the tank such as ullage hole or tank hold. This method exposes the gage user to the cargo and its vapors. - Restricted gaging is performed through a gaging device such as a sounding tube that penetrates the tank and

SUMMARY OF REGULATIONS - TANK VESSELS (Cont'd)

Agency	Regulation Code No./Title	Applicable Contents	Remarks
USCG	46CFR, Part 151, "Unmanned Barges Carrying Certain Bulk Dangerous Cargos"	Cargo tank gaging requirements for unmanned barges are listed in Table 151.05 on a per chemical basis.	- limits the amount of release of cargo vapor. If a sounding tube is used, the vent system shall be designed to prevent pressure buildup in the cargo tank. - Closed gaging is performed through a device that penetrates the cargo tank and prevents any release of cargo liquid or vapor during gaging (e.g., automatic float, and continuous tape).
		Cargo handling, personnel and procedures for unmanned barges.	A certified tankerman must be on duty to perform cargo transfer. Specific duties are similar to those described in 46CFR, Part 35.
	46CFR, Part 153, "Safety Rules for Self-Propelled Vessels Carrying Hazardous Liquids"	Cargo tank venting and vent height requirements for self-propelled vessels are listed in Table 1 of Part 153 on a per chemical basis.	Open and pressure/vacuum venting are as defined in 46CFR 151. For specific chemicals, discharge height of vents shall be in accordance with the B/3 (1/3 breadth of the ship) or 4m (4 meter) venting systems. For other chemicals there are no specific height restrictions. - B/3 venting system requires that the vent discharge shall be at least 15 meters from any air intake or openings to accommodation or service spaces and shall be at least B/3 or 6 meters above weather deck, whichever is larger. If the discharge is within 6 meters of a walkway, then its height must be 6 meters above the walkway. 4m venting system requires that the vent discharge shall be at least 10 meters from any air intake or openings to accommodation of service spaces and at least 4 meters above the weather deck or walkway if the discharge is within 4 meters of the walkway. - High velocity vents may be used in place of the B/3 or 4m venting systems as approved by the Commandant.
		Cargo tank gaging requirements for self-propelled vessels are listed in Table 1 of Part 153 on a per chemical basis.	Types of cargo tank gaging are open, restricted and closed. - Open gaging is as noted in Part 151. - Restricted gaging is as noted in Part 151 and cannot have an orifice diameter of more than 20 cm. If P/V venting is used in conjunction with restricted gaging, the P/V valve will be locked open or the P/V valve will be bypassed.

SUMMARY OF REGULATIONS - TANK VESSELS (Cont'd)

Agency	Regulation Code No./Title	Applicable Contents	Remarks
USCG	46CFR, Part 153, "Safety Rules for Self-Propelled Vessels Carrying Hazardous Liquids"	Cargo tank gaging requirements for self-propelled vessels are listed in Table I of Part 153 on a per chemical basis.	o Closed gaging is as noted in Part 151 and must have a vapor return connection and a high level alarm as described in Subpart 153.409.
		Personnel safety requirements for self-propelled vessels are listed in Table I of Part 153 on a per chemical basis.	The Master shall ensure that personnel on the ship wear tight fitting goggles or face mask when sampling, transferring, connecting or disconnecting a hose, tank gaging or opening a cargo hatch, ullage hatch or Butterworth. Additional protection such as coveralls and boots shall be worn for the handling of certain chemical cargos. Man-entry into spaces that have contained certain cargos cannot be performed unless the Master ensures that the space is free of toxic vapors and has sufficient oxygen to support life. The person entering the space must wear a 30-minute self-contained breathing apparatus and be closely supervised by an officer of the ship.
	46CFR, Part 154, "Special Interim Regulations for Issuance of Letters of Compliance"	Interim regulations for foreign vessels carrying certain hazardous bulk cargos.	Plan, review, and examination procedures for foreign shippers that carry dangerous cargos are listed in Table I of Part 154.
OSHA	29CFR, Part 1910 "Occupational Safety and Health Standards"	Definition of flammable liquids.	Flammable liquid - any liquid having a flash point below 100°F by closed cup method.
			Class IA liquids - flammable liquid with a flash point below 73°F and having a boiling point below 100°F.
			Class IB liquids - flammable liquid with a flash point below 73°F and having a boiling point above 100°F.
			Class IC liquids - flammable liquid with a flash point between 73°F and 100°F.

SUMMARY OF REGULATIONS - TANK VESSELS (Cont'd)

Agency	Regulation Code No./Title	Applicable Contents	Remarks
OSHA	29CFR, Part 1910, "Occupational Safety and Health Standards"	Definition of combustible liquid.	Combustible liquid - any liquid having a flash point above 100°F by closed cup method. Class II liquids - combustible liquid with a flash point between 100°F and 140°F. Class IIIA liquids - combustible liquid with flash point between 140°F and 200°F. Class IIIB liquids - combustible liquid with a flash point above 200°F
	29CFR, Part 1915, "Safety and Health Regulations for Ship Repairing"	Personnel jurisdiction.	Applies to all persons involved in ship repair other than Master, ship's officers, and crew of vessel.
		Precautions to be taken before entering ship spaces which may contain flammable or toxic vapors.	Atmosphere must not contain a concentration of flammable vapor or gas greater than 10% of the lower explosive limit. Atmosphere must be checked for toxic contaminants. Oxygen content must be at least 16.5% by volume.
	29CFR, Part 1918, "Safety and Health Regulations for Longshoring"	Personnel jurisdiction.	As noted in Part 1915.
		Handling of hazardous material.	Personnel handling hazardous cargo must be informed that the cargo is hazardous and must be provided with necessary personal and fire protection equipment.
	29CFR, Part 1918a, "Marine Terminals"	Safety of personnel is discussed in Subparts B and E.	Of special interest in Subpart B are sections 22 and 23. Of special interest in Subpart E are sections 91 through 95.
		Subpart B - Marine terminal operations	Section 22 - Hazardous Cargo (a) Procedures for informing employees of special precautions for hazardous cargo (b) Special handling of hazardous cargo (c) Instructions for clean-up of hazardous cargo Section 23 - Hazardous Atmosphere, Substances (b) Testing of atmosphere prior to employee entry into space previously containing a hazardous atmosphere (c) Testing of atmosphere during ventilation

SUMMARY OF REGULATIONS - TANK VESSELS (Concl'd)

Agency	Regulation Code No./Title	Applicable Contents	Remarks
		Subpart B - Marine terminal operations	(d) Man entry into hazardous atmosphere (1) Entering personnel shall be protected by respiratory and emergency protective equipment (see Subpart B). (2) Safety instructions to entering personnel as well as standby personnel (3) No ignition sources (4) Criterion for use of self-contained breathing apparatus
		Subpart E - Personal protection	Section 91 - Eye Protection Section 92 - Respiratory Protection Section 93 - Head Protection Section 94 - Foot Protection Section 95 - Other Protective Measures

APPENDIX D

PROPERTY DATA FOR CHEMICAL CARGOS

NOTES

- (1) All entries are closed cup flash points unless denoted as open cup (O.C.)
- (2) Nonflammable under conditions likely to be encountered
- (3) Composite of three gasoline grades: GPL, GRF and GSR
- (4) Temperature not stated
- (5) Abbreviations correspond to the U. S. Coast Guard CHRIS Manual
- (6) Total mist
- (7) 50 ppm vapor/10 mg/m³ particulate
- (8) 50 ppm vapor
- (9) in any 4-hour period
- (10) in any 3-hour period
- (11) in any 2-hour period
- (12) All concentrations in ppm unless otherwise noted
- (13) Pure sodium hydroxide

FLAMMABILITY PROPERTIES

Compound	Flash Point(^o F) (1)	UEL (Z Vol.)	LEL (Z Vol.)
Acetone(ACT) (5)	0.0	2.6	12.8
Benzene (BNZ)	30	1.3	7.9
Butyl Acrylate (BTC)	118(O.C.)	1.4	9.4
n-Butyl Alcohol (BAN)	84	1.4	11.2
Carbon Tetrachloride(CBT)	Non Flammable		
Caustic Soda (CSS)	Non Flammable		
Chloroform (CRF)	Non Flammable		
o,Dichlorobenzene (DBO)	155	2.2	9.2
p,Dichlorobenzene (DBP)	150	-	-
Diethanolamine (DEA)	305(O.C.)	1.6	9.8
Diethylene Glycol (DEG)	255	1.6	10.8
Epichlorohydrin (EPC)	100	3.8	21.0
Ethyl Acrylate (EAC)	44(O.C.)	1.8	9.5
Ethyl Alcohol (EAL)	55	3.3	19.0
Ethylene Dichloride (EDC)	55	6.2	15.6
Ethylene Glycol (EGL)	232	3.2	-
2-Ethyl Hexanol (EHX)	175	-	-
Gasoline (3)	-50 to 73	1.1-1.4	7.1-7.4
Glycerine (GCR)	320	-	-
n-Heptane (HPT)	250	1.0	7.0

FLAMMABILITY PROPERTIES
(Concl'd)

Compound	Flash Point(^o F) (1)	UEL (% Vol.)	LEL (% Vol.)
n-Hexane (HXA)	-7	1.2	7.7
Isopropyl Alcohol (IPA)	53	2.3	12.7
Methanol (MAL)	54	6	36.5
Methylene Chloride (DCM)	(2)	12	19
Methyl Ethyl Ketone(MEK)	20	1.8	11.5
Methyl Isobutyl Ketone (MIK)	73	1.4	7.5
Methyl Methacrylate (MMA)	50(O.C.)	2.1	12.5
Perchloroethylene (TTE)	Non Flammable		
n-Propyl Acetate (PAT)	58	2.0	8.0
Propylene Oxide (POX)	-35	2.1	38.5
Styrene (STY)	88	1.1	6.1
Toluene (TOL)	40	1.27	7.0
Toluene Diisocyanate (TDI)	270(O.C.)	0.9	9.5
1,1,1-Trichloroethane (TCE)	-	7.0	16.0
Trichloroethylene (TCL)	90	8	10.5
Vinyl Acetate (VAM)	18	2.6	13.4
m-Xylene (XLM)	84	1.1	6.4
o-Xylene (XLO)	63	1.1	7.0
p-Xylene (XLP)	81	1.1	6.6

OCCUPATIONAL EXPOSURE LIMITS⁽¹²⁾

Compound	ACGIH			OSHA		
	TLV-TWA (PPM)	TLV-STEL (PPM)	TLV-C (PPM)	PEL (PPM)	Ceiling (PPM)	Max. Acceptable Concentration Above Ceiling (PPM/Δt (min.))
Acetone (ACT) ⁽⁵⁾	1000	1250	-	1000	-	-
Benzene (BNZ)	10	25	-	10	25	50/10
Butyl Acrylate (BTC)	10	-	-	-	-	-
n-Butyl Alcohol (BAN)	50 (skin)	-	50 (skin)	100	-	-
Carbon Tetrachloride (CBT)	5	20	-	10	25	200/5 ⁽⁹⁾
Caustic Soda (CSS)	2mg/m ³ ⁽¹³⁾	-	2mg/m ³	2mg/m ³ ⁽¹³⁾	-	-
Chloroform (CRF)	10	50	-	50	-	-
o-Dichlorobenzene (DOB)	50	-	50	-	-	-
p-Dichlorobenzene (DBP)	75	110	-	75	-	-
Diethanolamine (DEA)	3	-	-	-	-	-
Diethylene Glycol (DEG)	-	-	-	-	-	-
Epichlorohydrin (EPC)	2 (skin)	5 (skin)	-	5 (skin)	-	-
Ethyl Acrylate (EAC)	5 (skin)	25 (skin)	-	25 (skin)	-	-
Ethyl Alcohol (EAL)	1000	-	-	1000	-	-
Ethylene Dichloride (EDC)	10	15	-	50	100	200/5 ⁽¹⁰⁾
Ethylene Glycol (EGL)	50/10 ⁽⁷⁾	-	50 ⁽⁸⁾	-	-	-
2-Ethyl Hexanol (EHX)	-	-	-	-	-	-
Gasoline ⁽³⁾	300	500	-	-	-	-
Glycerine (GCR)	10mg/m ³ ⁽⁶⁾	-	-	-	-	-
n-Heptane (HPT)	400	500	-	500	-	-

OCCUPATIONAL EXPOSURE LIMITS⁽¹²⁾
(Concl'd)

Compound	ACGIH			OSHA		
	TLV-TWA (PPM)	TLV-STEL (PPM)	TLV-C (PPM)	PEL (PPM)	Ceiling (PPM)	Max. Acceptable Concentration Above Ceiling (PPM/At (min.))
n-Hexane (HXA)	100	125	-	500	-	-
Isopropyl Alcohol (IPA)	400	500	-	400	-	-
Methanol (MAL)	200(skin)	250(skin)	-	200	-	-
Methylene Chloride (DCM)	100	500	-	500	1000	2000/5 ⁽¹¹⁾
Methyl Ethyl Ketone (MEK)	200	300	-	200	-	-
Methyl Isobutyl Ketone (MIK)	50	75	-	100	-	-
Methyl Methacrylate (MMA)	100	125	-	100	-	-
Perchloroethylene (TTE)	100(skin)	150(skin)	-	100	200	300/5 ⁽¹⁰⁾
n-Propyl Acetate (PAT)	200	250	-	200	-	-
Propylene Oxide (POX)	20	-	-	100	-	-
Styrene (STY)	50	100	-	100	200	600/5 ⁽¹⁰⁾
Toluene (TOL)	100(skin)	150(skin)	-	200	300	500/10
Toluene Diisocyanate (TDI)	0.02	-	0.02	-	-	-
1,1,1-Trichloroethane (TCE)	350	450	-	350	-	-
Trichloroethylene (TCL)	100	150	-	100	200	300/5 ⁽¹⁰⁾
Vinyl Acetate (VAM)	10	20	-	-	-	-
m-Xylene (XLM)	100(skin)	150(skin)	-	100(skin)	-	-
o-Xylene (XLO)	100(skin)	150(skin)	-	100(skin)	-	-
p-Xylene (XLP)	100(skin)	150(skin)	-	100(skin)	-	-

SELECTED PHYSICAL PROPERTIES

Compound	Molecular Weight	Boiling Pt. (°C) @ 1 atm	Surface Tension (Dynes/cm @ 20°C)	Liquid Specific Gravity @ 20°C	Solubility in Water (mg/l @ 20°C)	Odor Threshold (PPM)
Acetone (ACT) (5)	58.8	56.1	23.7	0.791	Infinit	100
Benzene (BNZ)	78.1	80	28.9	-	1780	4.7
Butyl Acrylate (BTL)	128.1	148.8	20.0	0.899	1600	-
n-Butyl Alcohol (BAN)	74.12	117.7	24.6	0.810	77,000	2.5
Carbon Tetrachloride (CBT)	153.8	76.7	27.0	1.59	800	>10
Caustic Soda (CSS)	40 (13)	130	-	1.50	-	-
Chloroform (CRF)	119.39	61.2	27.1	1.49	8000	205-307
o-Dichlorobenzene (DOB)	147.01	180.5	37.0	1.306	100	50
p-Dichlorobenzene (DBP)	147.01	174.2	-	1.458	69	15-30
Dichloroamine (DEA)	105.14	268.4	-	1.095	954,000	-
Diethylene Glycol (DEG)	106.12	245	-	1.118	Infinit	-
Epichlorohydrin (EPC)	92.53	115.2	37	1.18	60,000	10
Ethyl Acrylate (EAC)	100.12	99.6	25	0.973	20,000	0.00024
Ethyl Alcohol (EAL)	46.07	78.3	22.5	0.79	Infinit	10
Ethylene Dichloride (EDC)	99	83.3	32.2	1.253	8690	100
Ethylene Glycol (EGL)	62.07	197.6	-	1.115	Infinit	-
2-Ethyl Hexanol (EHX)	130.3	189.7	27.6	0.834	1000	0.14
Gasoline (1)	-	14.4-198.9	19-23	0.67-0.75	Insoluble	0.25
Glycerine (GCR)	92.1	290	63.4	1.26	-	-
n-Heptane (HPT)	100.21	98.4	19.3	0.684	2.4	223

SELECTED PHYSICAL PROPERTIES
(Concl'd)

Compound	Molecular Weight	Boiling Pt. (°C) @ 1 atm	Surface Tension (Dynes/cm @ 20°C)	Liquid Specific Gravity @ 20°C	Solubility in Water (mg/l @ 20°C)	Odor Threshold (PPM)
n-Hexane (HXA)	86.17	68.7	18.4	0.659	13	-
Isopropyl Alcohol (IPA)	60.1	82.3	-	0.785	Infinit	37
Methanol (MAL)	32	64.5	22.6	0.792	Infinit	100
Methylene Chloride (MCH)	84.93	39.8	-	1.322	20,000	205-307
Methyl Ethyl Ketone (MEK)	72.11	79.6	24.4	0.8	190,000	10
Methyl Isobutyl Ketone (MIK)	100.16	116.2	23.6	0.807	17,000	0.47
Methyl Methacrylate (MBM)	100.12	101	28	0.945	-	0.05
Perchloromethylene (TTC)	165.83	121	31.3	1.63	150 @ 25°C	5
n-Propyl Acetate (PAT)	102.13	101.6	24.3	0.886	18,900	20
Propylene Oxide (POX)	58.08	34.3	24.5	0.81	650,000	200
Styrene (STY)	104	145.2	32.16	0.906	300	0.15
Toluene (TOL)	92.1	110.6	29.0	0.867	515	0.17
Toluene Dicyanamate (TDM)	174.1	250	25	1.22 @ 25°C	-	0.4-2.1
1,1,1-Trichloroethane (TCT)	133.4	74	25.4	1.31	4,400	100
Trichloroethylene (TCL)	131.39	87	29.3	1.46	1,100 @ 25°C	50
Vinyl Acetate (VAM)	86.1	72.9	24	0.934	25,000 (4)	0.12
m-Xylene (XIM)	106.16	131.9	28.6	0.864	-	0.05
o-Xylene (XIO)	106.16	144.4	30.53	0.880	175	0.05
p-Xylene (XIP)	106.16	138.3	28.3	0.861	198 @ 25°C	0.05

REFERENCES

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6. Seidell, A., Solubilities of Organic Compounds, Van Nostrand Co., 1941.

APPENDIX E

BACKGROUND VOYAGE REPORT -
MANNED BARGE - GASOLINE

VESSEL AND CARGO DESCRIPTION

I. Vessel Description

I.1 Dimensions

- o Length Overall - 630 ft (approximate)
- o Length Between Perpendiculars - 600 ft (approximate)
- o Breadth (mid) - 90 ft (approximate)
- o Depth (mid) - 50 ft (approximate)

I.2 Tonnage - 39,000 DWT (summer mark) (approximate)

I.3 Propulsion - 14,000 hp diesel

I.4 Cargo Tanks - 18 (six rows of three across, wing capacities symmetric about center longitudinal)

I.5 Cargo Pumps - five 4500-gpm self priming, diesel driven deepwells; one 2500-gpm self priming diesel driven deepwell

I.6 Cargo Loading Method - open drop, open loading

I.7 Cargo Gauging Method - open gauging with Lufkin tape and crucifix through deck riser tubes. The deck riser tubes extend 28 in. upward from the deck plate. Tube inside diameter is 8 inches. The gauging tubes are not classified as a restricted gauging system.

I.8 Vapor Venting System - Vapors are vented through open ullage ports and open riser tubes during loading. Vapors are vented from secured tanks through VAC-REL P/V valves on each expansion trunk. The pressure-vacuum settings are 1.0 psi and 0.5 psi, respectively. The center of the P/V valve discharge is 42 in. above deck level.

I.9 Tank Cleaning Method - non-rotating water spray nozzle and water driven air blowers

I.10 Expansion Trunk Layout - The expansion trunks for the starboard wing tanks are colinear and parallel with the ship's longitudinal axis on the starboard side. The expansion trunks for the center tanks are colinear, as are the port wing trunks, both sets being located on the port side of the vessel.

I.11 Ballast Configuration - 1, 3, 5, and 6 center tanks are normally the ballast tanks.

II. Cargo Description

The cargo consisted of regular, unleaded, and super unleaded gasoline. During loading these products were distributed according to Table I.

TABLE I
Loading Plan

<u>Tank No.</u>	<u>Quantity (bbls)</u>	<u>Product</u>
1P	12,791	Regular
1C	19,657	
1S	12,784	
2P	14,902	
2C	31,660	
2S	14,909	
5P	9,302	Unleaded
5C	11,755	
5S	9,328	
4P	13,078	
4C	27,732	
4S	13,085	
6P	8,466	Super Unleaded
6C	18,236	
6S	8,450	
3P	18,723	
3C	38,527	
3S	18,740	

These products were subsequently discharged in three ports. The port times for loading and discharge are noted below.

<u>Port No.</u>	<u>Operation</u>	<u>Duration (hrs)</u>
1	Loading	39.50
2	Discharge	18.25
3	Discharge	19.25
4	Discharge	14.50

ENGINE DEPARTMENT

I. Propulsion System - 14,000 hp geared diesel

II. Engine Room Personnel and Assigned Responsibilities

- o Chief Engineer - Head of Engineering Department responsible for all technical aspects of entire vessel
- o First Assistant Engineer - overall responsibility for all engine room spaces and machinery. Specific responsibility for
 - o auxiliary engine/generator sets;
 - o main engine, engine controls, and water treatment;
 - o main reduction gears and shafting;
 - o steering gear;
 - o hydraulic systems and pumps;
 - o bow thruster; and
 - o main air compressor and starting air systems.
- o Second Assistant Engineer - responsibility for maintenance of
 - o windlasses, winches, and mechanical hoists;
 - o electrical systems;
 - o refrigeration and air conditioning systems;
 - o boilers (water testing and treatment, cleaning);
 - o fuel oil systems including purifiers, bunkering, and transfer;
 - o cargo pump diesel engines; and
 - o evaporators.
- o Third Assistant Engineer - primary responsibility for maintenance of
 - o lube oil systems including purifying, filtering, and straining systems;
 - o auxiliary air compressor;
 - o pumps and motors including bilge/ballast, main engines, and electric driven pumps;
 - o potable water systems;
 - o lighting systems;
 - o sewage treatment;
 - o batteries;
 - o cargo pumps; and
 - o tank cleaning pumps.

III. Watch Schedule

The three assistant engineers stand a conventional 4-on, 8-off rotating watch schedule at sea and in port. During a watch at sea, their responsibility is to conduct periodic inspection rounds of the engine room and control console to ensure that all systems are operating at a state that is consistent with the ship's maneuver. Repair and maintenance are not performed on watch at sea under normal conditions. Repair and maintenance may be performed by the Engineering Department

- o on overtime (off watch) at sea and in port; and
- o during regular watch in port.

IV. Typical Maintenance and Repair Activities

IV.1 In Port (Regular Watch and/or Overtime)

- o Inspect main engine, attached pumps, and gear train;
- o Correct oil leak on cam shifting detent;
- o Wash down engine and inspect valve gear, cams, fuel pump, and tappets;
- o Replace discharge nipple on starting compressor;
- o Clean and inspect reduction gear lube oil reduction strainers;
- o Top all oils to recommended levels;
- o Correct oil leak on No. 1 cylinder head shroud;
- o Clean sea suction strainers and lubricate parts;
- o Repair air leak on starting air system;
- o Repair salt water leak on injector cooling water over-board line;
- o Replace fitting on lube oil system;
- o Repair head cover on main engine;
- o Change final fuel filters on main engine; and
- o Clean strainers on fuel oil purifier.

IV.2 At Sea (Overtime)

- o Install lights (new) in engine room;
- o Change shaft seal on No. 3 main cargo pump;
- o Replace nipple on generator;
- o Replace union on ballast pump for sea water to generator for cooling;
- o Repair lube oil leak on generator spin filter line;
- o Replace light lenses in engine room;
- o Make up air hose for impact wrench in engine room;
- o Remount fire extinguisher in engine room;
- o Check hydraulic hoses on deck winches;
- o Make sea suction valve ready to replace;
- o Inventory oxygen and acetylene supplies for welder;
- o Install new fire pump relief valve;
- o Change oil and filter on generator;
- o Clean salt water side of compressor and repair leak on salt water piping;
- o Clean ballast pump suction strainers; and
- o Continue organization of engine room tool storage boards.

The maintenance and repair activities are posted in the Engine Control Room and are keyed to the responsibilities of the three assistant engineers.

V. Engine Room Ventilation System

Primary ventilation for the four-level engine room was provided by a push-pull system. Supply air was provided by two separate blowers, whose inlets were located on the central surfaces of the fairing supports for the flying bridge. Exhauster discharge grills were located on the aft end of these fairings.

Supply air was ducted to the first and second below-deck levels in the engine room. Forced ventilation for the forward third level was provided by one of the second level supply ducts located directly over the diesel engine. Air from the second level was transported to the third level through open floor gratings. Forced ventilation was confined primarily to the forward portions of the engine room that housed the main engine and other heat-producing pieces of equipment. The aft end of the first level, which housed the hydraulic steering mechanism as well as a welding shop and a general work shop, was separated from the forward portion of the engine room by a bulkhead with a hatch for access. Ventilation for this room consisted of infiltration through the door and natural ventilation as provided by a vertical duct that opened onto the main deck level aft of the deckhouse. The third and fourth levels housed the clutch, reducer gear assembly, and the drive shaft. A mechanical ventilation outlet was located over the propeller shaft assembly.

VI. Emission Inventory

The plan for assessing potential sources of occupational exposure consisted of

- o walk-through surveys to identify equipment systems and their functions;
- o walk-through surveys to observe the working environment and potential contaminant sources through smell (vapors) and sight and touch (oil mist and particulates);
- o informal discussions with engine room personnel, both on- and off-watch;
- o OVA surveys of the various engine room levels during cargo loading and at sea; and
- o area sampling for oil mist and airborne asbestos.

The first two items were conducted concurrently in port and at sea because of the different operating states of the engine room equipment. Item 3 was accomplished during two consecutive 4-hour watches at sea with the Third Assistant Engineer. The results of Item 3 are presented in a later section. These first three items yielded the following observations.

- o Odor levels were relatively low. There were no pronounced or distinctly identifiable sources of odor that could be related to cargo, oxidizing oil, or cleaning solvents.
- o Neither airborne particulates nor oil mist was observed visually.
- o In general, non-machinery-related surfaces were not covered with a dust layer or oil film.
- o The original asbestos insulation was being periodically replaced by a fiber glass substitute as a part of a long-term maintenance program. A material having the appearance of asbestos was in place on the generator and main engine exhaust header.

- o Leaks in the lube oil systems or high pressure diesel fuel delivery systems may be a potential source of mist and vapor if generator or engine manifolds are contacted.
- o A degreaser is commonly used in the engine room. Its use was not observed, and its odor was not distinguishable as a component of the odor background. However, discussions revealed that warm weather (elevated ambient and water temperatures) can enhance normal engine room temperatures to produce a noticeable degreaser odor.
- o Cargo vapor infiltration into the engine room was not commonly observed by the Engineering Department personnel.

Based on these inputs, personal sampling was not justified at this time, and an intermediate area sampling effort was conducted. As stated earlier, all engine room levels were surveyed using the OVA. Vapor concentrations as ppm methane are summarized in Table II for both engine room operations during cargo loading and at sea.

TABLE II
Engine Room Vapor Concentration Measurements
(ppm as Methane)

<u>Level</u>	<u>Location</u>	<u>In Port</u>	<u>At Sea</u>
I	Spare Parts Room	19-20	6-7
	Compressor	13-15	6-8
	Engine Exhaust Ducts	17-18	7-10
	Fuel Separator	15	9-10
	Hydraulic Steering Room	7	10
II	Work Bench and Tool Rack	12-15	8-9
	Engine Cylinder Covers	12-24	8-11
	Engine Cooling Air Outlet	10	10
III	Forward Transfer Pump	15-17	8-9
	Bucket of Degreaser	25	--
	Engine Fuel Racks	15-26	9-15
	Clutch and Reducer	25	10
IV	Propeller Drive Shaft	15-19	10-11

- NOTES:
1. Within a given level, locations progress from forward to aft end of engine room.
 2. Measurements made with OVA.
 3. Vapors were not analyzed for composition.

It is apparent that vapor levels were slightly, but consistently, higher in the engine room during product loading than during the laden voyage even though the prevailing wind during loading was from stem to bow. Since the gasoline odor was not detected (odor threshold = 0.25 ppm), the increase may be attributable to an elevated background level in the terminal area. The increase does not appear to be attributable to equipment operation since most engine room systems are geared down or on standby while in port. As will be noted later, a similar trend was observed in the deckhouse.

The following area samples were collected in the engine room during the laden leg of the voyage.

<u>Sample No.</u>	<u>Sampling Time (min.)</u>	<u>Sampling Rate</u>	<u>Concentration</u>
D-20	254	1.488 l/min.	asbestos N.D.
D-15	250	1.062 l/min.	0.2 mg/m ³ oil mist
D-11	360	1.475 l/min.	{ asbestos N.D. 0.06 mg/m ³ oil mist

Sample No. D-20 was collected on Level II of the engine room where the exhaust headers manifolded into the common exhaust stack. NIOSH Method No. P&CAM 239* was used to analyze the 0.8 μ mixed esters of cellulose filter for asbestos. The same type of filter (D-15) was used to sample for oil mist on Level III near the fuel injector rack. An infrared method was used to analyze this filter. Sample No. D-11 was analyzed for both asbestos and oil mist. This sample was collected on Level II of the engine room near the generator exhaust stack. Oil mist concentrations are based on mineral oil.

VII. Watch Activities

During the laden voyage, SwRI personnel stood two consecutive watches with the engineer on duty. The documentation of work activities from these watches has been condensed into a single scenario for a typical 4-hour watch.

The engine room watch at sea was structured around three inspection rounds. Each round was initiated near the beginning of each of the first three watch hours. The duration of each round is governed by the inspections to be accomplished, and they varied from 10 to 18 minutes each. Actual engine room time ranged from 34 to 40 minutes in a 4-hour watch. The remainder of the time was devoted to monitoring the readout displays of various engine temperatures and pressures and fluid levels in the engine control room.

<u>Round I</u>	Check valve settings; drain water from engine rocker arm lube system; check oil level in electrical generator; clean oil strainers using degreaser; general visual inspection of all systems.

* 100 fields counted at 500X on phase contrast microscope. Microscope field area was 0.004 mm².

Round II

Lubricate fuel rack, check valve settings; drain water from engine rocker arm lube system; check oil level in electrical generator; visual inspection of all systems; reset oil centrifuge.

Round III

Visual inspection of all systems, check valve settings, drain water from engine rocker arm lube system, read fuel oil counter for the day.

Prior to completion of a watch, the engineer may perform the following duties that can be accomplished from the engine control room area on the main deck level.

- o Gauge the fresh water tank.
- o Gauge the main engine crankcase sumps.
- o Record engine RPM totalizer.
- o Record exhaust temperatures on all cylinders.
- o Record oil and cooling water temperatures and pressures.

A potential dermal exposure exists during use of degreaser solvents. The hands are the area in contact with the solvent. Maximum duration of dermal contact is limited to the time required for an inspection round because the practice on the ship is to wash the hands thoroughly upon leaving the engine room.

DECKHOUSE

I. Deckhouse Configuration

The deckhouse consisted of three levels:

1. Main deck level - housed the galley, mess, engine control room, and quarters for unlicensed crew members.
2. Boat deck level - housed the hospital room and quarters for the licensed crew members.
3. Navigation bridge.

Access to the deckhouse from the forward deck was provided by two doors (port and starboard) on the main deck level and one door on the boat deck. Three doors, similarly located, provided access to the stern deck.

II. Deckhouse Ventilation

Conditioned air was provided to the main and boat deck areas by a central, closed-return heating and cooling unit. The compressor for the cooling unit was housed in the engine room. Air discharge grills were located in the ceilings of individual rooms with return air grills located in the interior doors. By design, this air conditioning system should not communicate with the outside ambient air unless the external air infiltrates into the deckhouse through the access doorways. Cooling air was provided to the navigation bridge by a window air conditioning unit. Due to the mild temperatures, the doors to the bridge wings were normally open.

III. Deckhouse Environment

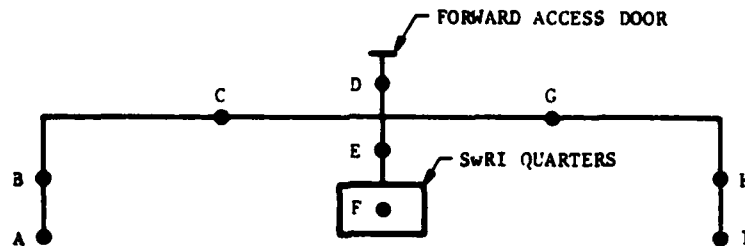
OVA surveys were conducted on the main and boat deck levels to assess the relative potential for vapor infiltration into living spaces. The surveys were conducted in the hallways, engine control room, and in the SwRI quarters during product loading and discharging, tank cleaning, and the laden leg of the voyage. The results of these surveys are shown in Table III where concentrations are expressed as ppm methane.

As in the engine room surveys, the deckhouse surveys indicated a general increase in vapor concentration during cargo loading and tank cleaning, which could be a result of infiltration through incompletely closed forward or aft access doors, or both. During loading, the odor of gasoline was noticeable, especially in the hallway to the boatdeck leading to the forward access door. On the deck side of the door, vapor concentrations ranged from 55 to 150 ppm. Vapor concentrations above the false ceiling in that hallway varied between 60 and 70 ppm. The source of that vapor access could not be determined.

Air velocity measurements were made in the SwRI quarters using a hot wire anemometer. The purpose of these measurements was to determine if the transport velocity exceeded 35 fpm, which is the minimum velocity that is recommended for use with passive dosimeters.

TABLE III
OVA Surveys of Deckhouse

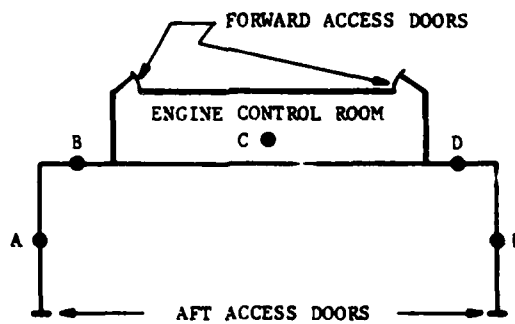
BOAT DECK LEVEL



Vapor Concentrations (ppm as Methane)

Point	Tank Cleaning	Loading	Laden	Discharging
A	12	12	7	7
B	12	12	7	7
C	12	12	7	7
D	10	15-37	7	12
E	12	12	7	7
F	13-17	9.5	7	7
G	11	12	7	7
H	11	12	7	7
I	11	12	7	7

MAIN DECK LEVEL



Vapor Concentrations (ppm as Methane)

Point	Tank Cleaning	Loading	Laden	Discharging
A	10	11	7	7
B	10	11	7	7
C	9	13	7	7
D	10	13	7	7
E	10	11	7	7

The measurements were made on the night stands next to the two beds in the hospital room as well as the ventilation discharge grill. The results are summarized below.

<u>Location</u>	<u>Transport Velocity (fpm)</u>	
	<u>During Loading</u>	<u>During Laden Voyage</u>
Stand No. 1	0-40, mostly 0-10 (door open) 0-10 (door closed)	0-50, mostly 5 with door closed
Stand No. 2	0-70, mostly 0-50 25 nominal average	0-20, average 5
Exhaust Grill	1100-1300	800-1000

These measurements suggest that passive dosimetry in crew quarters during sleeping hours may not produce valid samples. This result is meaningful because the alternative to passive dosimetry is active sampling. The air velocities at the discharge grill exceed the minimum, but because the discharge is coupled to a closed system, the vapor concentrations at the discharge point may not be representative of what is breathed.

DECK DEPARTMENT

I. Deck Department Personnel and Responsibilities

- o Chief Mate - Head of the Deck Department and second in command on the vessel. His primary responsibilities include
 - o administration and supervision of personnel in his department;
 - o training of personnel on safe work practices, applicable safety rules and regulations as well as fire, explosion, and pollution prevention;
 - o planning and executing maintenance of hull, deck, and cargo handling equipment;
 - o maintaining overtime records;
 - o assigning duties and responsibilities to other licensed and unlicensed crew members;
 - o maintain inventory of mooring line use and condition;
 - o maintaining a Deck Work Book as a current and historical record of daily maintenance activities and assignments;
 - o standing navigation watch at sea and deck watch during cargo transfer;
 - o operation and condition of all cargo handling and ballast systems;
 - o planning loading and discharging of cargo and ballast;
 - o all tank cleaning operations; and
 - o ship's firefighting, lifesaving, and personnel safety equipment and seeing that they are tested and in compliance with applicable governmental regulations.
- o Second Mate - Works under direction of Chief Mate and is responsible for
 - o the ship's navigation and radio equipment;
 - o updating navigation charts;
 - o testing of lifeboat radios;
 - o updating and reissue of flares and safety equipment;
 - o reorganizing tools on ship;
 - o supervising unlicensed personnel under his jurisdiction during watch standing, cargo transfer and ballasting operations, and other maintenance duties;
 - o standing navigation watch at sea;
 - o standing deck watch in port;
 - o repairing deck valves and installing grease fittings; and
 - o stencilling of signs on vessel.
- o Third Mate - Works under direction of Chief Mate and is responsible for
 - o standing navigation watch at sea and deck watch during cargo transfer operations;
 - o assisting the Chief Mate with maintenance of lifeboats and safety equipment;
 - o inspecting and maintaining firefighting equipment;
 - o flags and signalling equipment;
 - o maintaining proper oil and water levels on cargo discharge diesel engines;

- o replacement of filters on cargo diesel engines; and
- o assisting Second Mate with deck valve overhaul.

This vessel carried three Mates. Unlicensed personnel in the Deck Department consisted of a Bosun, three Able-bodied Seamen (A/B), and two Ordinary Seamen (O/S).

- o Bosun - The Bosun works under the direction of the Chief Mate. In this capacity he is essentially the foreman for deck work crews. His duties include
 - o operation of mooring line winches during docking and undocking;
 - o maintenance of deck rigging;
 - o preparing manifolds for hose connect and securing manifolds after cargo transfer;
 - o directing the deck maintenance of the A/B and O/S as identified in the Chief Mate's Deck Work Book;
 - o the Bosun did not stand navigation or cargo transfer watches.
- o A/B - The duties of the A/B include
 - o standing navigation watch at sea and deck watch during cargo transfer, ballasting, and tank cleaning operations;
 - o performing assigned deck work and maintenance at sea;
 - o participating in "all hands" preparation for docking and undocking.
- o O/S - With the exception of standing navigation watch, the duties of the O/S are similar to those of the A/B.

II. Work Schedules

For discussion purposes, it is convenient to distinguish between the work schedules of the licensed and unlicensed crew members.

At sea, all three Mates stand a 4-on, 8-off navigation watch. During off-watch hours at sea, each Mate may perform additional work activities on an overtime basis. If he so chooses, in port, the Mates stand a 4-on, 8-off deck watch during cargo transfer. Overtime work is also conducted off-watch. This overtime work may include "all hands" in preparation for docking and undocking, extending the deck watch hours if the Chief Mate's work load is too great, especially during the critical stages of cargo handling, and a variety of maintenance and housekeeping tasks, some of which were identified in the previous section.

At sea, the A/B's stand a navigation watch. The watch shifts of the three A/B's were scheduled such that they could also work a full (0800-1600) 8-hour maintenance and repair shift. Opportunities for overtime exist such as mandatory "all hands" for docking and undocking if it occurs outside of the regular work house and assisting with heel washing of tanks and flushing of cargo discharge lines.

The O/S's do not stand navigation watch. At sea, they perform deck work and general maintenance (0800-1600) as directed by the Bosun, who receives his daily work list from the Chief Mate. In port, both the A/B's and O/S's stand deck watch during cargo transfer. During cargo transfer operations, the deck watch work unit consists of a Mate, an A/B, and an O/S. The O/S also has opportunities for overtime such as "bow watch" during channel navigation and tank cleaning work at night or engine room maintenance.

It is to be noted that all work schedules include frequent, short, rotating work breaks for rest and mess time.

In general, extended work schedules arise because of

- o responsibility - Chief Mate's responsibility for tank cleaning. The duration of this activity is governed by the number of tanks to be cleaned.
- o overtime - Voluntary overtime is available without limit subject to the work that needs to be accomplished to keep the ship in a proper state of maintenance.
- o unique factors - These factors, such as shift exchange for free time in port, do not necessarily occur on a regular basis.

III. Deck Work Book Entries

As mentioned earlier, the Chief Mate maintains a Deck Work Book of the activities to be performed on the deck and in the deckhouse at sea. These activities may be of a housekeeping nature, or they may involve repair of ship's equipment. Certain repair work is timed so as to not involve any loaded tanks. The following entries were extracted from the ship's Deck Work Book for the SwRI voyage. These entries may be considered typical of day work at sea.

- Day 1 - o Paint forward bulwarks
- Day 2 - o All hands for undock
o Heavy seas, spray on deck, no deck work
- Day 3 - o Heavy seas, spray on deck
o Scrub down main deck
o Rig lifting beam on No. 3 pump house and change out leaky seal
o Grease butterfly valves forward
o Continue deck scrubdown
- Day 4 - o Paint forward bulwark and deckhouse
o Continue repair of blowers
o Overhaul butterfly valves forward
o All hands for docking
o Set up for product discharge

- Day 5 - o No work on deck this day
o Fire and boat drill
- Day 6 - o Very heavy seas on deck
o Hang lifeboat radio in starboard tower
o Rebrace Officers' Mess table
o Clean out forecandle and laundry room
o Miscellaneous projects
o All hands for docking
- Day 7 - o Set up deck for tank cleaning
- Day 8 - o All hands set up for product discharge
o All hands out for undocking
o River watches for tank cleaning
- Day 9 - o Gas free 2W, 3W, 4W
o Crew on river watches until next port
- Day 10 - o All hands for docking
o Rig staging
o After shift of Plimsoll marks, paint with zinc primer, yellow around marks, white on marks
o All hands secure for sea
o Stow six 55-gallon drums lube oil
o Send ashore No. 2 winch hydraulic motor and secure stage
- Day 11 - o Muck and inspect 4 P/S
o C/M prepare coating reports
o Continue painting and sandblasting on fore-castle bulwarks
o Fire and boat drill
o Rebuild strong back on No. 2 lifeboat
o Flush all pumps and lines
o Pressure Test No. 6 main cargo pump to find cause of slow discharge
- Day 12 - o Sandblasting
o Fix lifeline (new cable)
o Clean out No. 6 pumphouse with degreaser

IV. Potential Non-Cargo Related Occupational Exposures

Three deck day work activities involved the use of non-cargo chemical substances that could potentially contribute to the overall occupational exposure profile.

- o Spraying of rust deactivator
- o Spray painting
- o Sand blasting

Rusting of deck structures and components is a perennial problem. This rust may affect the performance of above-deck valve stems and make ullage ports, expansion trunk domes, and standpipe covers difficult to open or close. Rust must be deactivated before the affected surfaces can be painted. This deactivation was accomplished by spraying a phosphoric acid-based solution onto the rust. This liquid, which is a "balanced formula" of phosphoric acid, dichromate, wetting agents and extenders, is labeled as a corrosive. Further, the warning and labeling indicated that this material is an irritant to eyes and mucous membranes and that prolonged exposure may cause hand irritation, and rubber gloves should be worn. There was no suggestion that eye protection be worn.

This rust deactivator was applied with a garden type sprayer. The crewman wore chemical goggles, but no gloves. Other unprotected portions of the skin included the arms and legs. There is a potential for dermal exposure as evidenced by the fact that the crewman stated that the liquid is highly irritating to his skin. The duration and site of contact are governed by the wind conditions, body location with respect to wind vector, and the part to be sprayed. Spray duration per part was roughly 5 seconds. This potential problem could be minimized by clothing that covers the exposed surfaces.

Sandblasting is a continuing activity aboard ship. Blasting is employed when large areas are to be primed and painted or where excessive corrosion exists. The sandblaster wore full body coveralls, gloves, and a hood. Two types of hoods were available.

1. Loose fitting, leather hood with replaceable window shields. This hood is not meant for prolonged use, but offers good maneuverability and visibility when working in tight spots.
2. Full plastic hood with compressed air feed. This hood is quite bulky and hot, but is recommended for extended periods of time. Maneuverability and visibility are restricted. A spotter generally aids the blaster because the hood restricts hearing.

The first type of hood was used in preference to the second type. Because it is a loose-fitting hood, the worker occasionally experienced debris in his mouth and eyes. An area dust sample was collected at a nominal flow rate of 1.6 lpm and at a location approximately 8 ft downwind of the sandblaster. The sample was analyzed for particle size distribution on a Coulter Counter, Model TA. A logarithmic probability plot of particle size indicated a bimodal distribution with a break point at 40μ . It is postulated that particles above this size represent the blasting material, while particles less than 40μ represent paint and rust debris generated by the blasting operation. The count median diameter (CMD) for the entire distribution was 12.5μ . In the respirable range, 43.5 percent of the particles were less than 10μ .

After surfaces have been prepared by sandblasting or application of rust deactivator, they are ready to be spray painted. Painting was performed frequently at sea as a part of an ongoing program to upgrade the deck condition. Two-component epoxy paints and various strength thinners were mixed in the forecastle. Ventilation in this area was minimal. Mechanical ventilation was available, but was not used because the crew believed that the motor constituted an explosion hazard. The crew felt that the paint vapors made them nauseous and made breathing difficult both during mixing and spraying. The thinners were reported to be irritating to the skin. Given these reactions, all mixing and spray painting was conducted without respiratory protection or adequate skin protection. Exposed skin areas included the legs, thorax, and arms. Two types of respiratory protection were presumably available: organic vapor cartridge masks and surgical masks. Neither type was observed being used. There is, thus, a potential for respiratory and dermal exposure, which could be minimized or eliminated through administrative controls (training), engineering controls (explosion-proof ventilation motor), and protective equipment controls (clothing and respiratory protection).

PRODUCT LOADING

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I. Loading Work Scenario

The deck work unit during product loading consists of a Mate, an A/B, and an O/S. These three individuals stand a 4-on, 8-off work schedule. During their 8 hours off watch, they are replaced by two other work units that have the same labor composition. Thus, three work units rotate 4-hour deck watches.

Periodic tank gauging and tank toff were the two primary deck work activities during loading, and the three persons on watch worked as a team while performing these activities.

Periodic gauging has a definite pattern that is characterized by the "gauging round." The gauging round consists of sequentially measuring and recording the ullages on all tanks that are being loaded. The Mate performs the ullage measurements, and the A/B and O/S stand by the deck valves to adjust delivery flow rates as necessary. Ullage readings were taken with a Lufkin tape at the tank gauging tubes. Initially, the gauging rounds are performed on almost an hourly basis. The ullage measurements were used to calculate loading rates and to estimate the times to complete tank filling. The frequency of periodic gauging increased as the time approached to top off selected tanks. In this case, the emphasis was placed on the tanks that were nearly full, and the other tanks were temporarily eliminated from the gauging round. A summary of observed periodic gauging frequency is presented in Table IV. The elapsed time for a

TABLE IV
Frequency of Periodic Gauging Rounds

<u>Clock Time Start</u>	<u>No. of Tanks</u>	<u>Approximate Elapsed Time (min.)</u>
0030	11	10
0100	3	5
0130	9	7
0200	3	5
0309	11	16
0500	3	10
0900	3	5
1000	3	10
1230	4	4
1311	2	2
1321	2	2
1330	4	4
1334	3	3
1340	9	9
1355	2	2
1415	6	5
1615	3	3
1800	3	3

gauging round is a function of the number of tanks to be gauged and the distances between the gauging ports. Within a gauging round, each ullage measurement takes approximately one minute, which includes walking time between tanks. Actual gauging time is also variable, but it is roughly 30 seconds per tank. Interspersed between gauging rounds is random gauging of individual tanks.

A single product may eventually be loaded into as many as nine tanks. Normally, the product flow rates are adjusted so that the wing tanks (port and starboard tanks) are filled first, but at different rates. This staggering of delivery rates eliminates the possibility that two tanks will top off at identically the same time. Topoff of a single tank requires two workers. The Mate gauged the tank using a crucifix, and the gauging frequency was every minute initially and increased to every 15 seconds as the final ullage was approached. The Mate was assisted by an A/B or an O/S who manned the deck valves. Either of these two workers closed the valve to reduce product flow in response to the Mate's directions. When two wing tanks were being topped, the Mate gauged the tank that would finish first while the A/B gauged the other wing tank. When the first wing tank had been filled, the Mate relieved the A/B on the other tank. The O/S's function was to again man the delivery valves to each tank. The duration of crucifix gauging on selected tanks is summarized in Table V. The duration of final topoff gauging was quite variable and ranged from 5 to 37 minutes per tank.

When the three-man deck watch was not conducting a gauging round or topping off tanks, they would

- o Rotate work breaks. One individual at a time would take a break in the deckhouse. The duration of the break

TABLE V
Duration of Crucifix Gauging During
Tank Topoff

<u>Tank No.</u>	<u>Clock Time/Duration (min.)</u>	<u>Individual Involved</u>
5S	0928-0933 = 5 min.	3M
5P	0928-1005 = 37 min.	AB
1S	1045-1115 = 30 min.	3M
1P	1045-1118 = 33 min.	AB
2S	1250-1300 = 10 min.	2M
2P	1250-1307 = 17 min.	AB
3S	1420-1445 = 25 min.	2M
3P	1420-1447 = 27 min.	AB
	1447-1457 = 10 min.	2M
4S	1519-1526 = 7 min.	2M
4P	1519-1526 = 7 min.	AB

ranged from 10 to 30 minutes, with an average of 18 minutes. Rotation of work breaks is repeated on nearly an hourly basis.

- o Congregate near the manifold drip tray or a deck bit to chat.
- o Adjust mooring lines.

After a tank had been loaded, the ullage port and gauging tubes remained open. There was a visible discharge of vapor from the tanks. The discharge was periodic as a result of tank breathing and product expansion.

The direction of the wind on deck does not appear to be a factor in determining the location of the Mate or A/B with respect to the gauging tube while ullage measurements are being taken. The majority of the gauging was performed with the individual standing downwind of the vapors that are discharged from the gauging tube. Less frequently, the individual would stand crosswind. Rarely would the individual stand upwind.

II. Discharge Vapor Concentration Measurements

The vapor concentrations were monitored at the open ullage port of Tank 2S during loading of regular grade gasoline. This concentration-time history is shown in Figure 1. The emission profile has several interesting features.

- o The tank had not been cleaned after the previous contents were discharged, and the tank had been closed for several days prior to docking at the loading port. During this period of time, evaporation of residual product and mass transfer by diffusion resulted in an arrival component having a rather uniform vapor concentration of 11.9 to roughly 13% v/v. Discharge of the arrival component took place within roughly the first 100 minutes of loading.
- o The rise in vapor concentration during loading reflects discharge of the vapor blanket that had developed above the liquid surface as a result of evaporation of product.
- o The gasoline concentration at the end of loading was 39.8% v/v, which agrees very closely with the data points that have been measured by other researchers. For this particular grade of gasoline, that level may represent a saturated vapor concentration corresponding to the product temperature.

The indicated loading rate is applicable only to the initial stages of loading. The final loading rate approached approximately 17.12 m³/min as other regular gasoline tanks were topped off and the flows to these tanks were diverted to Tank 2S.

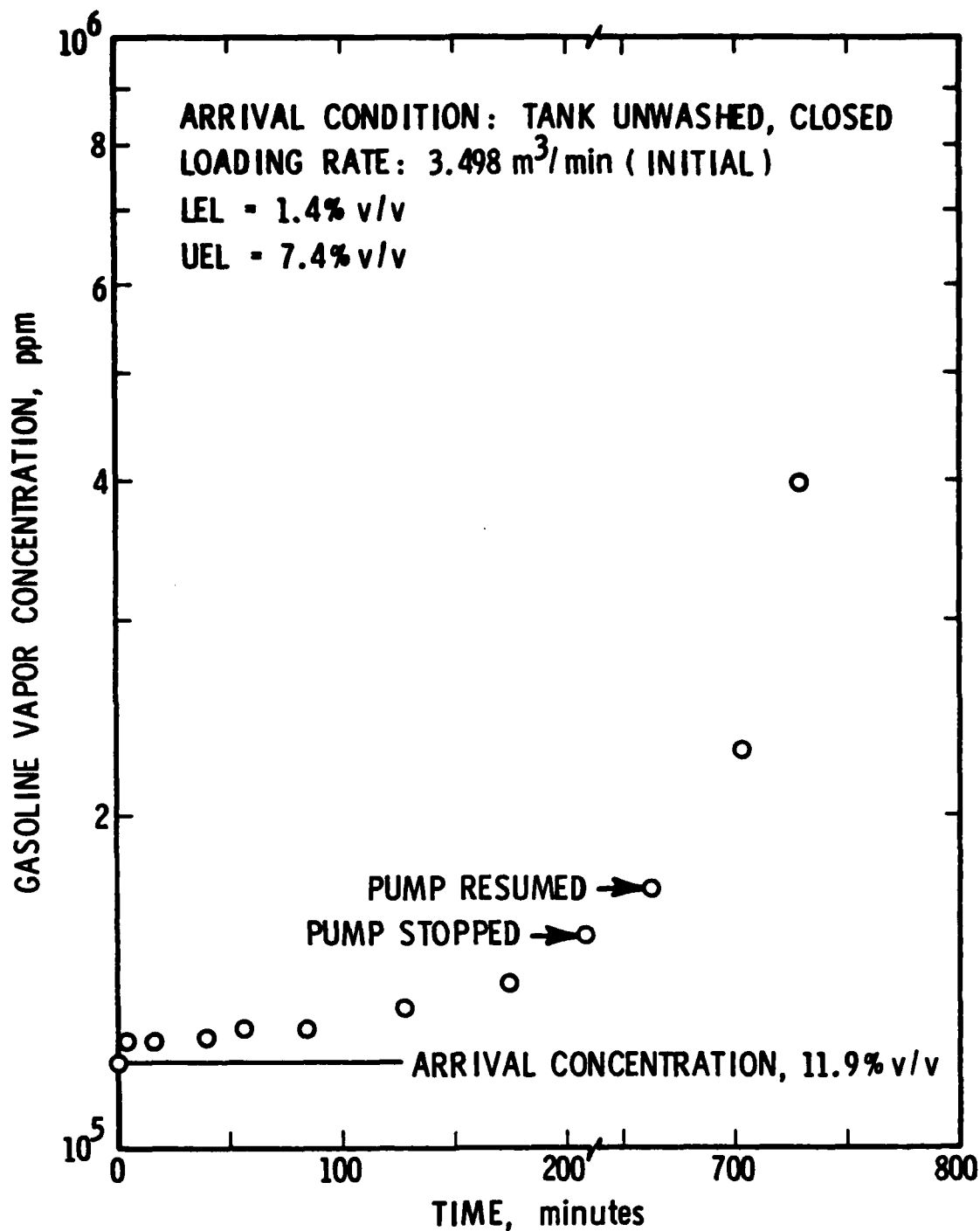


FIGURE 1. CONCENTRATION OF REGULAR GASOLINE VAPOR
DISCHARGED DURING LOADING OF TANK 2S

III. Occupational Exposures

Four groups of exposure samples were collected during loading. These samples reflect tank gauging with and without tank toff. All samples were analyzed for benzene content. Passive badge-type dosimeters were used in parallel with charcoal tube dosimeters on one of the sampling sets. The results are summarized below.

<u>Operation</u>	<u>Sample No.</u>	<u>Exposure Duration (min.)</u>	<u>Concentration (ppm)</u>
Periodic Gauging	SB-1 (2M) *	194	5.2
	SB-2 (CM)	165	2.4
Periodic Gauging & Topoff ^c of Four Tanks	SB-3 (3M)	254	7.8
Periodic Gauging	SB-4 (2M)	232	5.1
Periodic Gauging & Topoff of Three Tanks	SB-5	201	6.3
	47740 } †	196	1.5

† = Parallel sampling on Third Mate

* - Designator in parentheses after sample number indicates crew member sampled

**PREPARATION OF CARGO HANDLING SYSTEMS
FOR PRODUCT DISCHARGE**

I. Work Scenario

Preparation for cargo discharge begins well in advance of docking and takes place either at sea or in the inland waters leading to the discharge port. The following scenario describes these preparations as well as those cargo and tank related activities that take place prior to startup of the ship's discharge pumps.

- o All tools that will be used for removing flanges and connecting discharge hoses are assembled on the drip pan grating.
- o The following work activity is performed after the ship docks, if the ship's manifold system is set up to discharge from the same side of the vessel as was used at the previous port. This means that crossover piping on the opposite manifold remains intact. Crossover pipes are used to carry a single product grade to or from fore and aft tanks through a common manifold line. In this case, the work crew consisted of the Bosun, two A/B's, and two O/S's. The crew loosened the nuts on the manifold flange blinds for those pipes that would be used for product discharge. Excess product in the manifold system discharged into the drip tray. After the residual liquids stopped flowing, the flange bolts and blinds were removed. Three discharge hoses were to be used. Each hose was raised by the dock crane until the hose flange blind was positioned over the drip tray. As the hose blinds were removed, additional product fell into the drip tray. Each hose was then bolted and secured to a manifold flange. Manifold preparation and hookup of three hoses took 24 minutes. There was a potential for dermal exposure since protective gloves, etc., were not worn (see next item in this scenario for liquid contact times). There is also a potential for inhalation exposure to the vapors from the product that was released from the various lines as well as from the existing contents of the drip tray. On a round-trip voyage, product accumulated in the tray at the loading port and discharge ports. The liquid remained in the tray throughout the voyage and was flushed and drained only upon approach to the next loading port.
- o If the manifold crossover piping must be relocated from, say, port to starboard manifold because discharge will be through the port manifold, then the following activities are performed prior to docking. The work crew consisted of two A/B's and two O/S's. The first task was to loosen the bolts that hold the crossover pipes to the manifold flanges. When the flanges were unseated, excess product in the manifold lines drained from the lines into the drip tray. After the crossover lines had been disconnected, the manifold blinds were put in place and secured. The time to remove the crossover pipes and secure the blinds was roughly 30 minutes. Dermal contact time with the hands and arms was approximately 5 minutes. Contact was defined as the time for direct

exposure to bulk liquid. The crossover pipes were then transported to the other manifold where the flange blinds were removed and the crossover pipes were secured. The relocation process took about 30 minutes, and there was an additional dermal contact of about 5 minutes because liquid product also drained from the opposite manifold. Upon docking, the discharge manifold lines were opened. There was no dermal contact since these lines had previously drained. Hose hookup proceeded as outlined above, including the potential for dermal exposure from product in the loading hoses. At one discharge dock, the hoses were dry so that there was no spillage of product or dermal exposure during hose hookup.

- o Immediately upon docking, one crew member opened the ullage ports and gauging tubes on all of the tanks. This operation took 6 to 9 minutes. The potential for a short-term inhalation exposure is governed by the ullage space pressure and whether or not the crew member stands upwind, crosswind, or downwind of these tank openings. The wind direction on deck was generally such that this operation was performed downwind.
- o After the ullage ports and gauging tubes had been opened, the C/M accompanied a dock worker to each tank that was to be discharged. At these tanks, a liquid sample was collected, cargo temperature was measured, and the ullage space was gauged.

II. Occupational Exposures

Personal exposure samples were collected on the individual who opened tank ullage ports and gauging tubes after docking. Monitoring was conducted in two discharge ports. The benzene in gasoline exposure levels during tank opening were as follows.

<u>Sample No.</u>	<u>Sampling Time (min.)</u>	<u>Sampling Rate (l/min.)</u>	<u>Concentration (ppm)</u>
SB-10	6	0.186	ND
SB-11	9	0.186	ND

where ND denotes not detectable.

Dermal exposures were described earlier. Area samples were collected at the drip tray during product discharge, and the results are presented in another section of this documentation.

PRODUCT DISCHARGE

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I. Background

Gasoline cargos were discharged in three terminals. The discharge history for each tank is summarized below. Volumes are in approximate barrels of cargo remaining in a tank at each stage of the voyage.

Tank No.	Terminal No. 1		Terminal No. 2		Terminal No. 3	
	Dock	Undock	Dock	Undock	Dock	Undock
1P	12,791	12,778	12,778	MT	--	--
1C	19,657	7,323	7,323	MT	--	--
1S	12,784	12,753	12,753	MT	--	--
2P	14,902	5,987	5,987	MT	--	--
2C	31,660	31,553	31,553	31,553	31,446	MT
2S	14,909	5,994	5,994	MT	--	--
3P	18,723	16,948	16,948	11,850	11,850	MT
3C	38,527	MT	--	--	--	--
3S	18,740	17,018	17,018	11,885	11,885	MT
4P	13,078	13,078	13,078	13,078	13,078	MT
4C	27,732	10,401	10,401	3,831	3,831	MT
4S	13,085	13,054	13,054	13,054	13,054	MT
5P	9,302	9,302	9,302	9,302	9,302	MT
5C	11,755	MT	--	--	--	--
5S	9,328	9,311	9,311	9,311	9,311	MT
6P	8,466	8,462	8,462	MT	--	--
6C	18,236	MT	--	--	--	--
6S	8,450	8,438	8,438	MT	--	--

II. Discharge Work Scenarios

Three activities took place before discharge began.

- o opening of all ullage caps and gauging tubes
- o gauging and sampling of product in tanks to be discharged
- o hookup of discharge hoses to ship's manifold

The scenarios for these activities have been described elsewhere. After the appropriate deck valves had been opened, the diesel-driven deepwell pumps were turned on, and discharge was initiated.

During discharge, deck watch crews work a rotating 4-on, 8-off schedule. On each 4-hour watch, the work crew consists of a Mate, an A/B, and an O/S.

The work activities during a discharge watch may consist of

- o An hourly gauging round for those tanks that will be completely emptied. Periodic gauging enables the Mate to estimate the discharge rate (bbl/hr) and the corresponding time to empty the tank.

- o Stripping of tank heels to maximize product discharge to shore on those tanks that are to be emptied.
- o More frequent gauging of tanks that will not be completely emptied, but will remain slack until the next discharge port.

After product discharge was underway, the Mate used a Lufkin tape to gauge the ullage space in all tanks that were to be completely emptied. One hour later, these tanks were gauged again. From the ullage-time readings, the Mate estimated the time required to discharge the tank contents. After that calculation was completed, there was minimal gauging activity until the tank was nearly emptied. During this period of time, some tanks were randomly gauged, but the gauging frequency was considerably less than during loading. The ullage round took roughly 10 minutes to complete, and each tank gauging took 15 to 20 seconds. Generally, the A/B and O/S accompanied the Mate during his gauging activity. When not gauging, the three-man deck watch crew engaged in conversation at various points on the deck, especially at the downwind end of the drip tray on the discharge manifold. The drip tray contained residual product from the hose hookup procedure.

When the tank was nearly empty, the deck watch crew initiated a stripping operation. The objective of this activity was to discharge the maximum amount of product from the tank while not losing suction head on the deepwell pump. Generally, the ship is pitched bow up so that the heel accumulates at the aft end of the tank where the main suction and stripper inlets are located. During the stripping operation, the Mate visually watched the location of the product surface through either an open ullage port or a Butterworth opening. A flashlight or a mirror was used to illuminate the surface. In response to the Mate's directions, the A/S and O/S manned the deck valves that close down the main suction line and open the stripper line. The stripping operations took from 12 to 18 minutes, and during this time, the Mate's breathing zone was fully surrounded by the tank opening that he was using to view the liquid surface.

Tanks that will be partially emptied will be gauged more frequently to ensure that the correct quantity of product is delivered to the client. The Mate gauges the tank and directs the A/B to gradually close down on the deck valve for the main discharge line. When the correct product level has been reached, the A/B completely closes the deck valve, and the O/S may turn off the diesel engine that powers the deepwell pump if there are no other tanks on the common discharge line to be emptied. Termination of a split discharge requires the coordinated efforts of these three individuals for approximately seven minutes.

III. Discharge Vapor Concentration Measurements

Vapor concentrations were monitored at the ullage port during discharge of product from Tanks 1P and 2P. Tank 1P was initially full, and its 12,778 bbl were completely discharged. Tank 2P was initially slack, and it was emptied of its 5,987 bbl contents. The concentration measurements are tabulated in Table VI. Discharge rates were calculated using the ship's ullage tables and ullage-time measurements.

TABLE VI
Vapor Concentrations at the Ullage Port
During Product Discharge

TANK 1P

<u>Time From Start of Discharge (min.)</u>	<u>Gasoline Concentration (ppm)</u>
12	8-19
28	4
53	4
77	4-8
137	6
140	7
178	4
187 Discharge halted	
208	9702
223 Discharge resumed	
228	5-70
273	6-420
333 Discharge completed	4-41
873	70-4250

Discharge Rate: 6.519 m³/min. (initial), 4.611 m³/min. (final)

TANK 2P

<u>Time From Start of Discharge (min.)</u>	<u>Gasoline Concentration (ppm)</u>
18	12-41
28	8
53	4
78	4
137	4
178 Discharge completed	4
213	3131

Discharge Rate = 5.883 m³/min.

These data indicate that ullage port concentrations are quite low during discharge because deck air that is ingested into the tank replaces the cargo volume that is pumped out of the tank. All of the air flow is into the tank. There is a sizeable increase in ullage port concentration after the pumping is halted. This increase most likely results from a combination of molecular diffusion and free convection.

IV. Occupational Exposures

The potential for exposure to product vapors during actual discharge appears to be considerably less than during loading, ballasting, and tank cleaning. The low level concentrations at the ullage port, together with the lack of noticeable on-deck product odor, substantiates this hypothesis.

There is one possible exception, but it is difficult to quantify. During stripping, the pumping rate approaches zero, and under these conditions, ullage port concentrations may increase in a manner that is analogous to the termination of discharge. The Mate in charge of stripping has his head inserted into the ullage port or Butterworth opening. His potential exposure to a rise in vapor concentration is difficult to measure with conventional dosimetry techniques because the lapel-mounted sampler is not exposed to the breathing zone vapors.

Parallel active and passive occupational exposure samples were collected on two individuals during consecutive discharge watches. Parallel active and passive area samples were collected at the drip tray where the crew congregated. The results are summarized below.

<u>Identification</u>	<u>Sample No.</u>	<u>Sample Duration (min.)</u>	<u>Benzene Concentration (ppm)</u>
O/S	SB-12	81	0.86
	47,759 } †	74	ND
O/S	SB-13	225	0.17
	47,758 } †	222	ND
Area Sample	EX-11	383	2.1
	47,757	357	2.7

ND = not detectable

† = parallel sampling

BALLASTING

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I. Background

On this voyage, four tanks (1C, 3C, 5C, and 6C) were ballasted. Tanks 3C, 5C, and 6C were ballasted prior to undocking at the final discharge port. Tank 1C was ballasted in the previous docking port. The ballast plan was as follows.

<u>Tank No.</u>	<u>End Ballast Ullage (ft)</u>	<u>Comment</u>
1C	26	This tank short ballasted. The remainder of ballast space to be filled at sea with tank washing slops.
3C	27	Tank eventually overflowed at sea to produce a clean ballast state.
5C	4	Dirty ballast
6C	4	Dirty ballast

Dirty and clean ballast from the forward tanks was subsequently discharged over the side through the loading manifold while the ship was beyond the 50-mile limit.

II. Source Vapor Measurements

Two of the four ballast tanks were monitored for vapor discharge concentrations during ballasting. Tank 1C was ballasted shortly after its product had been discharged. Tank 5C was ballasted roughly three days after product discharge. The results of the concentration measurements are shown in Figures 2 and 3. All measurements were made at the open ullage port.

Tank 5C had been closed for three days prior to ballasting. During that time, the concentrations in the upper half of the ullage space had homogenized through diffusion at roughly 11% v/v. The rise in concentration during the latter half of ballasting reflects the discharge of a concentration gradient. The maximum concentration of 36% v/v at the end of ballasting is consistent with the near-saturation levels that have been observed by SwRI and others to occur at the end of a gasoline loading. The ballast and efflux rates were calculated from ullage-time measurements and the ship's ullage tables.

Tank 1C exhibits a different source concentration profile during ballasting. Since ballasting was begun shortly after discharge, the initially lower concentrations reflect air ingestion and dilution of the upper portion of the vapor space during product discharge. The concentration rises with time to a plateau that is analogous to the homogeneous layer in Tank 5C. If this tank had not been short ballasted, the final concentration would probably have risen to a level that was comparable to the end of ballasting on Tank 5C.

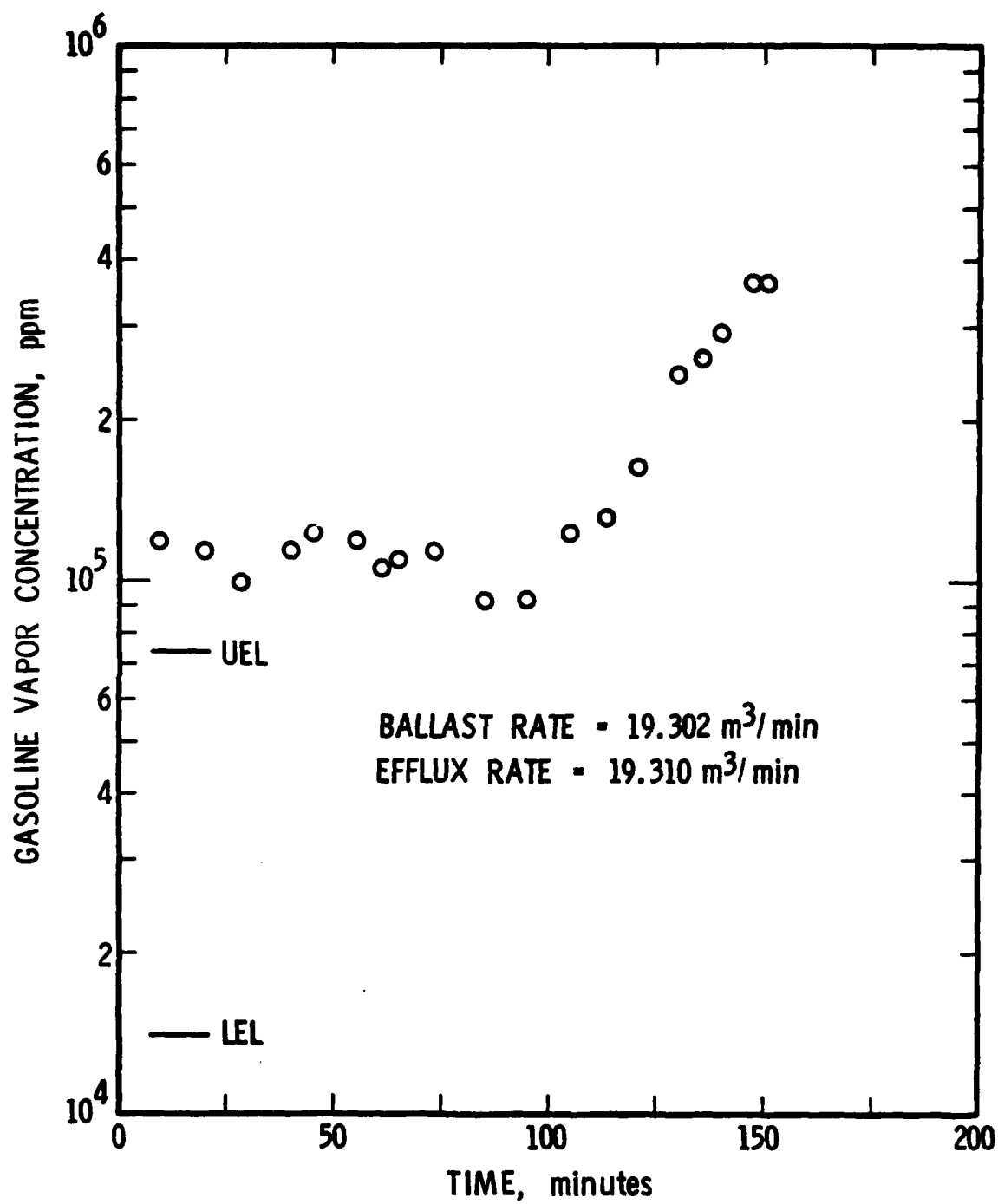


FIGURE 2. CONCENTRATION OF REGULAR GASOLINE VAPOR
DISCHARGED DURING BALLASTING OF TANK 5C

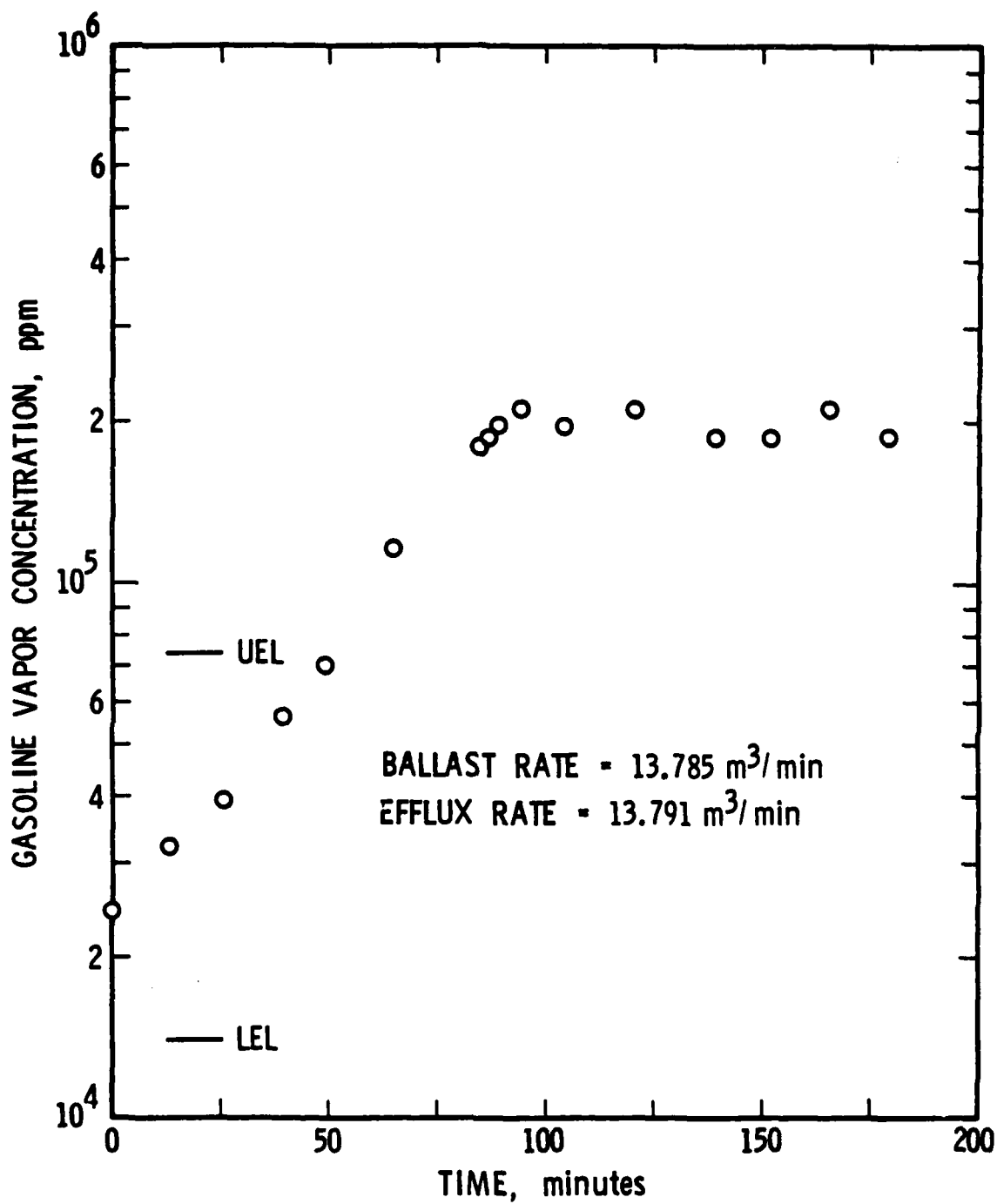


FIGURE 3. CONCENTRATION OF REGULAR GASOLINE VAPOR
DISCHARGED DURING BALLASTING OF TANK 1C

III. Ballasting Work Scenario

Ballasting in port took place after designated tanks had been discharged to shore and before undocking. The work activities during ballasting fell into three categories.

- o periodic gauging of ballast ullage;
- o preparation of the deck for undocking;
- o miscellaneous tasks unrelated to gauging and undocking.

The basic watch crew consists of a Mate, an A/B, and either a Bosun or an O/S. Other crew members may be on deck on an overtime basis.

Throughout the early and intermediate stages of ballasting, the vapor discharge concentrations are considerably higher than during comparable periods of cargo loading. For this reason, the crew members were generally on deck only for the brief periods of time that were necessary to perform required operations. There was one exception. In between various work activities, the crew members would occasionally congregate at the gangway near the discharge manifold. The number of workers on deck at any one time ranged from zero to four.

A ballast gauging round was conducted roughly once each hour. Gauging of an individual tank took approximately 20 seconds. Because the precise quantity of liquid is not as critical during ballasting as it is during product loading, there was no need to perform continuous gauging near toptoff.

Preparations for undocking that were conducted during the ballasting included

- o Disconnecting discharge hoses, blanking the manifold flanges, and removing crossover piping. This activity was performed by an A/B and an O/S and took roughly 35 minutes to complete.
- o Dogging down ullage hatches and ullage pipe covers on all tanks that were not being ballasted. This operation was performed by an A/B and an O/S and took approximately 5 minutes.
- o Collecting samples and gauging all tanks that still contained product. This activity was performed by a shore-based employee, but he was accompanied by a ship's Mate.

Activities unrelated to actual ballasting included adjusting mooring line tension and repair of a butterfly valve drive in a deep well pump line.

IV. Occupational Exposures

One dermal and one ocular exposure were observed. The ocular exposure occurred during ballasting, but did not involve the ballasting operation. The dermal exposure involved a tank that had been washed and then filled with clean ballast.

During hose disconnect prior to undocking, a flange nut fell into a drip tray bucket that had accumulated liquid product from the hoses and manifold piping. The liquid splashed into the eye of one of the crew members. Although the eye was irrigated quickly with fresh water, the contact produced irritation and reddening of the sclera and conjunctival membranes. Eye protection was not being worn.

Tank 3C was washed, but not ventilated. The tank was subsequently filled with sea water to the top of the expansion trunk and overflowed onto the deck to produce a "clean ballast" condition in the tank. The degree of cleanliness was unknown, but small patches of gasoline slick were apparent on the water surface. A potential dermal exposure occurred when one of the crew members washed his face in this ballast water.

TANK CLEANING

I. Background

The cargo compartments on a chemical tanker are generally cleaned on the ballast leg of each voyage. This cleaning may be a requirement for change of cargo grade or for guaranteeing product purity when a tank is to carry the same grade.

Conversely, large scale tank cleaning is not conducted routinely on each voyage of a gasoline tanker. Gasoline tanks may be washed and blown dry periodically so that tank coating materials can be inspected. Other tanks may be washed, stripped, and then loaded with clean ballast. Finally, tank cleaning is required if unleaded gas is to be loaded into a tank that previously carried leaded gas.

On this voyage, nine tanks were prepared, but the purpose was entirely different than was described above. The Plimsoll marks were to be lowered, and this operation involved grinding and welding on the hull exterior adjacent to Tank Nos. 3P and 3S. In accordance with a directive from a Marine Chemist, the following tank preparations were performed at sea prior to the load line modification.

- o Wash and gas free - Tank Nos. 2P, 2C, 2S, 4P, 4C, 4S
- o Wash and clean ballast - Tank Nos. 3P, 3C, 3S

Two of these wing tanks (2P and 2S) were washed and ventilated at sea prior to docking at the last discharge port. The remaining seven tanks were prepared during a 30-hour ballast voyage.

II. Tank Cleaning Procedure

A non-rotating washing machine was used. The washing head consisted of a cylindrical, closed tube with numerous water jet holes drilled through the wall of the tubes. This device was attached to a water hose that could be lowered through an open Butterworth deck plate. Depending upon the tank size, either two or three drops were made into the tank. The washing profile at each drop consisted of 15 minutes at each of three levels--15, 25, and 35 ft into the tank. The deep well pumping rate was synchronized with the water supply rate so that the liquid level in the bottom of the tank was slightly above the suction inlet of the discharge pipe.

The tanks were gas freed using water-driven blowers (Airscrew Fans, Ltd.).

Only two tanks could be processed simultaneously because there were only two water hoses on the vessel. Because of the common need for water to wash tanks and drive the blowers and the schedule to process seven tanks in a short period of time, blowers were frequently turned off so that the water supply could be used for washing another tank. The schedule did not permit uninterrupted washing and ventilation of a tank except in the case of Tank Nos. 2P and 2S.

III. Tank Cleaning Experiments

Two tank cleaning experiments were conducted. The purpose of these experiments was to monitor the concentration of the gasoline vapors that were discharged from the tanks during the cleaning operation. The first experiment included both the washing and gas freeing portions of the cleaning process. The second experiment concentrated on the gas freeing phase. Both the washing and gas freeing portions of the second experiment were interrupted because of the requirements on water usage that were described earlier.

Figure 4 shows the vapor concentration-time history during cleaning of Tank 2S. Concentrations were monitored at the expansion trunk, which was open throughout the entire operation. During ventilation, the tank gauging tube was closed. The blower was located on the Butterworth opening farthest from the expansion trunk; the two remaining Butterworth openings were closed.

The data suggest that the washing operation had a relatively small effect on the gasoline concentrations at the expansion trunk since the concentrations at the beginning and end of washing are of the same order of magnitude. The rise in expansion trunk concentration during washing may be due to (1) displacement of vapor-rich atmosphere as a result of water addition, and/or (2) convective currents generated by the water spray. Since gasoline is insoluble in water, the wash served primarily as a mechanism for aiding in stripping of raw product from the tank bottom. At the end of washing, the vapor concentration at mid-tank depth was approximately 15% v/v. The gas freeing curve exhibits a time delay relative to the ideal dilution curve. This delay probably reflects both the evaporation of residual gasoline on the tank bottom and the delay imposed by internal tank structure, since the vessel had a Type I hull, and the tank contained seven web frames. The relative contribution of these factors to the overall delay is reported in References 2 and 13 in the main body of this report. The time delay of roughly three tank turnovers at the TLV-TWA is consistent with the combined effects of structure and evaporation.

The initial expansion trunk concentration exceeded the UEL that is contained in CHRIS. Roughly 225 minutes were needed to ventilate the tank to an expansion trunk concentration equal to the TLV-TWA.

Tank 2P was cleaned at the same time as 2S. Both tanks received equal washing and ventilating times. The tank hatches remained open for roughly 18 hours following ventilation. At that time, the following gasoline concentrations were measured at the open expansion trunk.

<u>Tank No.</u>	<u>Concentration (ppm)</u>
2P	540-1180
2S	145-285

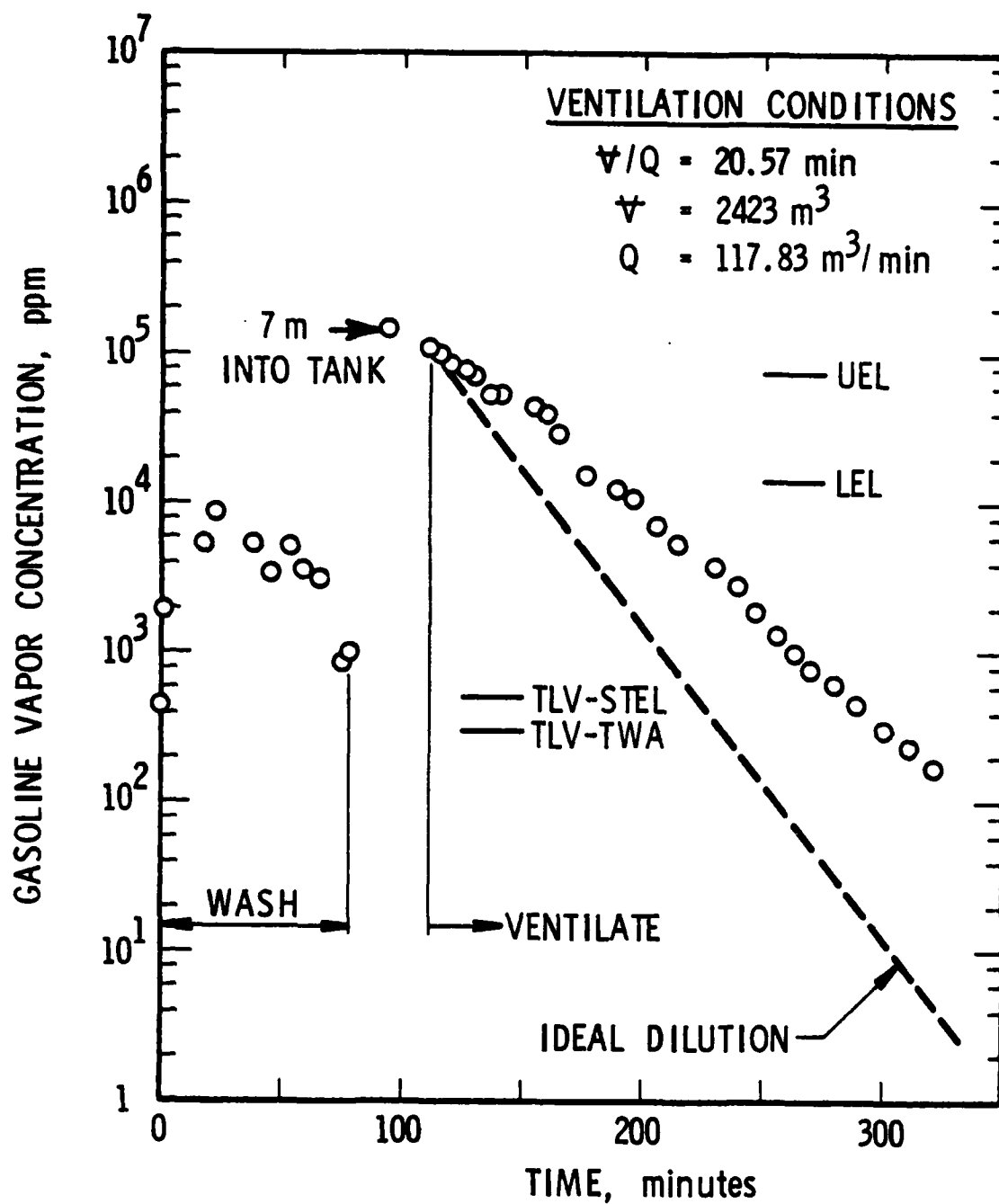


FIGURE 4. CONCENTRATION OF REGULAR GASOLINE VAPOR
 DISCHARGED DURING WASHING AND GAS FREEING
 OF TANK 2S

The tanks were then closed for five hours and then reopened. The expansion trunk concentrations were as follows.

<u>Tank No.</u>	<u>Concentration (ppm)</u>
2P	1950-2900
2S	220-285

Both tanks exhibited the anticipated rise in concentration with time after cleaning that results from (1) equilibration of the tank atmosphere, (2) evaporation of any cargo from tank bottom residues, and (3) evaporation of product that may be trapped by tank coatings. The rise was minimal in Tank 2S, which is characteristic of an efficient cleaning operation. By comparison, the rise in concentration for Tank 2P was quite pronounced. The blower pitch and water throughput on Tank 2P were observed to be lower than on 2S. This would have resulted in a lower blower flow rate, less efficient gas freeing operation, and elevated tank concentrations.

Figure 5 illustrates the gas freeing curve for Tank 4S. The differences between the gas freeing for Tanks 2S and 4S include the following points.

- o An interrupted ventilation process;
- o The initial gas freeing concentration on Tank 4S is roughly an order of magnitude less than the initial concentration on Tank 2S. This lower initial value may have resulted from (1) a 6- to 8-hour period between end of wash and beginning of ventilation, and (2) perhaps a more efficient washing and stripping of the tank heels. The separation period between washing and ventilating on Tank 4S may have been sufficient to permit vapor discharge by diffusion through the open expansion trunk and Butterworth openings.
- o The blower on-time to produce a TWA-TLV concentration was roughly 90 minutes as compared to 200 minutes for Tank 2S. The tanks are of comparable size with the flow rate on Tank 4S being approximately 12% greater than on Tank 2S.
- o The vapor discharge from Tank 4S was in the explosive range for about 12 minutes as compared to 55 minutes for Tank 2S.

The gas freeing history for Tank 4S also exhibits a time delay with respect to the ideal dilution curve; the contributing factors were discussed above.

IV. Tank Cleaning Work Scenario

The Chief Mate has responsibility for all tank cleaning. Because of this responsibility, he was present during the cleaning of seven tanks with the exception of a 4-hour navigation watch. The work unit consisted of the C/M, an A/B, and an O/S. The A/B's and the O/S's rotated watches with their counterparts so that no individual A/B or O/S was present continually during tank cleaning.

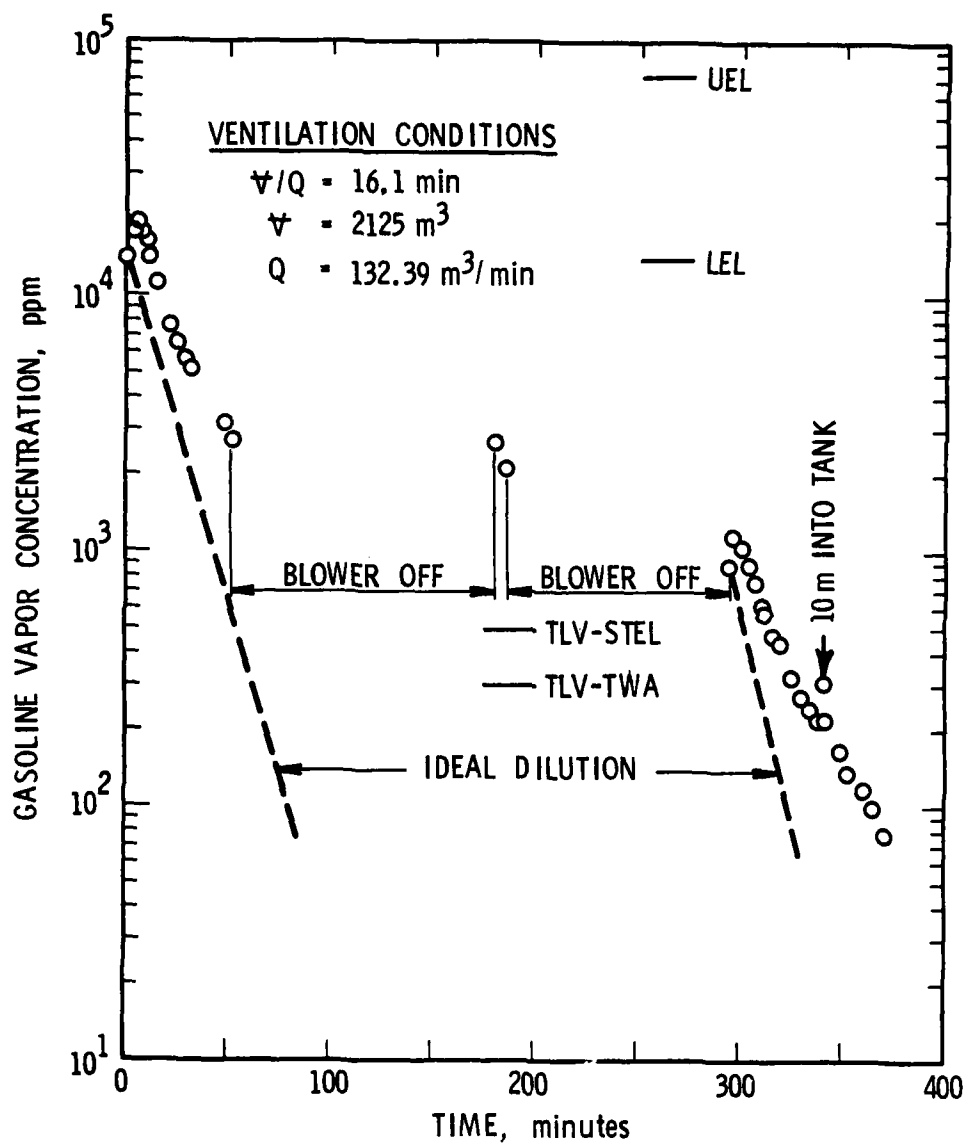


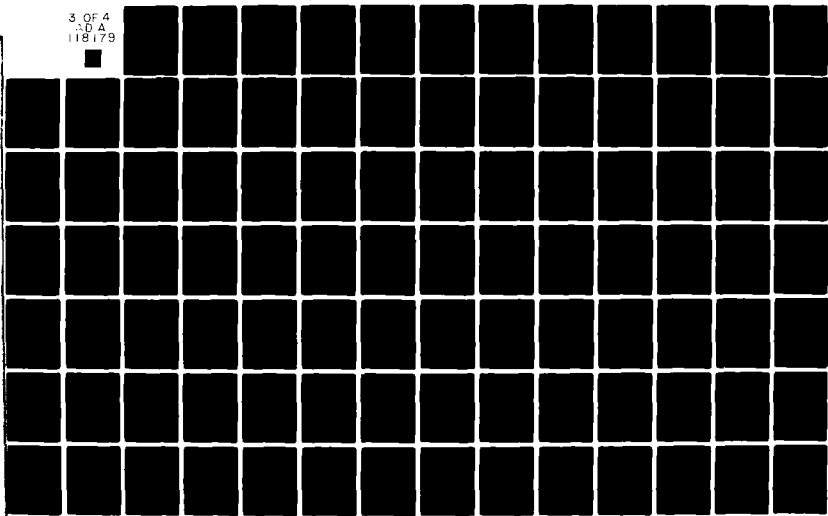
FIGURE 5. CONCENTRATION OF UNLEADED GASOLINE VAPOR DISCHARGED DURING GAS FREEING OF TANK 4S

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The tank cleaning operation can be characterized by major work tasks, but the duration and frequency of the elements of these work tasks may vary in a random fashion. The following scenario is a composite of the work activities that were observed during the tank cleaning period.

- o The initial activity involved hookup of the water hoses to the main supply line and the washing head. The blower was positioned near the Butterworth opening that would be used.
- o The expansion trunk hatch was opened, as was the Butterworth opening for the first drop of the washing machine.
- o The wash water was then turned on.
- o At this point, the Chief Mate's position was at the open expansion trunk. The other two members of the work crew may man the deck valve that controls pump discharge, or one member may be on that valve with the other member on the water supply valve.
- o During the initial stages of washing, it is important to balance the water inflow rate with the water discharge rate to yield a liquid free surface level on the tank bottom slightly above the inlet of the product discharge nozzle. If the liquid surface is too high, the pump will remove only water since the gasoline rides on the water surface. If the liquid level is too low, the pump may cavitate and lose suction head.
- o To achieve this balancing, the C/M used a flashlight (night) or mirror (day) at the open-expansion trunk to view the location of the liquid surface. This viewing was accomplished, generally, with the neck resting on the expansion trunk rim and the head over the open trunk. He remained in this position for two to three minutes, during which time he gave hand signals to the A/B and O/S to indicate the amount and direction of movement of deck valve or water supply valve. The C/M may alternate between two tanks being washed, spending two to three minutes viewing into each tank trunk. The time duration between successive viewings is a random variable that is governed by his experience, the distance between tanks, and the indicated need for additional balancing.
- o Characterization of the C/M exposure presents some practical problems. Lapel-mounted samplers are an approximation to the breathing zone. With his head in the indicated position, the sampler is outside of the expansion trunk and is not exposed to the breathing zone atmosphere. Shirts are frequently not worn during warm weather, and this presents an additional monitoring problem. These considerations are important because the total vapor concentrations are significant during washing.
- o After the water balance had been set, the three crew members worked together to lower the washing head according to the washing plan and switch the head to the next deck opening for the second drop.
- o During the intermediate stages of washing a tank, there is considerably less emphasis on viewing the liquid surface

- through the expansion trunk. The work crew stood upwind of the expansion trunk during this time.
- o Toward the end of washing, the viewing frequency increases, but viewing duration decreases. This increased activity by the C/M is needed to ensure that the maximum amount of liquid is stripped from the tank before gas freeing is initiated. A portion of this activity was conducted after the wash water was turned off. Viewing durations ranged from 22 seconds to 70 seconds, with an average of 54 seconds. In between viewings, the C/M may take charge of discharge valve adjustments.
 - o The A/B and O/S normally do not take part in the tank viewing activity. Their potential for high concentration exposure is reduced significantly. Their low level exposure is dictated by whether the deck valves are downwind or upwind of the expansion trunk.
 - o At the conclusion of washing, the C/M, A/B, and O/S remove the washing hoses, install the blower in a deck opening, attach the water hose to the blower, and turn the water on.
 - o After ventilation is initiated, the three-man work crew may begin a washing operation on another tank. The above description of work activities would be applicable to all tank washings.
 - o The C/M continues his intank observation during ventilation. He assumes the previously described position at the expansion trunk or he lays on the deck to view through an open Butterworth plate using a flashlight or mirror. The purpose of this viewing is to observe the status of the residual liquid and the state of dryness of the tank walls. The frequency and duration did not appear to be predictable. In one instance, four viewings were conducted within a five-minute period, with an average viewing time of 39 seconds. Earlier, three viewings were conducted in roughly two minutes with an average viewing time of 20 seconds.
 - o The potential for exposure during these viewings is greatest during the initial stages of ventilation.

V. Occupational Exposures

One occupational exposure sample was collected during each of the two tank cleaning activity periods. The charcoal tube samples were analyzed for benzene content, and the results are summarized below.

<u>Sample No.*</u>	<u>Sampling Rate (ℓ/min.)</u>	<u>Sampling Time (min.)</u>	<u>Concentration (ppm)</u>
SB-14	0.187	89	3.6
SB-20	0.196	387	1.6

* Chief Mate

TANK ENTRY

2

Tanks were entered on two occasions. Three tanks were entered during the docking to change the Plimsoll marks. Two tanks were entered the next day at sea.

Upon docking, a Marine Chemist boarded the ship and tested the atmosphere in Tank Nos. 2P, 2C, 2S, 3C, 4P, 4C, and 4S, which had been either washed and ventilated or deballasted at sea. Testing consisted of in-tank measurements of O₂ level and % LEL (as methane) using a combination oxygen meter and explosimeter and a drop that was inserted into the tank through the open expansion trunk. A gas free certificate was issued for these tanks, and it covered the following minimum conditions.

- o O₂ $\geq$ 19.5%
- o Toxic materials are within permissible concentrations.
- o Residues are not capable of producing toxic materials under existing atmospheric conditions.

Two SwRI personnel accompanied three ship's personnel into Tank Nos. 3C, 2C, and 2S. The purpose of the entry was to inspect the condition of tank coatings. OVA surveys were made of the tank atmospheres and an active charcoal tube dosimeter was worn by one of the SwRI project team members. The duration of each inspection and elapsed time between entries is given below. The dosimeter pump was turned off between entries.

<u>Tank No.</u>	<u>Inspection Time (min.)</u>	<u>Pump Off Time (min.)</u>
3C	45	
2C	22	4
2S	<u>15</u>	5
82 min. total sample time		

The results of the in-port tank inspections are as follows. All concentrations are referenced to breathing zone height unless otherwise specified.

Tank 3C

- o Gasoline vapor concentrations measured with OVA
 - First level into tank = 390 ppm
 - Second level into tank = 355 ppm
 - Tank bottom = 395 ppm
 - Above wet spot on floor = 430 ppm
 - Deposits on web frames = 660 ppm
- o O₂ concentration = 20.8%
- o Deck blower not operating during first 15 minutes of entry

- o Mate on deck for tank safety watch

Tank 2C

- o Gasoline vapor concentrations measured with OVA
First level down = 300 ppm
Second level down = 320 ppm
Tank bottom = 355 ppm
Above wet spot on floor = 1600 ppm
Above wet spot after disturbing it = greater than 4200 ppm
Behind loose chip of coating material on wall = greater than 4200 ppm
Deposits on hand rail = greater than 4200 ppm

- o O₂ concentration = 20.8%

Tank 2S

- o No one on deck for safety watch
- o Deck blower not operating
- o O₂ concentration = 20.8%
- o Gasoline vapor concentrations measured with OVA
First level down = 110 ppm
Second level down = 118 ppm
Tank bottom = 220 ppm
Mud on bottom = 1150 ppm

The following data apply to the personal dosimeter that was worn by SwRI.

- o Sampling time = 82 min.
- o Sampling rate = 0.203 l/min.
- o Adsorbent = charcoal tube
- o Concentration of benzene in gasoline vapor = 3.8 ppm

Tank Nos. 4P and 4S were entered by three crewmen at sea to inspect tank coatings and sweep up debris that had accumulated between the web frames. The results of these tank entries are given below. An occupational exposure sample was terminated due to pump failure. Vapor concentrations are referenced to breathing zone height unless otherwise specified.

Tank 4P

- o Deck blower on
- o Air rescue pack on deck

- o Safety watch on deck
- o Walkie-talkie in tank
- o Gasoline vapor concentrations measured with OVA
 - First level down = 70 ppm
 - Second level down = 85 ppm
 - Tank bottom = 70 to 100 ppm
 - Debris in bucket = 145 - 285 ppm with peaks to 880 ppm
 - Beneath pile of debris = greater than 4200 ppm. These piles existed mostly in the aft end of the tank near the loading/discharge drop.

Tank 4S

- o Gasoline vapor concentrations measured with OVA
 - Forward bays between web frames = 26 - 41 ppm
 - Directly above debris bucket = 145 - 285 ppm
 - Directly above coating chip pile = 285 - 355 ppm
 - Directly above rust pile aft end of tank near inlet to loading/discharge line = greater than 4200 ppm

The vapor monitor that was worn by an SwRI employee during entry of Tanks 2C, 2S, and 3C was analyzed for benzene content, and the results are summarized below.

<u>Sample No.</u>	<u>Sampling Rate (ℓ/min.)</u>	<u>Sampling Time (min.)</u>	<u>Concentration (ppm)</u>
SB-30	0.203	82	3.8

ADDITIONAL OBSERVATIONS

- o Vapor Regeneration in an Empty Tank
- o Tank Breathing
- o Discharge of Ballast at Sea

I. Vapor Regeneration in an Empty Tank

Residual product may remain in the pores of tank coating materials, in cracks of the coating material or in the silt deposits on the tank floor after the tank has been washed, ballasted, deballasted, and gas freed. An experiment was conducted to determine the rise in vapor concentration that results from evaporation of this residual cargo after the empty tank had received this treatment and had been sealed for a period of time.

As indicated in other sections of this document, Tank 3C had been treated as outlined above. During tank entry, the measured gasoline vapor concentrations ranged from 355 to 395 ppm in the bulk of the tank atmosphere with excursions to 660 ppm directly above deposits on structural members. All tank access openings were then closed in preparation for undocking, and the tank remained closed for 45 hours. At the end of this time, the tank was opened, and vapor samples were extracted from several vertical locations within the tank and analyzed on the OVA. The results are tabulated below.

<u>Distance Below Top of Expansion Trunk (ft)</u>	<u>Gasoline Vapor Concentration (ppm)</u>
0	220-940
15	1140
30	1140
45	1140

The oxygen content of each sample was also determined; its value was 20.8% at each location.

II. Tank Breathing

All tank expansion trunks were equipped with individual pressure relief valves that were set to release at 1.0 psig overpressure in the ullage space. Assuming that the tank is perfectly sealed, then the ullage space pressure could increase above this level as a result of (1) deck heating of the ullage volume, and/or (2) heating of the bulk cargo (increased water temperature) with increased surface evaporation. Alternately, if there is imperfect seating of hatch covers, ullage caps, Butterworth plates, and gauging tube covers, vapors could be released from the tank with ullage overpressures only slightly above atmospheric, but less than 1.0 psig, in which case the relief valve would not be actuated. It is also conceivable that liquid sloshing could generate localized pressures that could permit seat leaks, but the pressure would not be sufficient to actuate the relief valve.

Two classes of vapor release were observed on nearly full product tanks.

- Category I: Vapor release at seat leaks. Pressure buildup possibly caused by combinations of above factors.
- Category II: Vapor discharge at pressure relief valve.

Category I vapor releases were observed on Tank Nos. 6C and 2C. The release at Tank 6C was more or less continuous at the ullage port seat, and concentrations ranged from 11.6% to 18.7% v/v. The concentrations at the dome cover seat on Tank 2C varied between 26.2% to 36.3% v/v. The release at Tank 2C was not continuous; the tank appeared to inhale and exhale with a period of 3.4 to 5.8 seconds between successive exhales. The periodic nature of the discharge suggests that the release may have been associated with liquid sloshing.

Category II releases were observed on 3P and 3S. The vapors were discharged through the pressure relief valve, but the releases were continuous rather than periodic or intermittent. Vapor release time was 28.4 minutes on 3P and 66.7 minutes on 3S. Concentrations were not monitored.

III. Discharge of Ballast at Sea

The product/water residues generated during tank washing were pumped to a slop tank that also served as a normal product tank. Slops, also called dirty ballast, were carried aboard the vessel until the 50-mile limit was approached. They were then pumped overboard through the loading/discharge manifolds. Initially, the pumping rate was sufficient for the discharge stream to clear the side of the ship. The pumping rate decreased as the hydrostatic head of the slops also decreased. The result was that a considerable amount of the slops no longer cleared the vessel, but impinged on the deck. At this point, the valve on the discharge side of the pump was closed so that the pump could build up a discharge head. When the valve was opened, the slops again cleared the vessel, but soon the liquids began to impinge on the deck.

As the liquid struck the deck, retainer flanges on the deck prevented the slops from flowing over the side of the vessel. Because the vessel was bow-up in the ballast condition, the slops accumulated at the aft end of the deck and covered a sizeable area. Crew members going to or from the deck house passed by and sometimes walked through the dirty ballast, which contained a layer of gasoline that floated on the water surface.

APPENDIX F

BACKGROUND VOYAGE REPORT - PARCEL CHEMICAL TANKER

- o Vessel and Cargo Description
- o Engine Room
- o Deckhouse
- o Deck Department
- o Product Loading
- o Product Discharge
- o Ballasting
- o Tank Cleaning
- o Tank Entry
- o Miscellaneous Observations
- o Additional Observations

VESSEL AND CARGO DESCRIPTION

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I. Vessel Description

I.1 Dimensions

Length Overall - 660 ft (approximate)
Length between perpendiculars - 630 ft
Beam, molded - 90 ft
Depth - 49 ft (approximate)

I.2 Tonnage - 38,000 (approximate)

I.3 Propulsion - 15,000 hp. Steam Turbine

I.4 Cargo Tanks

Total of 27 tanks as shown in Figure 1. These include 12 wing tanks, 2 large center tanks and 4 center tanks that have been divided up into from 2 to 4 separate smaller tanks. Two of the 27 tanks (3CA, 6CA) contain double bottoms.

I.5 Cargo Pumps

Cargo can be off-loaded by 16 deep well pumps that are located on the ship's deck directly above the tanks they service. They are dedicated pumps driven by electric motors ranging in horsepower of 100-125 and capacities of 1286-1500 bbl/hr. The deep well pumps service such products as chemicals, lube oils and oil solvents.

The vessel also has a pumproom that contains 6 other main cargo pumps; five centrifugal and one steam reciprocating. Three of the five centrifugal pumps are steam driven and two have electric motor drives. Horsepower and capacities range from 385 to 600 hp and 4000 to 6857 bbl/hr. These pumps service the larger tanks that carry various grades of gasoline. The steam reciprocating pump is the only dedicated pump located in the pumproom. It services tank 6CA and has a capacity of 1000 bbl/hr.

These 22 main cargo pumps are assisted by 16 stripping pumps. Fourteen of the 16 are submersible air driven pumps with small capacities ranging from 21-29 bbl/hr. They are located within the tanks they serve. The two other stripping pumps are housed in the pumproom and service the remaining tanks. Their type and capacities are similar to the 6CA main cargo pump.

I.6 Cargo Loading Method

Twenty-six of the 27 tanks are open loaded. One of the tanks (3CA), which normally carries the chemical, epichlorohydrin (EPC), is closed loaded.

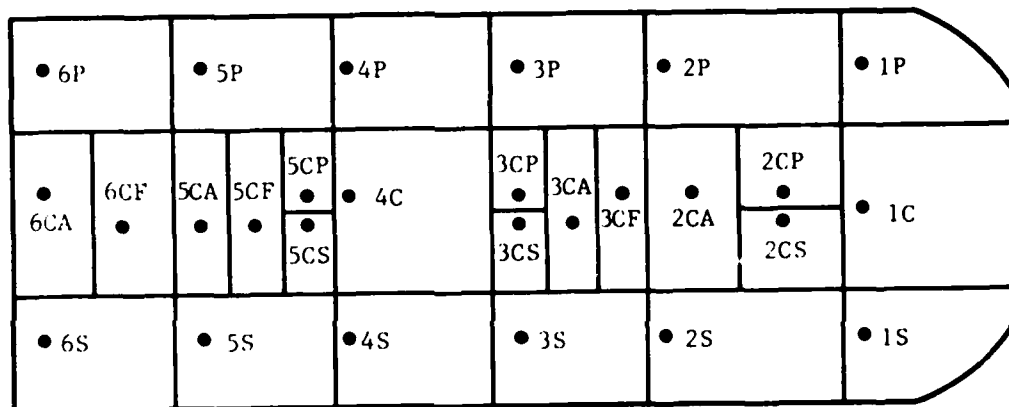


FIGURE 1. TANK SEGREGATION OF CHEMICAL TANKER

I.7 Cargo Gauging Method

Restricted gauging using Lufkin tape through standpipes that originate approximately 1 foot from tank bottom and extend about 2 feet above deck.

Closed gauging is used on Tank 3CA when EPC is being loaded. Ullage readings on 3CA are taken at a closed gauging device located on deck and from an automatic gauging sensor with remote readout in the ship's office.

I.8 Vapor Venting System

Vapors exhausted during loading from 26 of the 27 tanks are vented through ullage ports and open P/V valves. During loading, flame screens are in place over the ullage ports. P/V valves extend off of the tank expansion trunks at an elevation of 7 feet above deck.

The venting of tank 3CA, when EPC is loaded, is through vent piping that extends off the expansion trunk and discharges at a height of 30 feet above deck level (EPC is a hazardous chemical which, by Coast Guard regulation, requires the vent height be B/3).

I.9 Tank Cleaning Method

The majority of the tanks are first washed with water using a rotating type portable washing nozzle. Tank ventilation is accomplished either by air driven Coppus blowers which are mounted on deck butterworth openings or steam eductors which are set atop the tank standpipes.

I.10 Expansion Trunk Layout

The expansion trunks for the 27 ship tanks are signified by the dots shown in Figure 1.

I.11 Ballast Configuration

1P, 1S, 4C, 6P, and 6S are used as ballast tanks on the return voyage.

Two other tanks located aft of the six wings are also used for ballast and contain fresh water for tank cleaning. These tanks are located directly below the forward end of the deckhouse. The fresh water ballast tanks also act as a cofferdam space between the cargo tanks and the engine room. The access ports for man entry into these tanks are located inside the deckhouse.

II. Cargo Description

The types of cargoes carried during the voyage consisted of pure chemicals, gasolines, oil solvents and lube oil as shown in Table I.

TABLE I. LOADING PLAN

Tank No.	Cargo	Quantity
1P	AV Gas 100	(1) 50,000 (Total of 1P,1S,5P,5S)
1C	Super Unleaded Gasoline	(2) 76,136 (Total of 1C,4C,6P,6S)
1S	AV Gas 100	(1)
2P	Solvent 140	8,000
2CP	Tolusol 5	4,040
2CS	Cyclosol 53	3,530
2CA	MEK (Methyl Ethyl Ketone)	7,100
2S	Xylene	5,540
3P	EAL (190) (Ethanol)	10,000
3CF	EGL (Ethylene Glycol)	6,425
3CA	EPC (Epichlorohydrin)	2,410
3CP	EAL (190)	6,635
3CS	BAN (N-Butyl Alcohol)	6,600
3S	EAL (200)	11,712
4P	VM & P (Solvent)	10,800
4C	Super Unleaded Gasoline	(2)
4S	Solvent 340	10,000
5P	AV Gas 100	(1)
5CP	MVI 200	6,500
5CS	MVI 700	6,500
5CF	Bright Stock	13,200
5CA	HVI 100 TQ	8,800
5S	AV Gas 100	(1)
6P	Super Unleaded Gasoline	(2)
6CF	HVI 250 TQ	15,000
6CA	Empty	---
6S	Super Unleaded Gasoline	(2)

When the ship reached the loading port, where SwRI personnel were to board and commence the planned observation cruise, the vessel was already laden with cargo that had been loaded at two previous ports. The condition of the ship tanks was as follows:

150,000 barrels of SSU in Tank 1P,1C,1S,5P,5S,6P, and 6S
 6,425 barrels of Ethylene Glycol in Tank 3CF
 6,635 barrels of EAL (190) in Tank 3CP
 11,712 barrels of EAL (200) in Tank 3S

All other tanks empty.

The first operation that occurred at the observation loading port was the discharge of about one-half of the SSU from 1P, 1S, 5P and 5S. Following the discharge, loading of the other cargoes noted in Table I were carried out. These cargoes were subsequently discharged at two different ports on the East Coast.

ENGINE ROOM

I. Propulsion System - 15,000 hp steam turbine

II. Engine Room Personnel

Of the ship's 34 crewmen, 12 personnel comprise the engine room's staff. Five of the personnel are licensed and include the chief engineer, one first and second assistant engineers, and two third assistant engineers. The chief engineer and first assistant are considered day workers (8-5) and do not stand specific watches. The remaining assistant engineers, however, do stand typical 4 hour watches (4 on, 8 off). During each of the watches the assistant engineers each have an unlicensed personnel, called an engineman, that assists them in carrying out their specific watch duties. Cleanliness and house keeping of the engine room is the responsibility of the wiper, who is also a day worker.

Assisting the chief engineer and first assistant engineer during their daily work routine are engine room cadets. The cadets are individuals who have completed a specific amount of course work at one of the maritime colleges and are obtaining on-the-job training for their engineer's license.

The last individual listed under the engine room staff is the pumpman. As a result of the observation of the duties and work assignments of the pumpman, it appeared that it would be more appropriate to have him listed with deck crew. During the whole course of the round trip voyage, the pumpman was not observed in the engine room at all, but rather on deck working with the deck crew.

III. Assigned Responsibilities:

III.1 Chief Engineer

- o The chief engineer is the head of the engine room and is responsible for all technical aspects of the entire vessel.
- o Determines and schedules the specific work activities to be done during day work and delegates activities to first assistant.
- o Most of his time is spent in handling paper work such as purchase requisitions for parts and equipment and book-keeping of engine room personnel time sheets of regular and overtime work.
- o Normal work time is 8-5.

III.2 First Assistant Engineer

- o Supervises all day work activities which includes maintenance of ship's equipment.

- o Responsible for maneuvering ship from sea buoy to dock.
- o Normal work time is 8-5.

III.3 Second Assistant Engineer

- o Primary responsibility for maintenance of the ship's boilers.
- o Blowing of ship's boiler tubes (normally done during his watch once a day).
- o Care and treatment of boiler water.
- o Responsible for loading of fuel oil.
- o Fuel oil systems.
- o Stands (4-8) watch.

III.4 Third Assistant Engineer

- o Primary responsibility for the evaporation system for fresh water to boiler and potable water.
- o Addition of chemicals to evaporators to prevent scale building up.
- o Assist in maintaining electrical systems and generators.
- o Stands (8-12) watch.

III.5 Third Assistant Engineer

- o Primary responsibility for maintenance of lube oil system.
- o Change out of filter and oil as required.
- o Lubrication of main reduction gear.
- o Assist in maintaining electrical systems with 8-12 third assistant.
- o Stands (12-4) watch.

III.6 Engineman (Three)

- o Stands watch with respective assistant engineer.
- o Makes complete rounds of systems recording all temperature and pressure once each hour during watch.

- o Is stationed at control panel when not making rounds.
- o Stands a 4 hour watch.

III.7 Wiper

- o Responsible for cleanliness of engine room.
- o Clean walkways and handrail.
- o General cleanup as required depending on maintenance performed during day work.
- o Normal work time is 8-5.

III.8 Pumpman

- o Primary responsibilities for maintenance of all cargo and tank cleaning pumps.
- o Checks and maintains pump seals for all pumps.
- o Greasing of all valves on deck.
- o Is usually assisted by unlicensed deck crew.
- o Checks for proper connection of dock-to-ship loading hoses at loading and discharge port.
- o Opens tanks discharge valves and starts up pumps for discharge of product at the supervision of the mate on watch.
- o Handles tank ballasting at request of mate on watch.
- o Assists in gauging of tanks during discharge.
- o Normal work time is 8-5.

III.9 Cadets

- o Works with first assistant performing maintenance on equipment in engine room.
- o Normal work time is 8-5.

IV. Watch Schedule

A typical watch consisted of one assistant engineer and one engine-man standing a 4 on, 8 off rotating watch. Once every hour, each would conduct inspection rounds of the engine room equipment while the other

had to be near the control panel. It is the specific duty of the engineman to tabulate temperature and pressures of all operating equipment during his inspection rounds. No maintenance is performed by these personnel while they are on watch. Required maintenance is usually conducted during overtime or while in port. Approximately 75% of the time is spent near the control panel.

V. Typical Maintenance and Repair Activities

V.1 In Port (Regular Watch, Day Work, and Overtime)

- o Replace bearing on air compressor servicing Coppus blower.
- o Weld flange on new relief valve for tank cleaning pump.
- o Replace air filter on ventilation air inlet to living spaces.
- o Change out lube oil purifier filters.
- o Inspect main reduction gear and fill lubricating oil supply tank.
- o Clean walkways and stairway.

V.2 At Sea (Day Work and Overtime)

- o Water wash and ventilate one of the main fuel oil tanks in preparation for dry dock repair.
- o Scrape and paint walls in steering gear room.
- o Inspect and repair electrical wiring.
- o Scrape and paint interior hull on control panel level.
- o Replace seal on fresh water port ballast tank pump.
- o Oil port side cabin ventilation blower motor.

VI. Engine Room Ventilation System

Ventilation air was provided to the engine room by four fans each having a capacity of 33,000 cfm. These fans were located atop the 3rd level of the deckhouse directly behind the wheelhouse. Two of the fans, located at the forward end of the 3rd level, supplied air to the engine room through ducting and discharged the air from numerous outlets on each of the engine room levels. The other two fans, located at the aft end, exhausted the air outside. Each of the exhaust fans outlets were missing a disc seal which was to prevent downward discharge onto the 3rd

level roof. Consequently, some recirculation of exhaust air back into the engine room was occurring.

Within the engine room and located near the top level were two large blowers which provided air to the boiler burner assembly. Supply air for these blowers was obtained from an inlet located in between the supply and exhaust fan.

VII. Emission Inventory

The following tasks were performed to determine sources of hydrocarbon vapors and asbestos/oil mist emissions within the engine room and assess personnel occupational exposures.

- o Discussions with assistant engineers and engine-man on watch to identify what equipment or operations during the voyage produced noticeable emissions.
- o Walk-through survey of all levels of the engine room by SwRI personnel to inspect for visible deposits of particulates, oil mist and vapor odors.
- o OVA walk-through survey to determine the hydrocarbon background level.
- o Area sampling for oil mist and particulate (asbestos).

Informal discussions with the ship's two third assistant engineers, as well as with other engine room crew, suggested that the only time hydrocarbon vapors could be detected was during tank cleaning operations on the ballast leg of some voyages. As a result of the open ventilation system of the engine room and given the right wind conditions (bow to stern) vapor discharge during gas freeing of the cargo tanks could be injected into the engine room. No particular type of equipment in the engine room could be singled out as producing more vapors (odor) than another. In regard to oil mist, one possible source was identified by the engine room crew as the lube oil vent for the main reduction gear (MCR). This vent was located on the same level as the control panel. No mention of airborne particulates was noted.

All levels of the engine room were surveyed by SwRI Personnel to visually inspect for oil mist or asbestos. Oil mist was confirmed to be emitting from the vent pan of the MCR. Other locations where oil deposits were noted were in the area of the lube oil purification system and drip pans located beneath the air compressors and the boiler air-feed blowers. Handrails and walkways around these areas showed signs of oil on them. Although there was no visible particulates in the air, small pieces of the asbestos insulation were noticed on the flooring beneath some of the insulated piping. In general, most of the insulation was still intact. However, worn and cracked insulation was observed on the steam turbine piping.

During the visual survey of the engine room, total hydrocarbon vapor levels were measured using the Century System Organic Vapor Analyzer (OVA). Numerous surveys with the OVA were made during all phases of the voyage. The typical readings were found to be between 6 and 8 ppm as methane. A typical survey of the engine room and the hydrocarbon concentrations measured is shown in Table II. During the course of the voyage, a maximum variation of 2-3 ppm, both below and above those noted in Table II, were observed. The high levels, which were anticipated during the ballast leg of the voyage (during tank clean) failed to materialize since the prevailing wind direction was from port to starboard.

TABLE II. ENGINE ROOM VAPOR CONCENTRATIONS
(as ppm Methane)

Level	Location	Concentration
I	Motor drivers for cargo pumps in pumproom, main reduction gear, and propeller shaft.	7-8
II	High and low pressure turbine, evaporator, air compressors.	7-7.4
III	Control panel, boiler fuel oil tanks, vent pan for MCR, machine shop.	6-6.8
IV	Boiler uptake.	6
V & VI	Air blowers for boiler burner assembly.	7

To assist in assessing the exposure of the engine room personnel to oil mist and asbestos, a total of 8 area samples were collected using Millipore filter cassettes and an MSA model "S" sampling pump. The sampling flowrate was approximately 1.5 liter/min. Seven samples were analyzed for oil mist and five were analyzed for asbestos particles. The sample number and areas sampled are shown below.

<u>Sample No.</u>	<u>Location</u>
D9, D16	near main reduction gear vent (2 samples)
D1	at the control panel desk during 1600-2000 watch
D5	at the control panel desk during 1200-1600 watch

D10 at the control panel desk overlap of 1200-1600
and 1600-2000 watches

D3 near the lube oil purifier and main reduction
gear

D2 on walkway near boiler uptake

D19 next to low pressure steam turbine insulated piping

The NIOSH method No. P & CAM 239* was used to analyze the 0.8 μ mixed esters of cellulose filter for asbestos. The results of the sampling are shown below. The concentrations noted are fibers/cc for asbestos fibers greater than 5 μ .

Sample No.	Concentration (Fibers/cc)	Sample Duration (min)
D1	0.0032	225
D2	0	218
D5	0	226
D10	0.01	271
D19	0	222

The same filter material was used in collecting oil mist samples. The samples were analyzed by Fourier Transform Infrared Analysis (FTIR). The results of the analysis are shown below. Concentration of oil mist is expressed in mg/m³ as mineral oil.

Sample No.	Concentration (mg/m ³)	Sample Duration (min)
D1	0.43	225
D2	0.58	218
D3	0.73	223
D5	0.63	226
D9	4.10	180
D10	0.63	271
D16	1.62	253

*100 field counted at 500x on phase contrast microscope. Microscope field area was 0.004 mm²

DECKHOUSE

I. Deckhouse Configuration

The deckhouse was separated into five levels. The first level, at the same elevation as the ship deck, housed the unlicensed engine room and deck personnel. A large fire extinguishing foam supply tank complete with necessary pump was situated at the center of the deckhouse on this level at forward end. On each side of the foam tank and next to the forward wall were oval shaped openings which provided access to the two port and starboard fresh water ballast tanks. The fresh water ballast tanks were directly below the first level of the deckhouse and act as a cofferdam between the engine room and the 6P and 6S cargo tanks.

The officer's and crew's mess room and lounges were located on the second level along with the galley. Quarters for the bosun, chief cook, pumpman, and pilot, were also on the second level. SwRI personnel were housed in the pilot's quarters. The third level housed the licensed engine room and deck crew personnel. The captain's quarters and the radio room were located on the fourth level and the wheelhouse was located on the fifth level.

Access to the first and second levels was available through doors located on the port and starboard sides or at the aft end of the deckhouse. The remaining levels also contained at least one entry point from the outside.

II. Deckhouse Ventilation

Two separate ventilation systems provide conditioned air to the deckhouse. One system serviced the galley and operated open to the atmosphere. The supply and exhaust fans for the galley were located on top of the third level roof, one on each side of the base of the ship's stack. The other system, which provided ventilation air for the remaining part of the deckhouse living quarters, could operate either open to the atmosphere or in a closed recirculating mode. During the voyage, this system operated with fresh air supply louvers closed.

The heating and cooling units were located within the third level at the aft end of the deckhouse. Conditioned air discharged into all levels of the deckhouse with the exception of the wheelhouse and returned through two wall grills located on the third level.

The non-recirculating design of the galley ventilation system can permit ambient air to be discharged into the deckhouse. Consequently, any chemical vapors venting from the cargo tanks could infiltrate the galley and become recirculated into the other living spaces in the deckhouse. Discussions with the crew pointed out that odors of chemicals have been detected primarily during the ballast voyage when tanks were being cleaned and ventilated. However, during the SwRI observation cruise, no noticeable increase in hydrocarbon background was noted inside the deckhouse during the ballast voyage.

III. Deckhouse Environment

Total hydrocarbon vapor concentration was measured inside the deckhouse with a Century Systems Model 128 Organic Vapor Analyzer (OVA) to assess the infiltration of chemical vapors. These surveys were conducted during each leg of the voyage at all five levels of the deckhouse. Figure 2 illustrates the hallway locations where the measurements were made. The actual readings are tabulated in Table III.

With the exception of the laden voyage No. 1 and tank ballasting No. 2, no abnormal hydrocarbon levels were seen in the deckhouse. Although companion measurements made on deck during the same time showed levels between 50-200 ppm on deck, the prevailing wind direction dispersed the vapors away from the deckhouse. The source of high readings obtained during the laden voyage No. 1 were found to be from an internal rather than an external source. As shown in Table III, the highest readings were measured on the first level at point D. This location is aft of the fill piping for the fresh water ballast tanks. The actual source originated from an unbolted flange on the filling line for the port fresh water ballast tank. OVA measurements at the flange produced off scale reading on the OVA that were made using a 25 to 1 diluter probe (i.e. the concentration at the source was greater than 25000 ppm as methane).

The mate on watch was notified and the leak was fixed within a few hours, but not before the hydrocarbon reading in the SwRI quarters on the second level (between location A and B) had reached 70 ppm. During the next day, however, another OVA survey was made that resulted in much lower readings between 4-7 ppm. This concentration typified the deckhouse environment during the remainder of the laden voyage.

The reason that the fresh water ballast tank contained hydrocarbon gas was due to leakage of gasoline product from the adjacent 6P tank through the tank wall. The leaked gasoline product floated to the top of the water in the ballast tank and evaporated into the vapor space. Exactly why the filling line flange was unbolted allowing the gasoline vapors to vent out in the deckhouse was not determined. However, under the same condition with the flange properly bolted, the abnormally high hydrocarbon level in the deckhouse would probably have never been seen. It was mentioned that the bulkhead leak would be repaired after the completion of this voyage since the ship was going into dry dock for its biennial inspection and repair.

Above normal hydrocarbon levels were also obtained in the deckhouse during ballasting operations performed at the first discharge port. The tanks being ballasted were the 6P and 6S tanks. The first readings were made on the second level of the deckhouse. After traversing the second level, the SwRI personnel went outside to confirm high concentrations near the intake of the galley supply fan. Measurements around the supply fan of 50-300 ppm as methane were obtained. However, within minutes the concentration had dropped to approximately 10 ppm. The sudden drop resulted because the ballasting operations had ceased. Another deckhouse

survey was made and the hydrocarbon background was back to normal as shown in Table III.

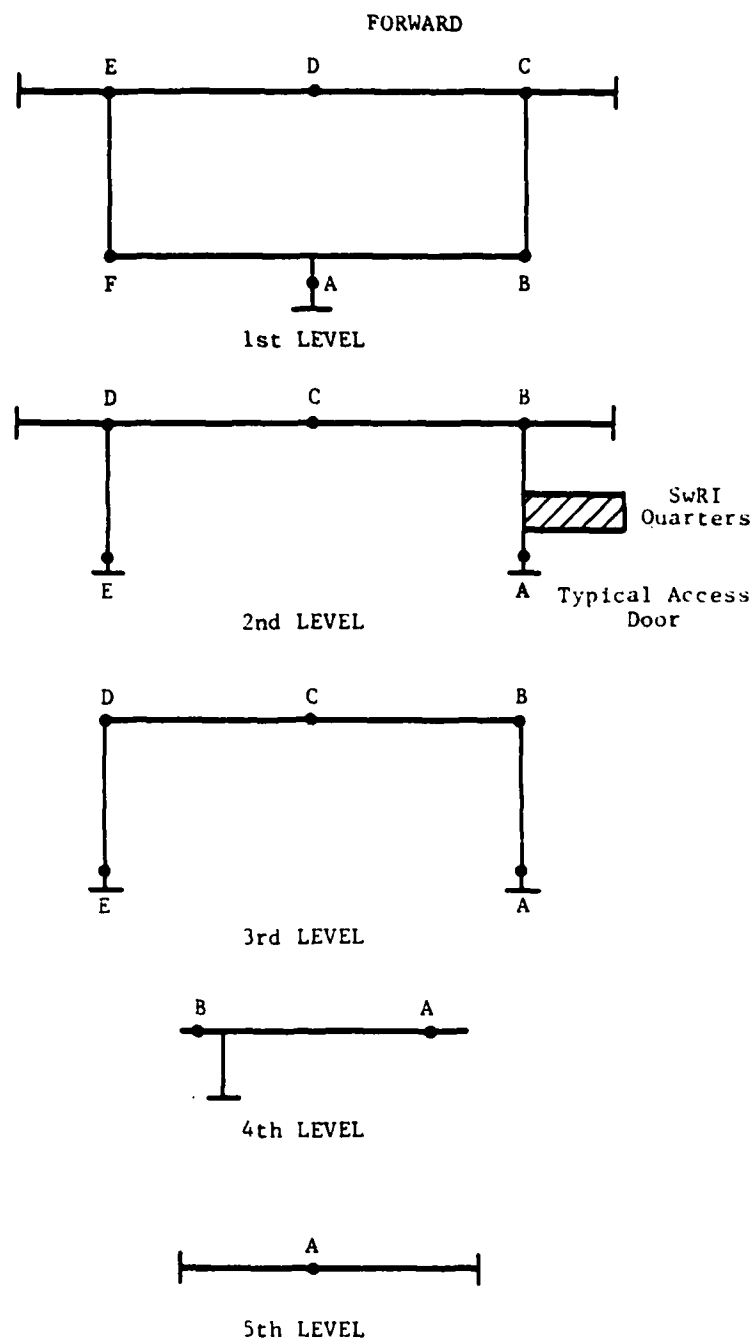


FIGURE 2. OVA SURVEY LOCATIONS INSIDE DECKHOUSE OF CHEMICAL TANKER OR TANKSHIP.

TABLE III. TOTAL HYDROCARBON *READING IN DECKHOUSE DURING EACH LEG OF THE VOYAGE

DECKHOUSE LEVEL	LOCATION	LOADING	LAIDEN No. 1	DISCHARGE No. 1	BALLASTING DURING	DISCHARGE No. 2	BALLAST VOYAGE (TANK CLEANING)
1	A	5-7	4	4-5	6-7	5-6	1-5
	B		11				
	C		12				
	D		50-100				
	E		14				
	F		15				
2	A		4		14		
	B		22		16		
	C		22		16-20		
	D		13		30-40		
	E		6				
3	A		5				
	B		10				
	C		10		10		
	D		11				
	E		6				
4	A		8				
	B		8				
5	A		7				

*Expressed as ppm methane
 1 Refer to Figure 1

DECK DEPARTMENT

I. Deck Department Personnel and Responsibilities

The deck department was comprised of four licensed and ten unlicensed crewmen. The four licensed crewmen included one chief mate, one second mate and two third mates. Of the ten unlicensed crewmen there were three quartermasters (QM), three able-bodied seamen (AB), three ordinary seamen (OS) and one bosun. Although the pumpman is a member of the engine room department, his work station was observed to be primarily on-deck with the deck crew. With the exception of the chief mate, bosun, and pumpman, who were day workers (8-5), all deck crewmen stood a normal 4 hour on, 8 hour off watch.

Each of the deck crew personnel have specific responsibilities that are assigned to them. Listed below is a summary of the responsibilities pertaining to each of the personnel in the deck department.

I.1 Chief Mate

- o Head of the deck department.
- o Determines daily work tasks that need to be performed on deck.
- o Decides cargo loading and discharging plan and tank ballasting ullages.
- o Coordinates the daily work activities with the bosun.
- o Responsible for maintenance and operation of all safety equipment on board.
- o Certifies tanks to be safe for man entry using ship's safety equipment.
- o Determines tank cleaning requirement and schedules.
- o Maintains regular and overtime records for deck crew.
- o Primary responsibility for all cargo transfer and handling.
- o Normal work time - 8-5.

I.2 Second Mate

- o Works under direction of chief mate.
- o Responsible for supervising docking and undocking at the forward mooring stations under the authority of the master.

- o Updates navigation charts.
- o Navigates the ship at sea during his watch.
- o Responsible for gauging tanks during loading, discharging and ballasting during port watch.
- o Responsible for maintenance of lifeboats.
- o Supervises quartermaster standing watch with him while ship is in transit.
- o Does not participate in deck work activity while ship is underway.
- o Stands the 4-8 watch.

I.3 Third Mate (Two)

- o One 3rd mate is responsible for supervising docking and undocking at the after mooring stations under the authority of the Master.
- o Stands 4 hour navigation watch at sea with quartermaster.
- o Responsible for gauging tanks during cargo transfer operation while in port during his watch hours.
- o Maintains navigation charts during at-sea watch.
- o Does not participate in any deck work activities while ship is underway.

I.4 Bosun

- o Works under direction of chief mate.
- o Coordinates with chief mate the necessary deck work maintenance required.
- o Responsible for upkeep of all deck equipment such as winches, mooring lines and tank washing and ventilation equipment.
- o Supervises all deck work activities of QM, AB and OS while ship is in transit.
- o Does not participate in cargo transfer activities while ship is in port.
- o Day worker - 8-5.

I.5 Quartermaster (Three)

- o At sea, assists mate on watch in maneuvering of ship.
- o In port, stands deck watch during cargo transfer operations to assist mate on watch to open or close tank cargo valves, and occasionally gauge tanks.
- o Operates ship's booms for picking up stores from dock.
- o Only participation in deck work at sea is performed on overtime and not during regular hours.
- o On deck work at sea consists of painting or scraping of deck surfaces, man entry to muck tank, ready hoses and equipment for tank washing and ventilation, and assist in repair of deck equipment.

I.6 Ablebodied Seamen (Three)

- o Stands bow watch at sea during his night watch hours.
- o Relieves QM in wheelhouse for 30 minute break during both day and night watches at sea.
- o Assists in taking on stores while in port.
- o Stands deck watch in port to assist mate on watch during cargo transfer operations.
- o During day watch at sea, he participates in the same work activities as QM.

I.7 Ordinary Seamen (Three)

- o Stands night watch, at sea, in crew's mess for any assistance needed by mate in wheelhouse.
- o Relieves AB on bow watch at night for 30 minute break.
- o 8-12, OS performs housekeeping duties on 2nd level of deckhouse during day watch at sea.
- o 12-4 and 4-8, OS participates in deck work activities at sea as noted for QM.
- o Stands deck watch, in port, ready to assist mate on watch during cargo transfer operations.

II. Work Schedule

The observed hourly work schedules of the deck crew varied between licensed and unlicensed crewmen and also depended on what leg of the voyage the ship was on.

As mentioned previously, the chief mate's regular hours were 8-5. Except for operations occurring upon arrival in port and during the ballast leg of the voyage (tank cleaning), the chief mate's work responsibilities were usually accomplished within an 8 hour work day. In-port operations such as docking and undocking and coordination of loading or discharging hose hook up were activities that extended the chief mate's normal 8 hour work day to approximately 16 hours. During the ballast voyage when tank cleaning was performed, the chief mate was observed to work, on some days, for as much as 15 hours straight (0800-2300). The necessity for putting in long hours during this particular ballast voyage may have been exaggerated since all tanks had to be cleaned to prepare the ship for dry dock and repairs. The typical tank cleaning schedule for a normal ballast voyage may significantly reduce the chief mate's work schedule.

The other licensed crewmen (second and third mates) worked a strict 4 on, 8 off schedule while the ship was in transit (laden and ballast leg). However, in port, they were observed to extend their normal watch hours due to docking and undocking operations and occasional shift exchange for free time in port. Also, while the ship is in port one of the mates has to stand a day watch (0900-1700) in addition to his normal watch hours. The day watch duty rotates between each of the three mates. During the loading observation, the second mate was observed working in a total of 16 hours straight since it was his turn for day watch.

The unlicensed crewmen (QM, AB and OS) were observed to put in extra overtime during the laden and ballast legs. Most of them averaged from two to four hours overtime during the laden voyage. The types of work performed other than their normal watch duties included painting and scraping the deck surface and repair of tank washing machines. During the ballast voyage, overtime hours increase to six hours due to the extensive tank cleaning that had to be performed during this voyage. During cargo loading and discharge the unlicensed crewmen worked the standard 4 on, 8 off routine except when one would work another's watch to allow him free time in port.

The bosun and the pumpman kept to a normal 8 hour day during the laden voyage. However, during the ballast voyage, their overtime was equal to that mentioned for the chief mate. Other activities requiring the bosun to work overtime were readying of mooring lines and operating the ship's winch during docking and undocking. The pumpman was observed to put in numerous hours at the discharge port. His responsibility in operating the cargo pumps for cargo discharging and tank ballasting resulted in a 24 hour work period.

III. Deck Work Activities During the Voyage

During the voyage on the chemical tanker, SwRI personnel recorded various activities that were performed by the deck crew. It should be noted that the activities shown for Days 1 through 4 do not reflect those typical during the laden voyage. Normal work tasks of scraping and painting ship's surface, repair of equipment, and greasing of valves were not performed. Instead, the crew was readying those tanks or spaces to be cleaned and gas freed in preparation for dry dock repairs after the ballast voyage.

- Day 1
 - o Set up Coppus blower on forward ballast tank
 - o Gas free forward ballast tank
- Day 2
 - o Paint surfaces around forward locker
 - o Gas free forward ballast tank
- Day 3
 - o Move stripping and water hoses aft from bow locker storage
 - o Muck and clean pumproom bilge
 - o Muck and clean forward ballast tank
 - o Repair portable washing machine
 - o Connect elephant trunk vent ducting to fresh water ballast tank access in deckhouse
- Day 4
 - o Gas free fresh water ballast tank
 - o Scrape and paint forward loading manifold valves
 - o Withdrawing tank product sample from ullage port
 - o All hands on deck for docking at first discharge port
 - o Normal watches during cargo discharge
 - o All hands on deck for undocking
- Day 5
 - o Moving tank cleaning equipment to vicinity of first cargo tanks to be washed and gas freed.
- Day 6
 - o All hands on deck for docking
 - o Normal watches during cargo discharge
 - o Ballasting of 6P, 6S and 4C
 - o All hands on deck for undocking
- Day 7
 - o Setup of tank cleaning equipment on 1P, 1C, 1S tank
 - o Rigging of discharge piping to loading manifold to discharge wash water over deck railing
 - o Washing and gas freeing of 1P, 1C, 1S
 - o Setup of tank cleaning equipment on lube oil tanks 5CP, 5CS, 5CF, 5CA
 - o Tank washing of 5CP, 5CS, 5CF, 5CA
- Day 8
 - o Washing and gas freeing of 2S, 4S, 4P, 3CP
 - o Re-gas freeing and stripping of 2S tank
 - o Washing and gas freeing of 2CA, 3CP
 - o Man entry into 3S and 3P to position eductor lines

- Day 9
 - o Hot water wash and ventilation of 3CF, 3CA and 3CP
 - o Replace all tank washing equipment into storage locker
- Day 10
 - o All hands on deck for docking up to dry dock

PRODUCT LOADING

I. Loading Work Scenario

The work unit, during cargo loading of a chemical carrier, varied from four to five individuals. During daytime hours (0800-2000 hrs.), the unit is comprised of one mate and three unlicensed seamen (QM, AB, or OS). The three unlicensed crewmen rotated half-hour breaks during their watch so that only two are on deck at any one time. From 1700 hours to 0800 hours, another mate, called a night mate, is added to the watch compliment. This port relief mate is a licensed officer who assists the ship's mate in cargo transfer operations. The night mate was responsible for gauging the tanks aft of the midship loading manifold while the forward tanks were gauged by the ship's mate.

Normally, each of the ship's personnel stand a 4-hour on, 8-hour off watch during loading. However, situations did occur that resulted in extended work periods. It was not uncommon to request for leave whenever the ship docked. Those crewmen, whose hometown was near the loading port, would swap their watch with those who lived near the discharge port. The compliment would be returned when the ship arrived at the discharge port. Another occasion for extended work hours involved only the licensed officers. Each time the ship came into port, one of the mates, other than the chief mate, was required to stand the "day watch" from 0900-1700 hours. The mate on "day watch" is also required to work his normal watch schedule. During product loading, the second mate stood the "day watch," his regular watch, and a 4-hour watch for a third mate who had taken shore leave. This combination resulted in a 16-hour continuous work period.

Prior to the start of loading, blinds are removed from the manifold valves by the unlicensed crewmen. Dock side workers then come aboard and bolt up the loading hoses to the valves. Loading normally does not commence immediately after hoses are connected. Delays can occur due to the unavailability of a shore side pump or a shift change of the dock workers. During this time the unlicensed crewmen station themselves near the gangway. The mate uses this time to become more familiar with the loading plan. When word is received that the dock is ready to start loading, the AB's and OS' position themselves near the manifold loading valve and open the valve slightly. Once flow has started, the mate verifies that the product is flowing into the proper tank by putting his handkerchief over the tank ullage port to observe the outflow of tank vapors. Once this has been determined, the mate signals the AB or OS to open the valve to the maximum. One of the unlicensed crewmen withdraws a line sample from a sample valve located between the product valve and the loading hose. This scenario is repeated until all tanks have commenced loading. From this time until a tank nears completion, the unlicensed crewmen will move away from the loading manifold to a place near the gangway. The mate, on the other hand, starts the routine of gauging the tanks.

The mate will initially make two or three successive rounds of the tanks he is gauging to determine approximate loading rates and

completion times. The length of time that he stays at one tank to take ullage readings may vary from 20 seconds to 4 minutes. Once he feels secure that the tanks are filling at a predictable rate, the frequency of tank visits are reduced. Table IV illustrates the number and duration of tank gauging performed by the second mate during his watch.

TABLE IV. FREQUENCY AND DURATION OF TANK GAUGING ACTIVITY

Tank No.	Cargo	Tank Gauging Visit/Gauging Time (sec)						Total Time Near Each Tank (sec)
		1	2	3	4	5	6	
1P	Av. Gas 100	20	20					40
1C	Super Un- leaded Gas	10						10
1S	Av. Gas 100	20	20					40
2P	Sol 140	20						20
2CP	Tolusol 5	20	20	20	15			75
2CS	Cyclosol	20	20	20	20	15		95
2CA	MEK	120	10	60	20	15		225
3P	EAL (190)	20	20	240	20	30		330
3CA	EPC	20	20	20	30			90
3CS	BAN	20	40	20	20	120	20	240

The table reflects a total time of 20 minutes spent gauging tanks over a 3 hour period. The remaining time was spent near the loading manifold coordinating the start of product loading with the dock crew as well as break time.

When a tank approached top-off, the mate had one of the unlicensed crewmen man the product loading valve while the other positioned himself so that he was visible to both the mate and the man on the valve. During this time the mate made less frequent visits to the other tanks he had been gauging. The mate would take a few ullage readings in succession and signal to unlicensed crewmen to close down on the valve. The time spent by the mate during top-off ranged from 5 to 10 minutes per tank.

II. Discharge Vapor Concentration Measurements

Vapor concentration measurements were made at the ullage ports of four tanks being loaded with pure chemical. These tanks were 2CA, 3CS, 3P, and 2S. The first three tanks were loaded simultaneously during a 5 hour period. Loading of 2S did not commence until approximately 8 hours after completion of the three tanks.

Due to the short loading time, coupled with a misinterpretation of the start of loading, complete vent concentration time histories were not obtained for tanks 2CA, 3CS, and 3P. Table V, however, illustrates the measurements that were made on these tanks.

TABLE V. VAPOR DISCHARGE CONCENTRATION DURING LOADING

Tank Number	Chemical	Time	Ullage	Concentration ppm	% of Final Ullage
2CA	MEK	1620	52' 0"	NM	0
		1819	23' 4"	9488	74
		1900	13' 1"	NM	100
3CS	BAN	1730	52' 0"	NM	0
		1830	35' 9"	114	30
		1945	15' 0"	174	70
		2030	1' 0"	NM	100
3P	EAL (190)	1735	52' 0"	NM	0
		1836	42' 5"	776	22
		1933	31' 6"	1568	46
		1942	29' 4"	1656	52
		2135	8' 4"	NM	100
NM = Not Measured					

Inspection of tank cleaning records from the previous ballast voyage indicate that these tanks had been cleaned and gas freed. The vapor discharge concentrations shown in Table V, appear to confirm this since an untreated tank would have resulted in much higher discharge concentrations during the early stages of loading. The concentrations measured in each tank also reflect different magnitudes that corresponds to the relative volatility of each chemical being loaded.

The vent concentration for the loading of xylene into tank 2S is shown in Figure 3. Since the nominal depth of the tank was 52 ft, Figure 3 indicates that tank 2S was short-loaded to roughly one-half of its capacity. During the initial stage of loading, the vent concentration increased slowly. During the latter stage, the concentration increased more rapidly, which suggests that a very thick vapor blanket was developing above the liquid.

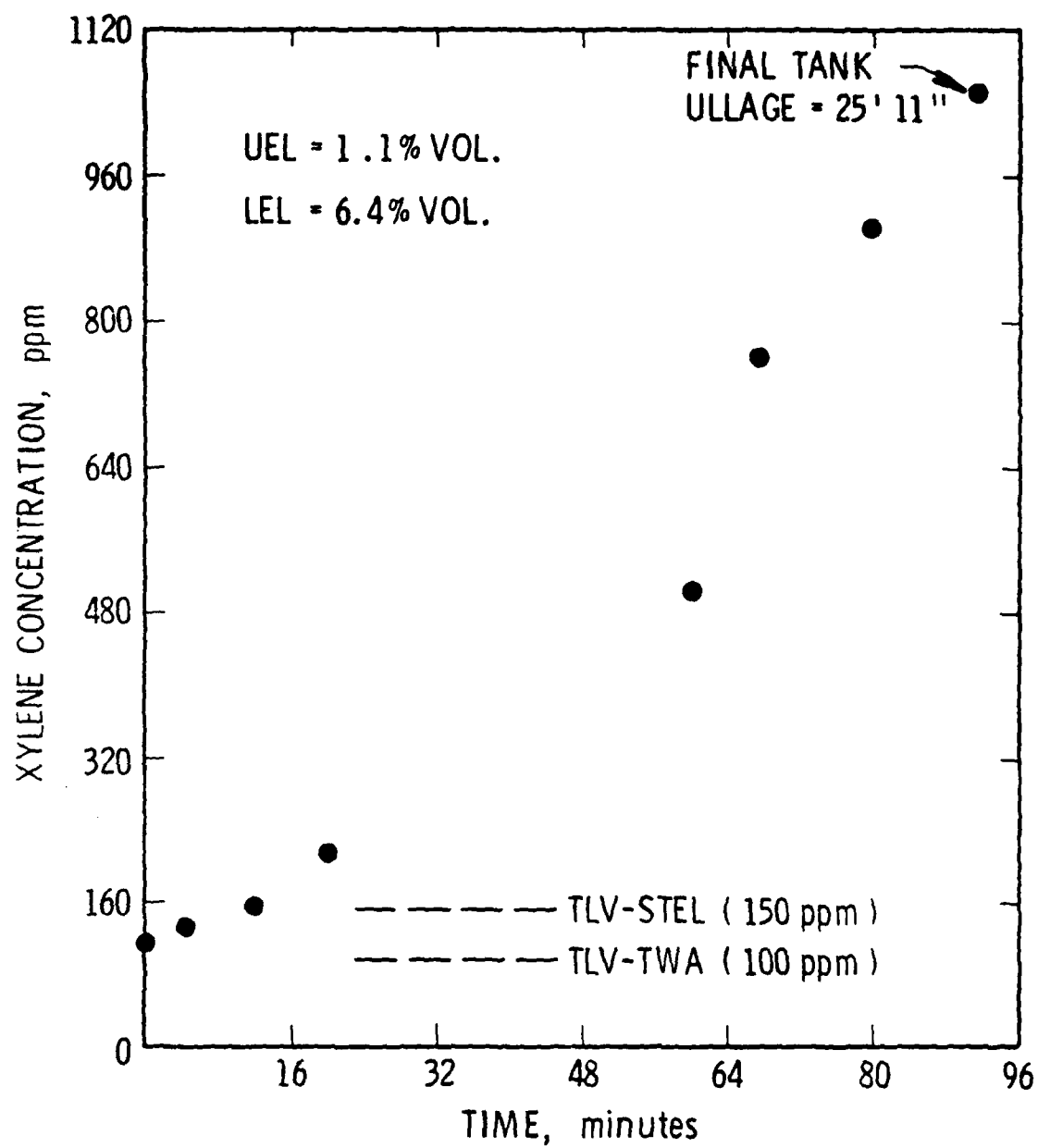


FIGURE 3. VENT DISCHARGE CONCENTRATION DURING LOADING OF TANK 2S WITH XYLENE

III. Occupational Exposures

Three separate exposure samples were collected during the loading of the chemical carrier. Two were personnel samples collected on the second mate while gauging and one was an area sample taken downwind of the EPC (tank 3CA) tank. Passive badge type dosimeter was used in parallel with one of the charcoal tube dosimeters as noted. The results of the sampling are shown below.

Operation	Sample Number	Chemical	Exposure Concentration, ppm	Exposure Duration, min
Restricted Gauging	VF5	{ MEK *EPC EAL	{ 0.92 0.47 0.16	172
Restricted Gauging	VF6 47754	{ +Xylenes	{ 0.28 0.47	106
Area sample downwind of EPC tank at man breathing height	VF4	EPC	0.22	188

*EPC tank was closed loaded and closed gauged

+Parallel sampling on second mate

PRODUCT DISCHARGE

I. Background

SwRI personnel witnessed cargo discharge operations at three different terminals. The first terminal was the same one at which the loading observation was conducted. Since only a small amount of cargo was discharged at this terminal, the test team utilized this time storing their test equipment and becoming familiar with the ship's crew. The description of cargo discharge activities was primarily observed at the second terminal. Essentially, all of the products on board the chemical carrier were discharged at this terminal with the exception of a portion of the VM&P and Av. Gas 100 cargo. These remaining products were off-load at the third and final discharge port.

II. Discharge Work Scenarios

Prior to the ship's arrival at the second discharge port, two activities were observed to be typical in preparation for arrival at the discharge port. One of the activities involved retrieval of a tank sample of each tank. The work group involved in obtaining the sample consisted of the bosun and two unlicensed seamen. Before samples could be retrieved, the tank P/V valves were opened. Once pressure was relieved, the pins on the ullage ports were removed and a quart sample bottle connected with a chain was lowered through the ullage port to withdraw the sample. Dermal exposure was witnessed to occur during this activity. No gloves or protective clothing were worn by the crewmen performing this activity. One particular tank, 6P, which contained unleaded gasoline, was observed to have a tremendous amount of pressure on the tank. The pressure was so high that the vapors venting through the ullage port could be heard on the flying bridge of the deckhouse where one of the SwRI personnel was stationed. It appeared that the crewman was having trouble releasing the pin on the ullage port of 6P. Consequently, he called over the bosun to help him push the lid down to release the pin. After the pin was removed, the tremendous pressure in the tank blew the ullage port open and rocketed the flame screen about 20 feet in the air. The two crewmen appeared dazed for a short period due to the direct contact with the gasoline vapors.

Removal of product loading valve blinds were also performed by the unlicensed seamen at this time. The potential for skin contact with the cargo liquid was greater during this activity than any other operation. The main reason is that primarily pure chemical is in the product load lines. Again, no gloves or protective clothing were worn by the crew when this was performed.

After the ship docked at the discharge terminal, a similar work unit, as was described for loading, was present during discharge. In addition to the mate and unlicensed seamen, one other person who is believed to be the primary individual during discharge became visible. This person was the pumpman. As his name implies, the pumpman is responsible for the care and maintenance of all of the ship's pumps.

While the ship is in transit, he normally worked his standard 8-5 day watch routine. However, during discharge he was observed being on deck a total of 24 consecutive hours for the complete discharge, including ballasting of tanks in preparation for the ballast voyage. The pumpman's duties included start up of all cargo pumps (both deep well and those located in the pumproom), assisting mates in gauging of tanks, and ballasting and gauging of ballast tanks.

The sequence of work activities during discharge is initiated with the hook up of the loading hoses by the dock crew. While this is being performed, one of the dock inspectors comes aboard to obtain tank samples, initial ullage readings and tank temperatures, for each of the product tanks. This activity is accomplished in the presence of the mate on watch. Once the initial readings have been taken, a certain amount of time is required to coordinate the start up of discharge of all products with the shore. With the exception of the lube oil, cargo commencement of discharge of all cargo was underway within 2-1/2 hours after the ship had docked.

As during loading, tank gauging became the dominant work activity once discharging operations were underway. Gauging rounds were performed in the same way as observed for loading. The personnel involved in gauging consisted of the pumpman and the mate. In some cases, the AB on watch was allowed to take ullage measurements. The mate and unlicensed crewmen worked a 4 on, 8 off watch.

As anticipated, the exposure to chemical vapor was expected to be minimal during gauging of discharging tanks. This occurs because of the inflow of fresh air into the tanks as the product level drops. However, significant chemical concentration levels were measured on deck during discharge. The source of the high measurements were traced to a number of leaking drain valves located in various product lines. During product discharge, the line pressure is much higher than during product loading. As opposed to seeing near atmospheric pressures during loading, the product line pressures reach upwards to 100 psig because they are just down stream of the cargo pump discharge. The leaks from the drain valves fall to the deck and form a thin stream which runs aft toward the deckhouse. One of the SwRI personnel mentioned to one of the mates about the leaking drain valve. His statement was that leaks are typical during discharge. To contain them, the mate usually puts a coffee can under the leaking valve.

As tanks are nearing completion of discharge, the frequency of gauging increases. The mate also starts closing down on the product discharge valve to keep from losing suction. As the pressure decreases, the valve is closed more. When no more product can be pumped, the submersible stripping pump is activated to remove the residual.

III. Occupational Exposures

A total of eight exposure samples were collected prior to and

during product discharge operations. Five of the eight were obtained on personnel while performing various activities described previously. The remaining three were area samples taken within the ship's pumproom and at the pumproom exhaust fan which discharged pumproom vapors near the deckhouse area frequently passed by the mates on watch. The pumproom area samples are significant because the pumpman has to periodically descend into the pumproom to check on the condition of the equipment during product discharge. Parallel passive dosimeter samples were also obtained. The results are summarized on the following page.

Operation	Sample Number	Chemical	Exposure Concentration, ppm	Exposure Duration, min
Obtaining tank sample through ullage port	VF10(AB)	{ MFK Xylene	{ 1.21 0.09	{ 13
Predischarge tank ullage and temperature reading, restricted gauging.	VF14(2M)	{ EPC MEK EAL Xylene	{ 0.10 0.09 0.41 0.25	{ 202
Restricted gauging	VF12 (pumpman)	{ EPC MEK EAL Xylene	{ 0.38 0.78 2.76 0.21	{ 110
Restricted gauging	VF18 (3rd Mate)	BAN	4.44	176
Restricted gauging	VF20 (3rd Mate)	{ EPC MEK EAL Xylene	{ 0.12 0.00 0.80 ND	{ 93
Area sample near pumproom exhaust fan discharge (area frequently passed by mate on watch)	VF1 47756 } *	Benzene+	{ 5.23 10.50	{ 208
Area sample at bottom level of pumproom	VF2 47741 } *	Benzene+	{ 4.07 2.0	{ 193
Same as above except after pumproom bilge was mucked clean	VF16	Benzene+	0.02	566

* Parallel active and passive samples

+ From gasoline product

ND - Not detectable

Note: NBA exposures were sacrificed on samples VF14, VF12, and VF20 due to difference in desorption method for various chemicals of interest.

BALLASTING

I. Background

Four tanks on the chemical carrier were ballasted following completion of product discharge. Ballasting was performed at the second discharge terminal. The tanks ballasted were 1C, 4C, 6P, and 6S. Final ullages were recorded for all ballast tanks, except for 1C, and these are shown below.

<u>Tank Number</u>	<u>Final Ballast Ullage</u>
4C	14' 2"
6P	29' 0"
6S	28' 3"

II. Source Vapor Measurements

Vent concentration was measured during the ballasting of tank 4C, 6P, and 6S. Figure 4 shows the concentration time history for 4C. Similar data is plotted for 6S and 6P in Figure 5.

The concentration shown in Figure 4, for tank 4C, represents the vapor measurements taken after ballasting had started. The first data point coincides with a ballast ullage of 22' 9". Tank 6P and 6S were monitored from the start of ballasting. Over the first 110 minutes, a constant discharge concentration was measured in 4C. This reflects a well mixed vapor space in the tank. However, soon after the third data point, a sudden rise in concentration occurred. This behavior usually signifies the presence of the vapor blanket that is constantly expanding by diffusion above the liquid level.

Inspection of tanks 6S and 6P discharge concentrations shown in Figure 5, illustrates an interesting observation. The concentration for 6S stays relatively constant, while 6P shows an erratic but rising concentration. This may be explained by the difference in the ballasting rate of the two tanks. Since 6P (2806 BBL/Hr) has a lower ballast flow rate than 6S (3477 BBL/Hr) there is more time available for the gasoline rich vapor layer to expand by diffusion. Consequently, at about the same ullage level a higher vapor concentration is sensed at the discharge ullage port.

III. Ballasting Work Scenario

The work unit during ballasting is similar to that explained for product discharge. The activities performed consisted of periodic gauging of ballast tanks and preparing for undocking.

The mate and the pumpman performed the gauging rounds. The frequency of gauging is reduced during ballasting in comparison to loading because the exact quantity of ballast is not critical. The pumpman was observed making ullage readings once an hour. The remaining

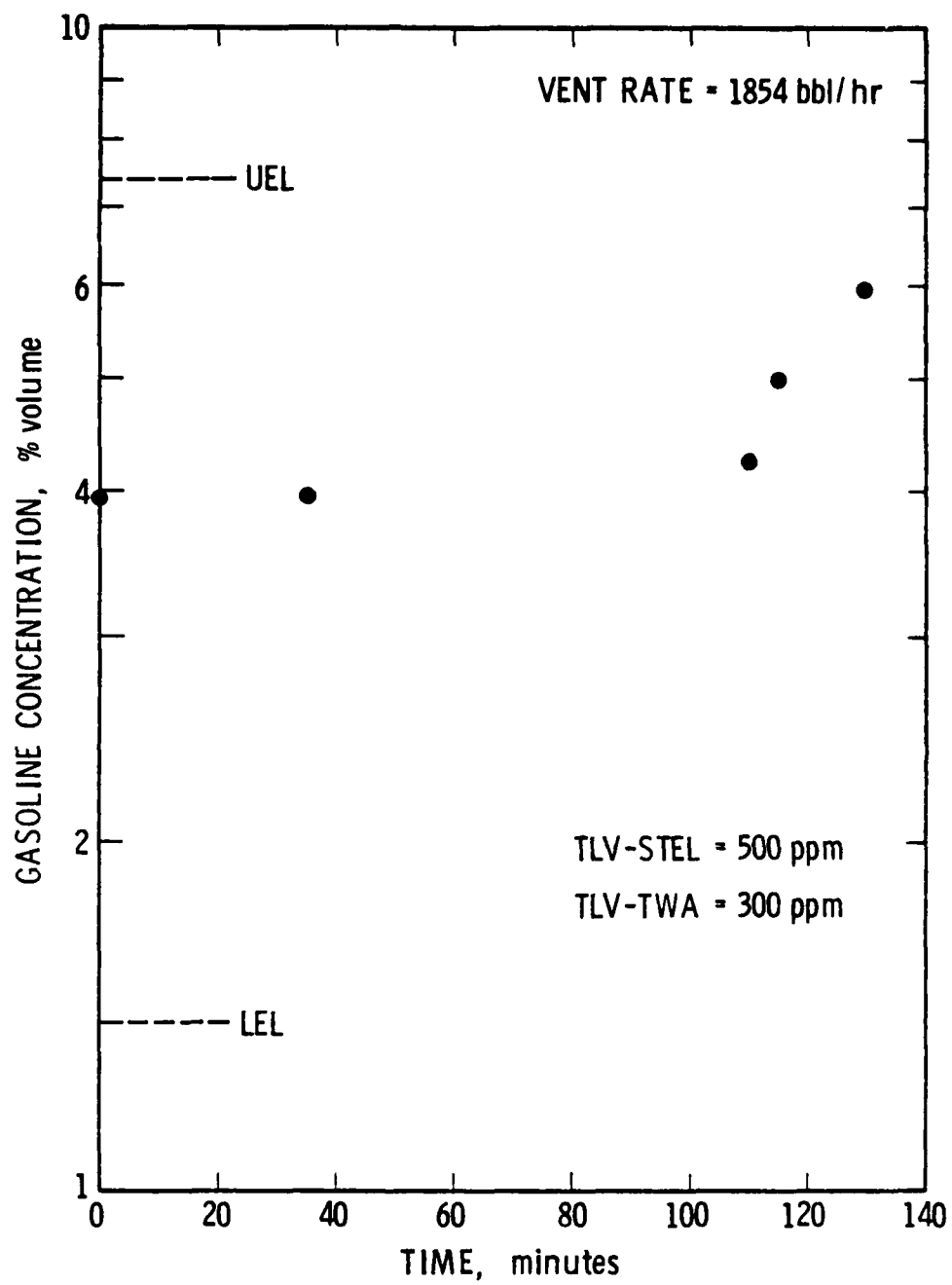


FIGURE 4. VENT DISCHARGE CONCENTRATION DURING BALLASTING OF 4C.

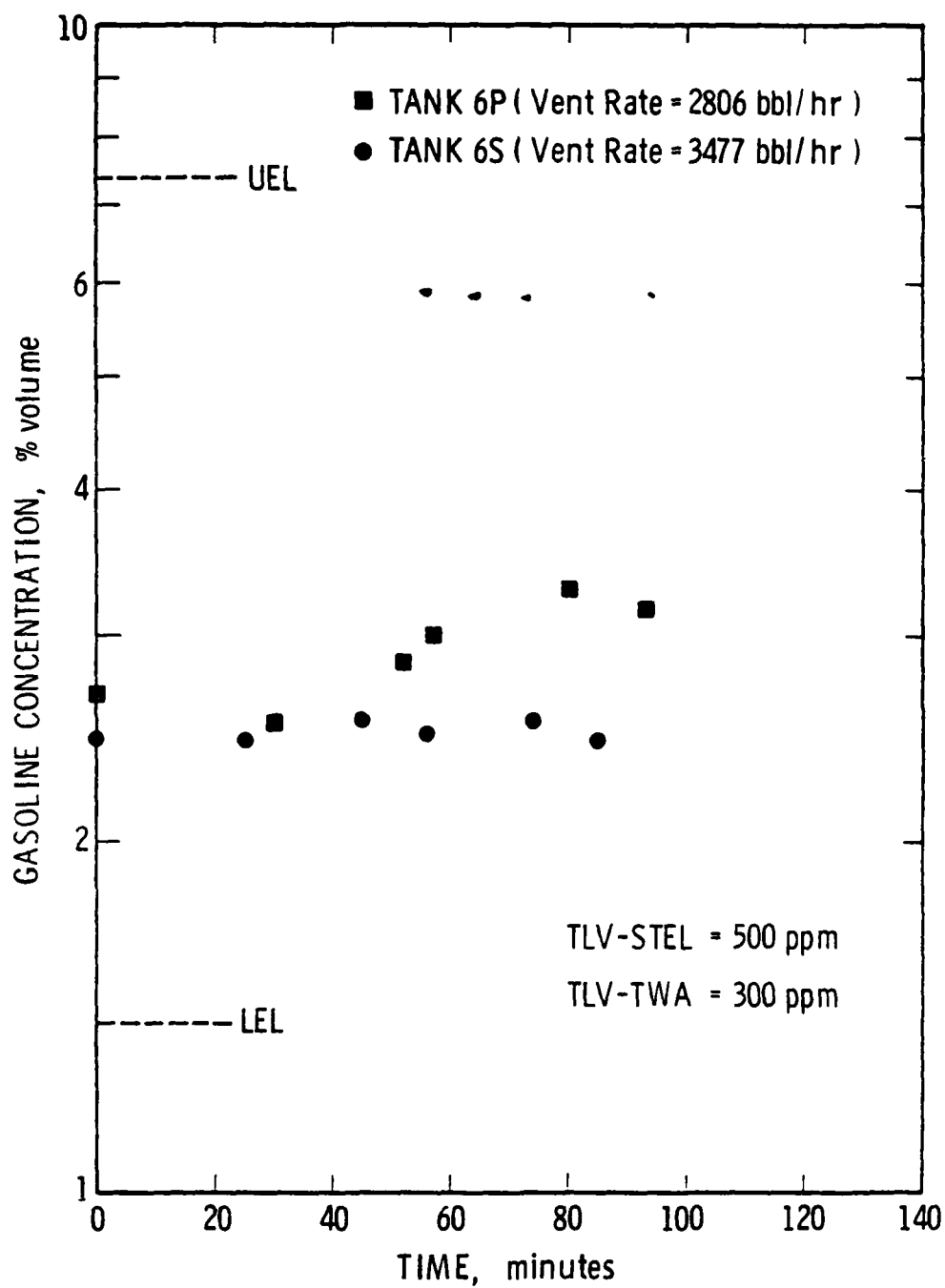


FIGURE 5. VENT DISCHARGE CONCENTRATION DURING BALLASTING OF 6P and 6S.

time was spent resting in the shade or checking the operation of the ballast pump in the pumproom.

The mate also gauged the tanks. In addition, the mate directed the unlicensed crewmen to prepare for undocking. Blinds were put back on to the manifold loading valves. This activity lasted for about one-half hour to one hour depending on the number of people involved. Vapor exposure occurred from evaporation of product leftover in the drip pans. Skin contact was also witnessed whenever a dropped bolt had to be removed from the drip pan. Another activity involved battening down of tank hatches and closing of P/V valves.

IV. Occupational Exposure

One personnel exposure sample was collected on the pumproom during ballasting. The results are shown below.

Operation	Sample Number	Chemical	Exposure Concentration-ppm	Exposure Duration-min
Gauging ballast tanks	VF15	Benzene+	0.14	141

+ From gasoline product

TANK CLEANING

I. Background

From time to time, the cargo tanks on a chemical tanker require cleaning. In most cases, tank cleaning is necessary whenever a different product is loaded into a tank than what was previously carried. Although some tank cleaning is performed in port, the majority is done at sea on the ballast leg of the voyage. Because of the many types of chemicals and petroleum products transported, the marine department of most chemical companies provide the chief mate with the proper tank cleaning procedure for readying a tank for a new cargo.

In addition to preparing a tank for a different product, tank cleaning is also required for man entry for inspection and repair. Such was the case during the SwRI observation cruise. In fact, all tanks on the chemical tanker were cleaned and gas freed in preparation for this ship's biennial inspection as required by Coast Guard regulation.

II. Tank Cleaning Procedure

The bulk of the work performed by the deck crew during the ballast leg of the voyage was spent in washing and gas freeing all cargo tanks. Table VI illustrates the washing procedure scheme used to clean the tanks. All solvent and gasoline product tanks were washed with cold water for a period of 30 minutes with the washing machine left at one level in the tank. Two of the eight chemical tanks containing MEK and xylene were treated in a similar manner. The remaining cargo tanks, with the exception of the ethyl alcohol tanks, were hot water washed at a temperature of 135°F. The ethyl alcohol tanks were not washed but only stripped dry of residual product prior to gas freeing.

Before tank washing commenced on each tank, the bulk of the residual product was stripped out by one of two methods. As noted in the first section of the report, 14 of the 27 tanks contained submersible stripping pumps within them that were used to remove leftover product. The remaining tanks utilized a sea water jet ejector, called a Motivator manufactured by Vita Motivator Company (New York), for stripping operations. The latter device was more cumbersome to work with and required the lowering of long hoses into the tank, usually through the tank gauging standpipe. Product stripping rates from 10 to 15 gpm were obtained when using the Motivator.

Following the stripping operation, tank washing commenced using a Dasic (England) two nozzle rotating portable washing machine. These machines were normally lowered into the tanks through the butterworth opening and left to wash for a period of time at a specific height. The tank size and previous product determined the number of drops required to clean the tank. During the washing cycle, wash water was continually discharged through the product line with the tank cargo pump. It was important to balance the washing rate with the discharge rate for efficient tank washing. After tank washing was complete, the ventilation equipment was started to gas free the tank. Air driven Coppus blowers

TABLE VI. TANK WASH PROCEDURE ON CHEMICAL CARRIER

TANK NUMBER	PREVIOUS PRODUCT	WASH WATER TEMPERATURE	NUMBER OF MACHINES	NUMBER OF DROPS PER MACHINE
1P	Av. Gas	Cold	2	1
1S	Av. Gas	Cold	2	1
1C	Mo. Gas	Cold	4	2
2CP	Solvent	Cold	1	1
2CS	Solvent	Cold	1	1
2CA	MEK	Cold	1	1
2P	Solvent	Cold	1	1
2S	Xylene	Cold	1	1
3S	EAL (200)	THESE TANKS WERE NOT WASHED		
3P	EAL (190)			
3CP	EAL (190)			
3CS	BAN	Hot	1	1
3CF	EGL	Hot	2	1
3CA	EPC	Hot	2	1
4P	Solvent	Cold	1	1
4S	Solvent	Cold	1	1
4C	Mo. Gas	Cold	4	2
5CP	Lube Oil	Hot	2	4
5CS	Lube Oil	Hot	2	4
5CA	Lube Oil	Hot	2	2
5CF	Lube Oil	Hot	4	4
5P	Av. Gas	Cold	2	1
5S	Av. Gas	Cold	2	1
6CF	Av. Gas	Hot	8	2
6CA	Empty	NO WASHING OR GAS FREEING PERFORMED		
6P	Mo. Gas	Cold	2	1
6S	Mo. Gas	Cold	2	1

(C-12) were used on most of the tank. These blowers were set over a butterworth opening that was farthest away from the tank's expansion trunk. For some of the tanks, congested on-deck piping made the butterworth openings inaccessible for blower mounting. Consequently, steam driven Air Jax (New Jersey) exhaustor eductors were used. The eductors were mounted upon the top of the tank gauging standpipes. In this setup, fresh air entered the tank through the expansion trunk and displaced the tank vapors from the tank bottom up and out through the standpipe.

III. Tank Cleaning Experiments

A total of five tank cleaning experiments were performed during tank cleaning operations on the ballast leg of the SwRI observation voyage. Two of the five tanks (2CA, 2S) tested were washed and gas freed while the other three tanks (3P, 3S and 3CP) were gas freed without being water washed. Due to a misunderstanding of start time of washing on the 2CA and 2S tanks, vapor concentration measurements were not obtained during washing. Consequently, only tank vapor concentration time histories were measured during the gas freeing phase of the tank cleaning process.

Figure 6 illustrates the discharge concentration measured during ventilation of tank 2S. The previous cargo carried in the tank was xylene, a relatively water insoluble chemical. Two separate ventilation periods were required to gas free the tank. During the first period, a rapid increase in the concentration occurred initially, followed by a substantial drop down to a level of approximately 500 ppm. Comparison of the experimental data with the theoretical dilution curve illustrates the characteristic time delay caused by the evaporation of chemical from the residual liquid layer at the bottom of the tank. Further tank ventilation past 60 minutes did not reduce the concentration. It is theorized that during this time, the evaporation of chemical was equal to the rate of vapor discharge. This condition usually occurs when a tank is ventilated in the presence of a thick layer of pure chemical in which a constant surface area is maintained. Analysis of a wash water sample, taken prior to gas freeing, confirmed that the water was super saturated with xylene forming an immiscible liquid mixture.

Approximately 24 hours later, gas freeing of tank 2S was resumed. A similar steady concentration was measured for a period of 90 minutes during the second ventilation period. At this time, arrangements were made to have a Motivator stripping line lowered to the tank bottom to remove more of the residual chemical/wash water liquid. Immediately after tank stripping was started, a decrease in tank vapor concentration was observed. From Figure 6 the rate of concentration decrease was significantly lower during the second period as compared to the first period, which is attributed to the lower ventilation flow rate.

The tank vapor concentration time history measured at the tank hatch during the ventilation of tank 2CA is shown in Figure 7. Although MEK is more volatile than xylene, a significantly lower MEK initial

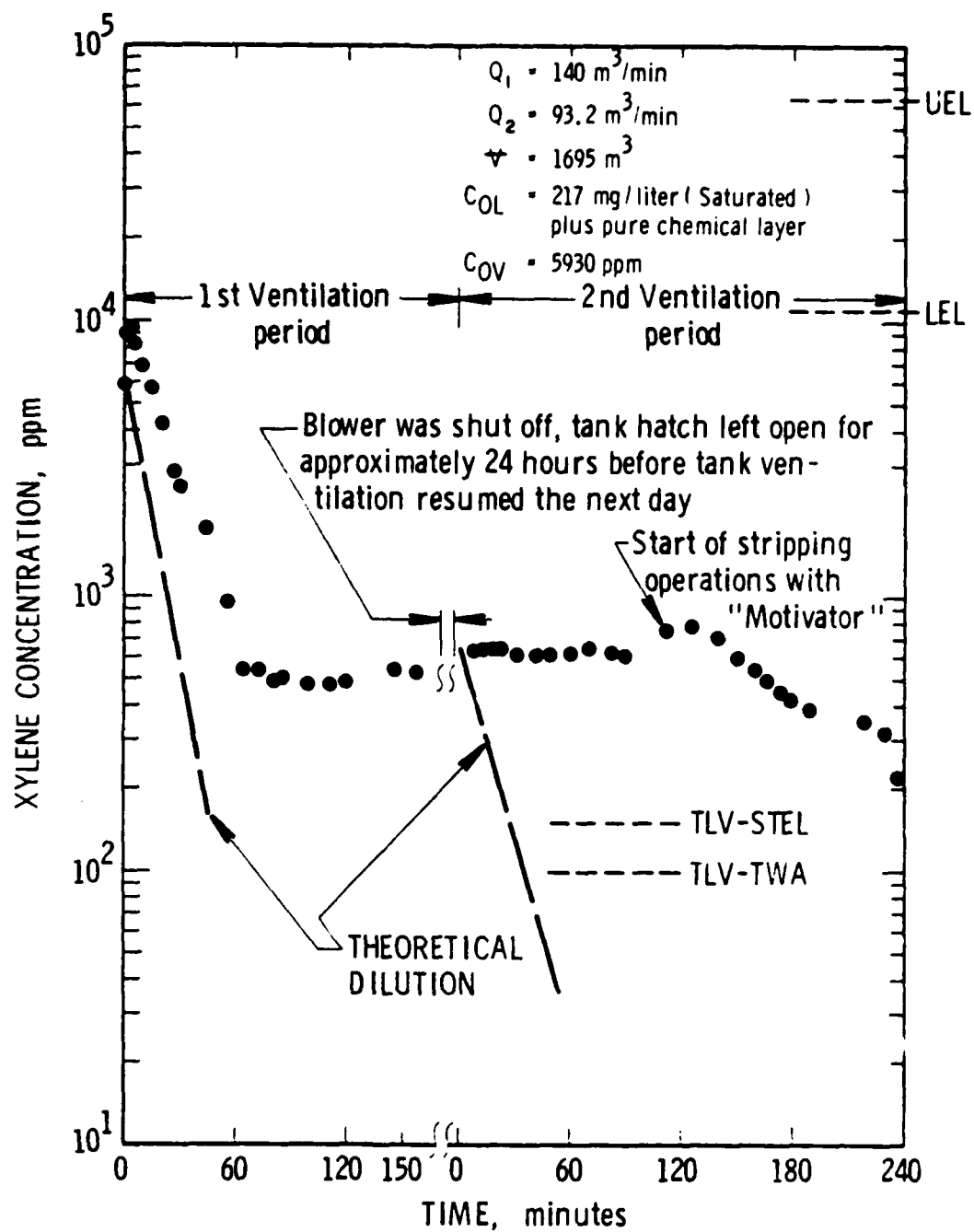


FIGURE 6. TANK VENTILATION OF 2S

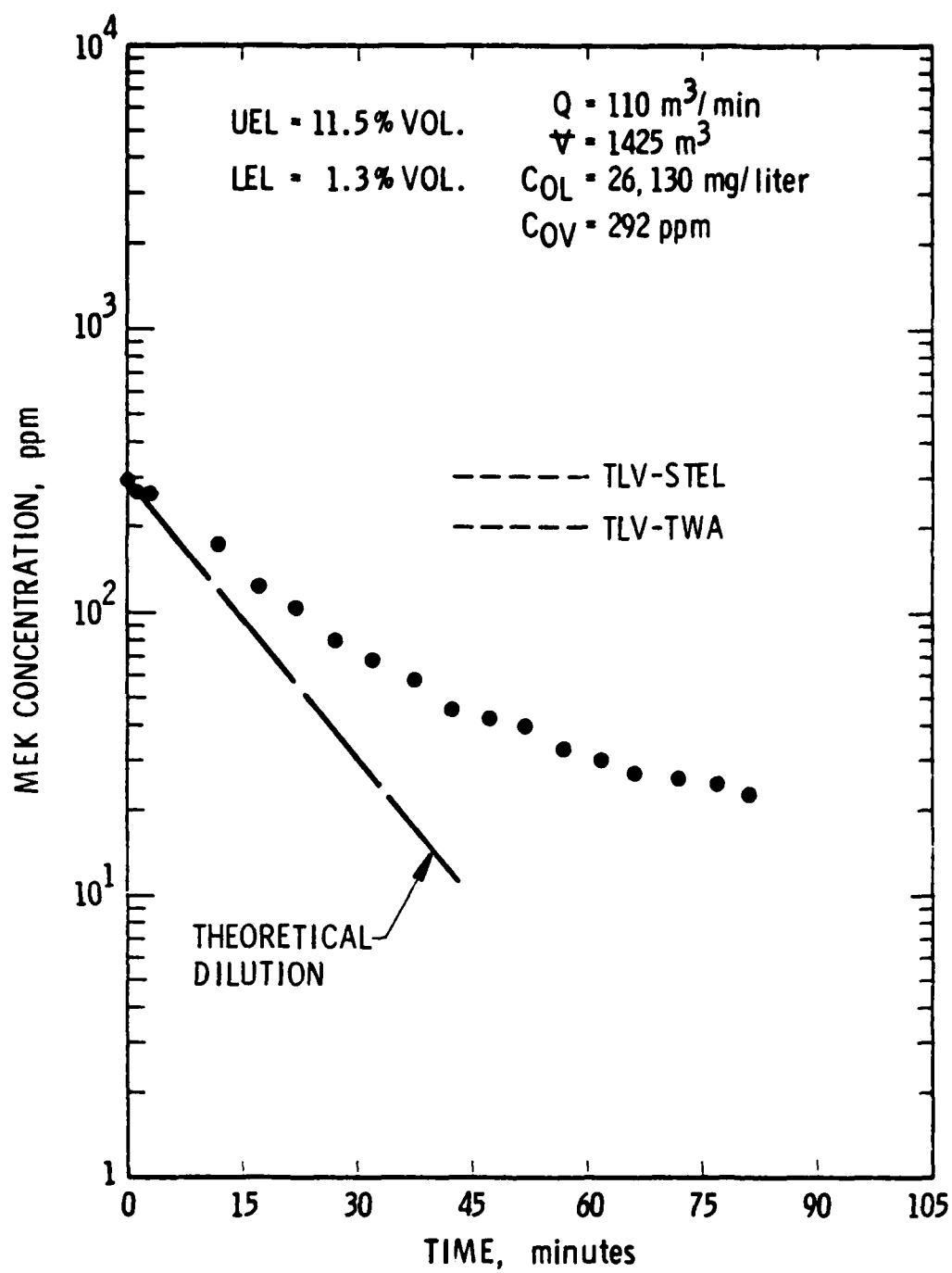


FIGURE 7. TANK VENTILATION OF 2CA

concentration was measured. The exact reasons why this occurred is not known but it may be attributed to one of the following:

- o Tank 2CA contained its own stripping pump and did not have to use the Motivator stripping device. The stripping pump could remove residual wash water at a faster rate thus shortening the time for evaporation of chemical into the tank vapor space.
- o Water washing would be more efficient in removal of a chemical that has a higher solubility. The solubility of MEK and xylene in water at 25°C is 353 and 0.2 gram/liter respectively. Unless the wash water level is kept extremely low for xylene, undissolved chemicals will float to the top without being discharged, resulting in more evaporation into the vapor space.

The remaining three gas freeing tests were carried out in tanks that were not water washed. All three tanks had contained ethyl alcohol. Two of the tanks (3S, 3P) were ventilated with Coppus blowers. Tank 3CP, however, was gas freed with a steam driven Air Jax exhauster.

The concentration time histories for the ventilation of tanks 3S and 3P are shown in Figures 8 and 9 respectively. Both tanks were equivalent in size and gas freed at similar flow rates. Although the tank hatches were opened simultaneously, tank 3S was the first to be ventilated. Gas freeing operations on tank 3P were not started until two days later. Inspection of the two curves illustrates that the initial concentration of tank 3S (27700 ppm) was much higher than for tank 3P (550 ppm). The lower concentration in tank 3P probably resulted from natural venting of tank vapors through the tank hatch during the two day period. In addition, the additional stripping and blowing performed on tank 3S (Figure 8) suggests that there was more residual product at the bottom of 3S.

The lower tank vapor concentration in 3P may explain the difference in the initial portion of the concentration profiles for the two tanks. In tank 3P, a gradual rise is observed from the initial value of 550 ppm to a peak value of 1050 ppm, whereas tank 3S's vapor concentration decreased from the start of ventilation. The increase in the vapor concentration of tank 3P stems from enhanced evaporation resulting from the high initial concentration driving force. Comparison of the remaining experimental data for both tanks with theoretical dilution curves again demonstrates the time delay caused by evaporation from residual chemical product.

The last gas freeing test performed on the observation voyage of the chemical carrier was conducted in tank 3CP. As opposed to the dilution type method which characterized the ventilation of tanks 2S, 2CA, 3P, and 3S, tank 3CP was gas freed by the displacement method. In the

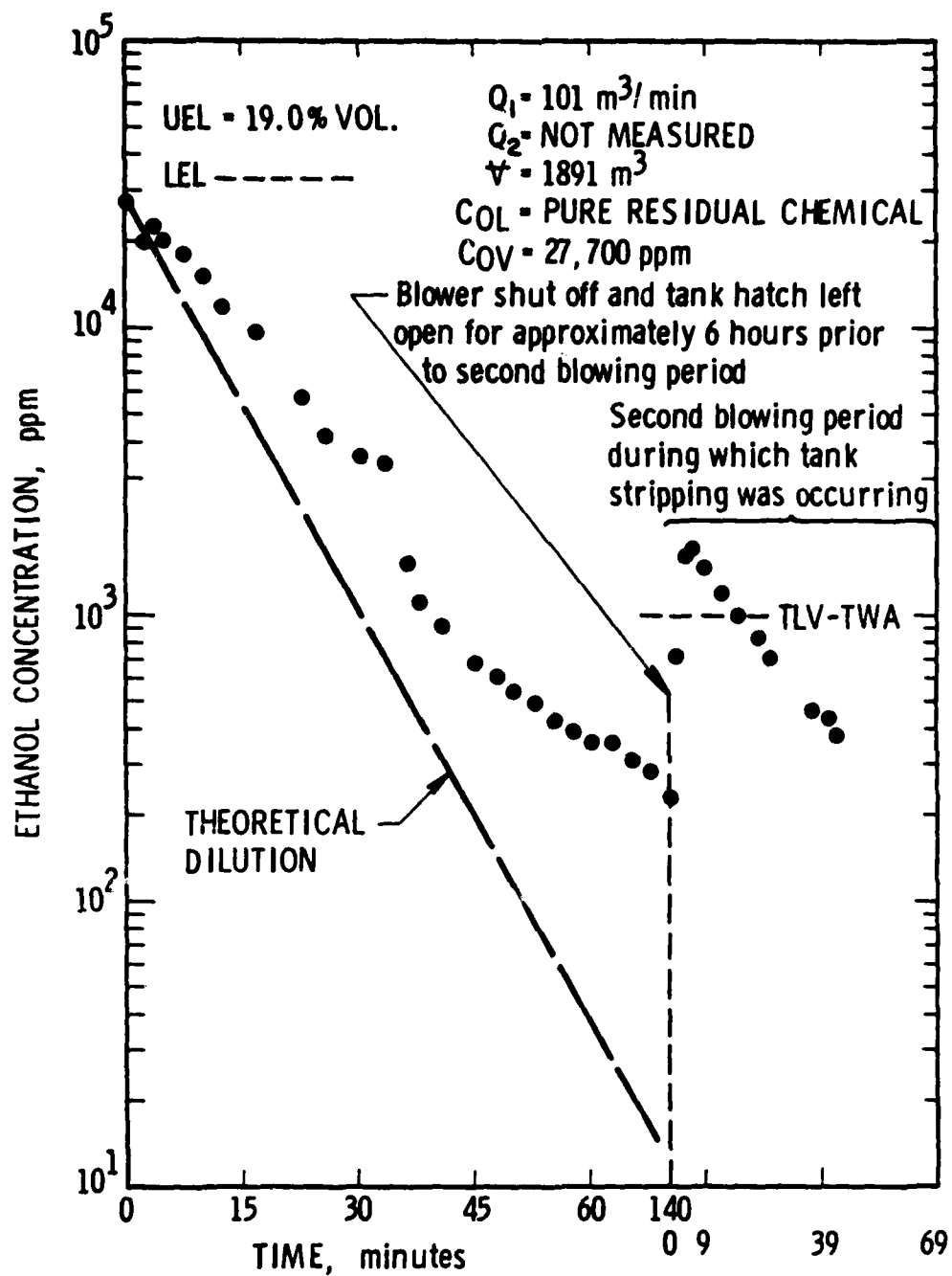


FIGURE 8. TANK VENTILATION OF 3S

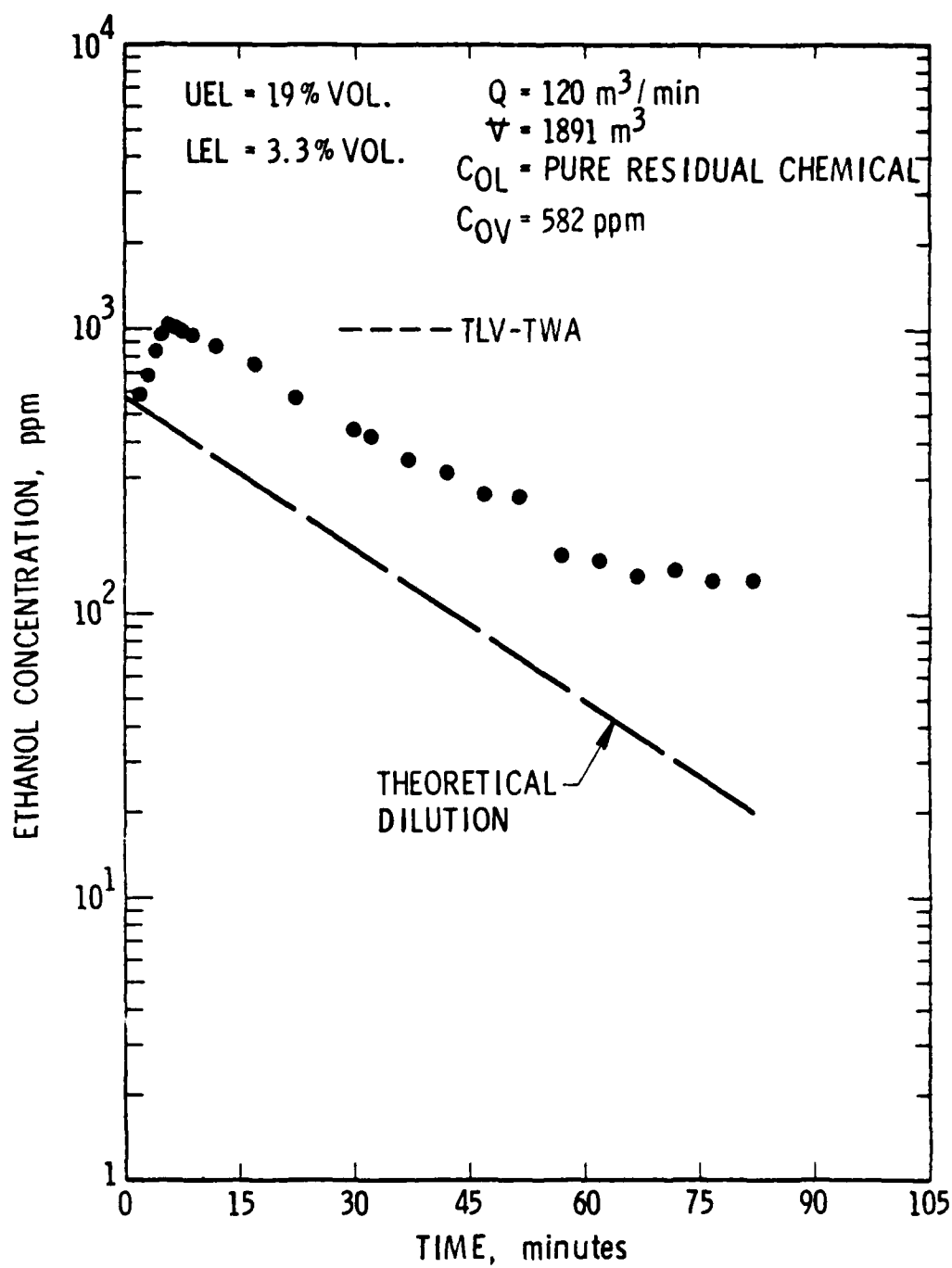


FIGURE 9. TANK VENTILATION OF 3P

displacement method, a large inlet area (tank expansion trunk) is utilized to reduce inlet vent velocity and minimize mixing of tank vapors with incoming fresh air. The fresh air and tank vapors form an interface which slowly moves downward in the tank as ventilation proceeds. As the air enters the tank, an equivalent volume of tank vapors are exhausted from the bottom of the tank through a standpipe (restricted gauging pipe). Theoretically, it should take one tank volume changeover (V/Q minutes) to gas free the tank by the displacement method. However, due to the time delay caused by chemical evaporation, as well as internal tank structure, more time is actually required.

The concentration time history for tank 3CP is shown in Figure 10. Vapor samples were retrieved from the bottom of the tank directly below the tank hatch using teflon tubing and an MSA Model "S" sample pump. Initially, during displacement gas freeing, and prior to time for one tank changeover, there should be no change in the vapor concentration at the tank bottom. Unfortunately, due to a misinterpretation of ventilation start time of tank 3CP, only one vapor measurement was made prior to one tank turnover (12.9 minutes). Combination of the first two data points, however, does suggest some stability in the vapor concentration up to a ventilation time of 17 minutes. Past 17 minutes, a sharp drop is observed characteristic of the passage of the fresh air/tank vapor interface. During the remaining part of ventilation, the inlet jet is able to reach the tank bottom and the concentration decreases similar to the theoretical dilution curve.

IV. Tank Cleaning Work Scenario

The deck personnel involved in tank cleaning consisted of the chief mate, bosun, pumpman, and the three unlicensed seamen on watch (QM, AB and OS). In addition, due to the extensive tank cleaning required in preparation for the ship's dry docking for inspection, extensive overtime hours were put in by those unlicensed seamen that were not on watch. The chief mate worked, in mainly a supervisory capacity, insuring that the tank washing plan was being followed. The activities performed by the chief mate consisted of periodic checking of the status of tank cleaning and verifying that the tanks were gas freed. It was the bosun's responsibility to arrange to have the necessary crewmen present and to delegate the actual work assignments. A major concern during tank cleaning operations involved the length of time that the ship has to discharge its dirty wash water. Government regulation requires that a ship has to be 50 miles or more away from shore to discharge any chemical product into the ocean. Consequently, normal crew work hours had to be extended in order to meet this requirement.

The general worker scenario during tank cleaning operations on the ballast leg of the voyage consisted of the following activities.

- o One AB or OS removed the butterworth plate and opened the tank hatch of the specific tank to be cleaned.

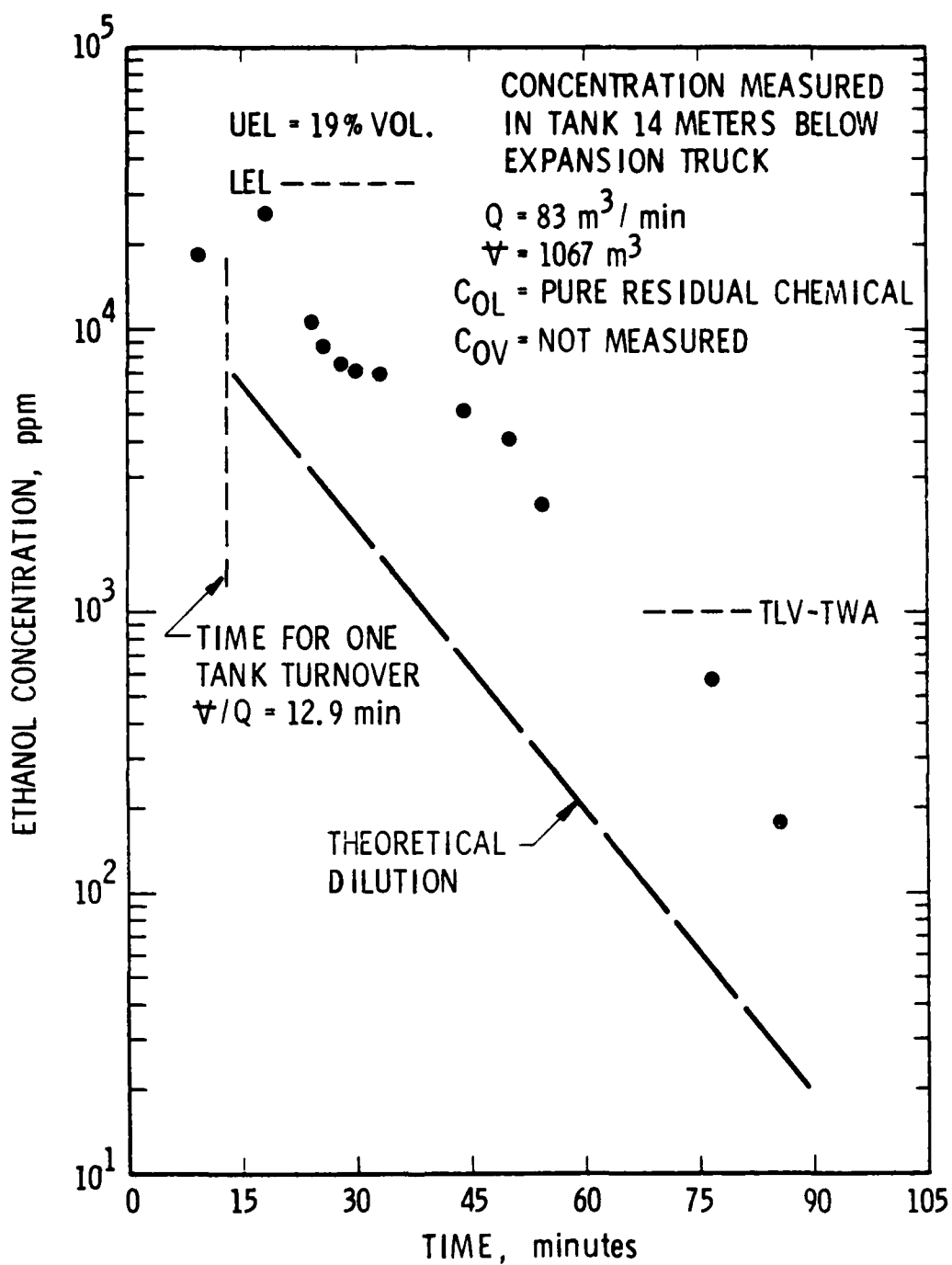


FIGURE 10. TANK VENTILATION OF 3CP

- o Two or more other unlicensed crewmen would be moving the necessary hoses, washing machines, and ventilation equipment in the vicinity of the tank. These hoses would be hooked up to the utility supply connection on deck and to the tank cleaning equipment. The washing machine would then be lowered into the tank to the first prescribed washing height.
- o Blinds on the manifold loading valves were removed by the deck crew and long pipe extensions were bolted to some of the product valves to allow the wash water discharge to clear the deck. Prior to removing the blinds, the small sample valves on the product loading valve spool piece were opened to drain any residual product from the lines into the drip pan below. In most cases, skin contact with the chemical occurred.
- o After these activities were completed, the water was turned on by the pumpman to start the washing operation.
- o At this point, the pumpman would start up the tank cargo pump to discharge the wash water. On most tanks after washing commenced, the AB's and OS's would move from the prepared tank to ready a new tank. This left the pumpman as the only crewman near a tank being washed.
- o The main task performed by the pumpman consisted of balancing the wash water input to pump output. Maintaining the lowest wash water level in the tank, short of losing suction head, was critical for efficient tank washing. Consequently, repeated discharge valve adjustment and viewing of tank wash water level through the tank hatch was performed by the pumpman during the initial portion of the tank washing. Once the optimum level was reached usually the pumpman would also move away from the tank until washing was completed.
- o After the tank had been washed at one level for the prescribed time, two or more unlicensed crewmen would move back to the tank and lower the washing machine to the next prescribed level. The procedure would be repeated according to the washing plan for that tank. On some tanks the operation had to be shut down in order to withdraw the washing machine and insert into a different butterworth opening. Restart of washing at the new location was simplified since optimum product valve setting versus water washing rate had already been adjusted for at the first location.
- o Once the washing schedule approached completion for a particular tank, the pumpman would move over to the tank and shut off the water. Considerable care was necessary in ensuring that the pump did not lose suction prematurely before discharging as much wash water as possible. In order to maintain the suction

head, while the wash water level was dropping, the pumpman would go through a sequence of valve closing and openings while maintaining suction pressure each time keeping his eye on the pump discharge pressure. As the pressure would drop, the valve would be closed slightly until the pressure rose at which time the valve was backed off. This sequence continued until the level was too low to continue pumping.

- o When stripping operations were completed, the blowers or exhausters were set on the proper tank opening by the unlicensed crewmen. The ventilation equipment was started and the tank was left unattended. Periodically, the chief mate would measure the chemical vapor and oxygen concentration in the tank using a combination explosimeter/oxygen meter. In most cases the equipment was left on even after the chief mate considered the tank "gas freed."
- o One last activity performed along with the tank cleaning operation that was observed to give rise to potentially hazardous exposure, was the draining of on-deck product lines. The type of exposure obtained during this activity was mainly by skin contact. The hazardous situation occurs due to the inaccessibility of some of the drain valves. The addition of on-deck piping over existing product lines required a person to crawl underneath the piping to reach the valve. The bosun, who was responsible for draining the line, mentioned that it is almost impossible to move away from the liquid fast enough to prevent coming in contact with it.

V. Occupational Exposures

From the description of the work scenario during tank cleaning, the pumpman and bosun were identified as being more susceptible to exposure to chemicals than the other crewmen. The level of exposure, however, was not quantified because these individuals were somewhat reluctant to wearing the personnel sampling equipment during tank cleaning activities.

TANK ENTRY

A total of five different tanks were entered by the ship's crewmen during SwRI's observation voyage. Two of the tanks were segregated ballast tanks which had not been cleaned in a long time and had been suspected of having leakage of gasoline product from adjacent cargo tanks. Two other tanks (3S, 3P) were cargo tanks which had been gas freed without prior water washing. These tanks had previously contained ethyl alcohol. The last tank entered was the pump room for the purpose of mucking of bilge. The following summarizes the hydrocarbon level measured in the tank and the safety precautions taken during man entry.

Forward Ballast Tank

- o Total hydrocarbon concentration as methane 150 ppm
- o Concentration homogeneous through tank
- o O₂ concentration 20.8%
- o Coppus blower in operation during man entry
- o Man on standby at tank hatch

Fresh Water Ballast

- o Total hydrocarbon concentration
 - 30-50 @ 25' level
 - 100-130 @ 52' level
- o O₂ concentration 20.5%
- o Steam driven exhaustor in operation during man entry
- o Man on standby on deck

Tank 3S

- o Discharge concentration during gas freeing was 230 ppm ethanol
- o Concentration reading was homogeneous throughout tank
- o O₂ concentration 20.8%
- o Coppus blower in operation during man entry
- o Man on standby at tank hatch

Tank 3P

- o Discharge concentration during gas freeing was 132 ppm ethanol
- o Concentration reading was homogeneous throughout tank
- o O₂ concentration 20.8%
- o Coppus blower in operation during man entry
- o Man on standby at tank hatch

Pumproom

- o Concentration at bottom of pumproom = 50 ppm as methane
- o From top to bottom, concentration was 7-50 ppm as methane

- o O₂ concentration not measured
- o Ventilation provided by fixed exhaust fan
- o Man on standby on deck

Exposure samples were collected on charcoal sampling tubes for all five tank entries. The individuals wearing the sampling gear were unlicensed crewmen.

Operation	Sample Number	Chemical	Exposure Concentration, ppm	Exposure Duration, min
Mucking out of forward ballast tank	VF11	Benzene+	ND	144
	VF13 } 47753 }	* Benzene+	ND	165
Muck out of fresh water ballast tank	VF100	Benzene+	ND	17
Man entry into BS tank for: 1) Placement of portable stripping line 2) Removal of access cover plate to double bottom of adjacent ECH tank	VF102	EAL EPC	66.65	84
			0.40	
Man entry into 3P tank to mop up pure chemical	VF103	EAL	239.29	30
Mucking of Pump-room bilge	VF7	Benzene+	0.51	22
	VF8	Benzene+	0.84	22

+From suspected leak of gasoline product

*Parallel active and passive samples

ND- Not detectable

ADDITIONAL OBSERVATIONS

Discharge of Ballast/Wash Water at Sea

I. Discharge of Ballast at Sea

Residual product and wash water was discharged through the product loading valves during tank cleaning. The final stripping of pure product was pumped into the drip pans below the product valves. The separate drip pans were connected together by their drain lines. One of the drains was connected with a rubber hose which extended over the ship's deck and discharged the product. During tank washing, low flow rates were encountered which resulted in a steady stream of chemical/wash water onto the deck. On-deck readings near chemical/water surface were high in total hydrocarbon. The liquid was present through the entire washing cycle.

APPENDIX G

EXPERIMENTAL TEST PLAN

I. CRITERIA FOR VESSEL SELECTION

1. Crew size will affect the basic work schedule. On a ship with minimum crew size, extended work schedules have generally been longer and more frequent than on vessels with maximum crew size. On the latter vessels, there appears to be more adherence to the conventional 8-hour work-day and/or the traditional 4-on, 8-off schedule, or variations thereof.
2. On a vessel with Type I hull, cargo tanks may be ballasted, thus creating a potential on-deck vapor exposure situation. Double-bottom tanks (Type III hull) are not normally ballasted; thus, there would be no chemical vapor exposure potential during ballasting. Integral tanks are more difficult to gas free prior to entry than are double-bottom tanks because of internal structure. A variable potential for exposure may exist.
3. Vessels with two deckhouses create more opportunities for regions of recirculating air flows. Vapors are entrained and retained in the work area and are not as readily removed by the ambient wind stream. Vessels with midship deckhouses may have vapor discharge points and gauging stations in dead air zones created by the structural configuration of the main deck level of the house.
4. Exposure monitoring efforts have indicated that restricted gauging reduces exposure potential relative to open gauging. Where closed gauging has been employed, it has been effective. The minimum requirements for gauging systems for certification purposes may not reflect operational procedures.
5. Vapor return systems have been observed; their effectiveness is a function of the physical condition of the vapor transport lines which have been quite variable. B/3 or 4m vents have been observed, but they have not generally been used for vapor venting during loading. With respect to Subchapter D products, the minimum venting requirements during loading may be preempted by operational factors.
6. The trend in ship design is toward dedicated deepwell pumps for product discharge. Pumproom discharge is generally not used for pure chemicals, although one chemical was discharged through the pumproom on a recent voyage. The primary products flowing through the pumproom are gasolines and blended solvents. The interest in the pumproom centers around pump seal leaks and product accumulations in the bilge as potential exposure sources.
7. Based on experience to date, the engine room is not of primary interest for occupational exposures. Ingestion of cargo vapors into the engine room is possible. The use of asbestos as an insulation material is rapidly disappearing. Measured oil mist levels were not significant.
8. Engine room operations on the ballast leg are similar and, thus, representative of laden leg operations.

9. Experience has indicated that appreciable pumproom activity occurs only during discharge of product and tank washing slops.

II. PRODUCT CARRIERS MEETING SELECTION CRITERIA

1. Crew Size

a. Minimum Crew

- o Vessel No. 1
- o Vessel No. 2

b. Maximum Crew

- o Vessel No. 3
- o Vessel No. 4
- o Vessel No. 5
- o Vessel No. 6
- o Vessel No. 7

2. Tank/Hull Type

a. Tank Walls Integral with Hull

- o Vessel No. 5
- o Vessel No. 1
- o Vessel No. 3

b. Double-Bottom Tanks

- o Vessel No. 4
- o Vessel No. 2
- o Vessel No. 6
- o Vessel No. 7
- o Vessel No. 5

3. Deckhouse Configuration

a. Single Aft Deckhouse

- o Vessel No. 2
- o Vessel No. 1
- o Vessel No. 4
- o Vessel No. 7
- o Vessel No. 5

b. Aft and Midship Deckhouse

- o Vessel No. 3
- o Vessel No. 6

4. Gauging Systems

a. Open

- o Vessel No. 3
- o Vessel No. 1
- o Vessel No. 2
- o Vessel No. 7

b. Restricted

- o Vessel No. 5
- o Vessel No. 6

c. Closed

- o Vessel No. 5
- o Vessel No. 4

5. Venting Systems (Loading)

a. B/3 or 4m (or high velocity)

- o Vessel No. 5
- o Vessel No. 7
- o Vessel No. 4

b. Reasonable Height

- o Vessel No. 3
- o Vessel No. 5
- o Vessel No. 1
- o Vessel No. 2
- o Vessel No. 6
- o Vessel No. 7

c. Vapor Return

- o Vessel No. 6
- o Vessel No. 4

6. Cargo Discharge Systems

a. Dedicated Deepwell

- o Vessel No. 1
- o Vessel No. 2
- o Vessel No. 5
- o Vessel No. 6
- o Vessel No. 7
- o Vessel No. 4

b. Pumproom

- o Vessel No. 3
- o Vessel No. 4
- o Vessel No. 5

7. Propulsion System

a. MV (Diesel)

- o Vessel No. 1
- o Vessel No. 2
- o Vessel No. 4

b. SS (Steam)

- o Vessel No. 7
- o Vessel No. 6
- o Vessel No. 3
- o Vessel No. 5

III. VOYAGES BASED ON DECK DEPARTMENT CRITERIA (1 THROUGH 5)

Voyage #1 (Vessel No. 1): 1a, 2a, 3a, 4a, 5b
Voyage #2 (Vessel No. 2): 1a, 2b, 3a, 4a, 5b
Voyage #3 (Vessel No. 3) 1b, 2a, 3b, 4a, 5b
Voyage #4 (Vessel No. 5): 1b, 2a, 3a, 4b, 5ab
Voyage #5 (Vessel No. 6): 1b, 2b, 3b, 4b, 5bc
Voyage #6 (Vessel No. 7): 1b, 2b, 3a, 4a, 5ab
Voyage #7 (Vessel No. 4): 1b, 2b, 3a, 4c, 5ac

IV. VOYAGES BASED ON ENGINE/PUMPROOM CRITERIA (6 AND 7)

Voyage #8 (Vessel No. 3): 6b, 7b,
Voyage #9 (Vessel No. 4): 6b, 7a

Notes:

1. Dedicated deepwell operations are implicitly contained in the Deck Department Voyages.
2. Limit Voyages 8 and 9 to product discharge and ballast leg per Selection Criteria 8 and 9.

V. OPTIONAL DECK DEPARTMENT VOYAGE

Thus far, vessel and voyage selection has been based on noncargo-related criteria. Because of the significant quantities of crude oil that are shipped or lightered in U. S. coastal waters, it is logical to make provisions for one voyage that is specifically directed towards that commodity. Therefore, we recommend that testing during Voyage No. 10 be performed aboard a crude oil tanker that would be identified at a later date.

The philosophy for monitoring occupational exposures aboard the crude carrier would be similar to that which is contained in the body of this plan with the exception that the contaminants of interest would most likely be hydrogen sulfide, straight chain and aromatic hydrocarbons, as well as toxic gases that may be present during loading, crude oil tank washing, and inert gas system operation. The details of this sampling activity would be defined in Phase II.

VI. VOYAGE SUMMARY

- o Seven chemical tanker voyages to monitor exposure profiles in the Deck Department.
- o Two chemical tanker voyages to monitor exposure profiles of Engine Room and Pumproom personnel.
- o One crude oil tanker voyage to monitor occupational exposures in the Deck Department.

VII. SAMPLING PLAN - DECK DEPARTMENT

The probability of exposure to cargo vapors is not uniform throughout a voyage. The probability is greatest during loading, ballasting, tank cleaning, and tank entry. A much lower probability exists during discharge (pumproom considered separately), the laden voyage, and those portions of the ballast voyage where tank cleaning is not performed. Negligible exposures are anticipated during a navigation watch or day deck work watches while the vessel is underway. Therefore, for planning purposes, it would be logical to postulate a voyage scenario and tailor the sampling plan according to the probability of exposure.

VII.1 Voyage Scenario

1. 14-day round trip voyage beginning and ending at same port.
2. 2 days' loading (48 hours) at Gulf Coast port.
3. 3 1/2 days' laden voyage (84 hours) to East Coast port.
4. 2 days' discharge (48 hours)

5. 1-day slack voyage (24 hours) to another discharge port to the north.
6. 1-day discharge (24 hours) at second port.
7. 4 1/2-day ballast voyage (108 hours) to home port.
8. Tanks are cleaned for first 72 hours of ballast voyage.
9. 7 chemicals of interest.

VII.2 Scenario Work Breakdown

There are basically three labor grades* in the Deck Department: Mates, A/Bs, and O/Ss. The sampling plan is based on monitoring one Mate and one unlicensed seaman on each voyage. We will assume that the Mate is the C/M for planning purposes because his responsibilities and work hours will define the maximum requirements for sampling equipment. Depending on the actual work structure of the mates on a given vessel, the 2/M or 3/M could be selected and would not impose any additional requirements on sampling equipment. With the exception of the A/B's navigation watch, the work activities and schedule of the A/B and O/S are nearly identical. Because of the low exposure potential during navigation watch, we can select either an A/B or O/S. Assume that it will be an A/B because he is more senior than the O/S and may be more intimately involved in cargo transfer operations.

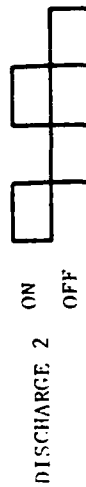
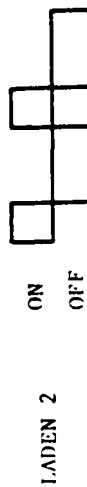
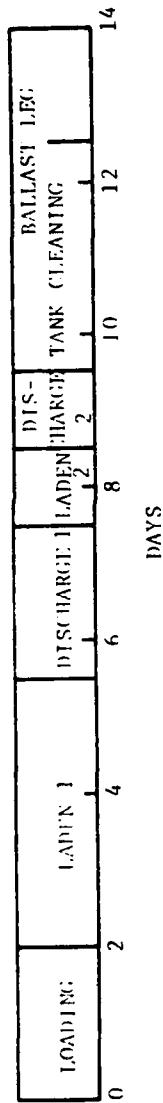
Based on the voyage scenario, work schedules have been generated for the Chief Mate (Figure 1) and Able-Bodied Seaman (Figure 2). These schedules form the basis for the sampling plan and equipment requirements.

VIII. CHIEF MATE

VIII.1 Product Loading (48 hours)

- a. Assume that the C/M is on duty for the entire loading period of 48 hours.
- b. There will be times when the C/M is absent from the deck, but it is assumed that the majority of the time he is on deck and is actively involved in cargo gauging.
- c. Assume that there are seven chemicals of interest on the ship and that the C/M tops all tanks (ship stop as opposed to shore stop). These seven chemicals are assumed to be loaded into 12 tanks.

*The vessel generally carries a Bosun and may or may not carry Quarter Masters.



- NOTES:
1. ON = ON DUTY
 2. OFF = OFF DUTY
 3. CE = CLEAN AND ENTER CHEMICAL TANKS
 4. CTC = CONTINUED TANK CLEANING

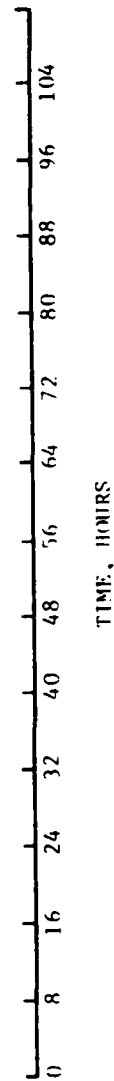


FIGURE 1. WORK SCHEDULE SCENARIOS FOR CHIEF MATE

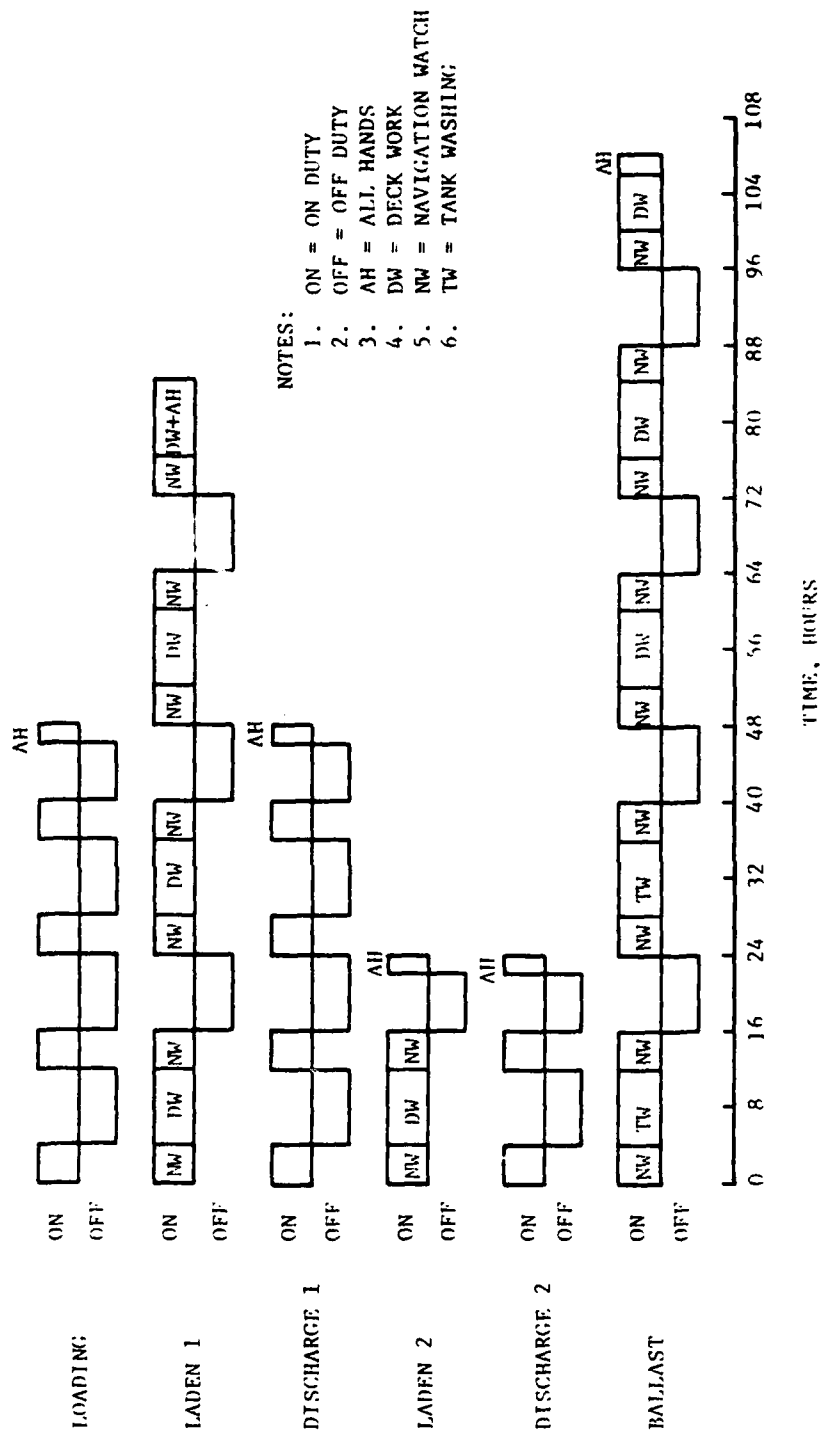
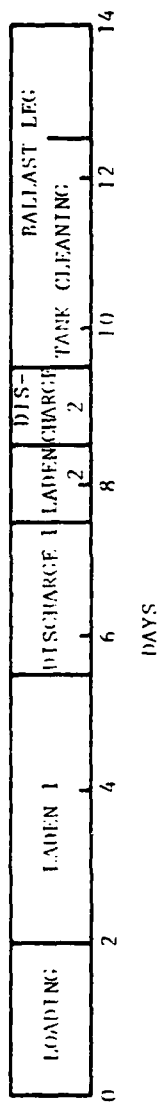


FIGURE 2. WORK SCHEDULE SCENARIOS FOR ABLE-BODIED SEAMAN

d. Sample requirements

- o 48 one-hour samples
 - o 12 short-term top-off samples
 - o 7 blanks
 - o 67 charcoal tubes
- } 60 active samples

e. Pump requirements (excluding backups)

- o 8 pumps at 6 hours/pump

f. At the end of the loading, all 8 pumps will have been used and will be ready for recalibration and charging. These two operations would be performed after the first 4-hour laden watch following undocking.

VIII.2 Laden Voyage 1 (84 hours)

a. Assume C/M works traditional 4-on, 8-off schedule.

b. The pumps used during the loading operation will be ready for reuse 20 hours after loading ends and the ship undocks.

c. Sample requirements (on watch)

- o 7 four-hour samples
 - o 7 blanks
 - o 14 charcoal tubes
- } 7 active samples

d. Pump requirements

- o There are 7 four-hour watches during Laden Voyage 1.
- o One additional pump is required to handle the first two 4-hour watches. The remaining five 4-hour watches will utilize the pumps from the loading operation at 8 hours/pump.

e. At the beginning and end of each 8-hour-off watch period, the living environment would be monitored with the OVA in GC mode (including strip chart recorder). If unusual concentrations are found, then a pump and charcoal tube would be placed in the room for the 8-hour period. The first 8-hour period after loading terminates would likely present the highest concentrations if there is vapor infiltration as a result of adverse atmospheric conditions. Subsequent 8-hour periods should be relatively vapor free because cargo tanks are sealed and the room environment has been purged. Similar logic would be applied to the bridge environment during navigation. Items c and d may be deleted pending results of the OVA survey.

- a. Assume that the C/M works a 6-hour-on, 6-hour-off schedule. The 2 additional hours each shift reflect responsibility, but discharge does not demand his full-time attendance.
- b. Sample requirements
 - o 4 six-hour samples (charcoal tube)
 - o $\frac{4}{8}$ blanks (4 of 7 chemicals discharged at this port)
 - o 8 tubes
- c. Pump requirements
 - o No additional pumps are needed for this discharge.
- d. Off-hour sampling to follow previously outlined plan.

VIII.4 Laden Voyage 2 (24 hours)

- a. Assume normal 4-on, 8-off routine for this leg of the voyage.
- b. Sampling requirements (on-watch)
 - o 2 four-hour samples
 - o $\frac{3}{5}$ blanks (3 chemicals of interest remain onboard)
 - o 5 tubes
- c. Pump requirements
 - o No additional pumps required.
- d. Off-watch monitoring to follow previous plan with OVA.
- e. a and b may be deleted pending results of OVA survey in bridge.

VIII.5 Discharge 2 (24 hours)

- a. Assume same work schedule as Discharge 1.
 - o That is, 6 on, 6 off.
- b. Sampling requirements
 - o 2 six-hour samples
 - o $\frac{3}{5}$ blanks (for 3 remaining chemicals)
 - o 5 tubes

- c. Off-watch sampling as previously outlined.

VIII.6 Ballast Leg (108 hours)

- a. There are 7 chemicals of interest on board. These chemicals are amenable to sampling by the charcoal tube (activated carbon) methods. The remaining materials (cargos) are assumed to be either not amenable to charcoal sampling or are complex proprietary blends for which the composition is unavailable (excluding gasoline). Therefore, only the cleaning of the tanks that have held these cargos is of interest. Assume that these 7 cargos have been carried in 12 tanks and each tank requires 3 hours for washing, ventilating, and man-entry (by C/M). Assume for planning purposes that these 12 tanks are cleaned as a group during the first 36 hours of the 72-hour cleaning period. During the second 36 hours, the remainder of the tanks that have held other cargos are cleaned.
- b. Assume that the C/M is on duty and is supervising and participating in the entire 36-hour cleaning of chemical tanks.
- c. Sampling requirements
 - o 36 one-hour samples
 - o 12 short-term samples (tank entry)
 - o $\frac{7}{55}$ blanks tubes
- d. Pump requirements
 - o 6 pumps at 6 hours/pump
 - o No additional pumps required
- e. During the remainder of the ballast voyage, the other cargo tanks would be cleaned, but exposures would not be monitored for the reasons given earlier. During this phase of the operation, work schedules and duration in proximity to cargo vapor sources would be documented.
- f. The sampling plan would be modified to account for any alterations of the tank cleaning scenario. The chemical vapors of interest would remain the same.
- g. Liquid samples of all products on board will be collected.

VIII.7 Chief Mate's Summary

Number of pumps for voyage = 9 (low flow)

<u>Leg</u>	<u>No. Tubes</u>	<u>No. Blanks</u>
Loading	60	7
Laden 1	7	7
Discharge 1	4	4
Laden 2	2	3
Discharge 2	2	3
Ballast/cleaning	48	7
Ballast/remainder	--	--
	123	31 + 154 tubes

IX. ABLE-BODIED SEAMAN

IX.1 Product Loading (48 hours)

- a. From experience, the A/Bs have stood a conventional 4-on, 8-off schedule during loading. Assume that the "all-hands" call for hose disconnect and undocking occurs when he would normally be off-watch, but he is now required to work 2 hours of overtime. Since the ship is in port, there is no navigation or bridge watch.
- b. Assume that the A/B assists the C/M and he also periodically gauges ullage on the 12 tanks that are loading 7 chemicals.
- c. Sample requirements

o 18 one-hour samples (on watch)	} 30 active samples
o 12 short-term samples (near top-off, but C/M actually performs top-off)	
o 7 blanks	
o 37 tubes	
- d. Pump requirements
 - o 3 pumps at 6 hours/pump
- e. These pumps are ready for posttest calibration, charging, and pretest calibration.
- f. The pumps used during loading will be ready for reuse in roughly 16 to 20 hours after undocking.

IX.2 Laden 1 (84 hours)

- a. The A/B works a 16-hour day (2 four-hour navigation watches separated by an 8-hour day deck work period (worst case).
- b. Following the logic for sampling of C/M,

- o OVA in GC mode used to sample bridge and living quarters environment at beginning and end of navigation and off-watch periods.
- o Personal sampling with pumps is not envisioned because of the low probability of exposure in these areas. However, 3 additional low-flow pumps will be available for use if OVA readings justify personal monitoring.
- c. During deck work, the potential for exposure to cargo vapors is quite low because tanks are sealed. However, an additional 3 pumps (low flow) will be available to react to special situations such as cleaning and mucking of a chemical slop tank. Primary exposure monitoring would be for dust from sandblasting operations (NIOSH P & CAM S315) and chemical vapors emitted from mixing epoxy paints (P & CAM 127). Vapor exposure samples to be collected during hose hookup for Discharge 1.
- d. Dust sampling requirements
 - o 3 six-hour filter samples from the first 3 deck work periods.
 - o 1 blank filter
 - o Analyze for silica, Fe_3O_2 .
- e. Pump requirements
 - o 3 MSA high-flow pumps with cyclone separator and filter cassette
- f. Vapor sampling
 - o 2 one-hour tube samples during hose connect
 - o 4 blanks (4 of 7 chemicals to be discharged)
 - o 4 short-term tube samples for paint vapor
 - o 1 blank tube
 - o 11 tubes

IX.3 Discharge 1 (48 hours)

- a. Assume that the A/B works a conventional 4-on, 8-off schedule with the exception that the last 8 hours off is cut short for "all hands" at undocking.
- b. OVA/GC sampling during off hours will follow previously outlined logic.
- c. Sampling requirements
 - o 18 one-hour tube samples

- o $\frac{4}{22}$ blanks (4 of 7 chemicals discharged at this port)

d. Pump requirements

- o 3 pumps at 6 hours/pump. No additional pumps required in excess of those previously allocated.

IX.4 Laden 2 (24 hours)

- a. OVA/GC samples during navigation and off-watch periods to be applied as previously outlined.

b. Sampling requirements

- o 2 one-hour tube samples (hose connect)
- o $\frac{3}{5}$ tube blanks
- o 1 six-hour dust filter sample (sand blasting)
- o 1 blank filter

c. Pump requirements

- o No additional pumps required in excess of previously defined need.

IX.5 Discharge 2 (24 hours)

- a. The A/B works a 4-on, 8-off schedule except for a 2-hour "all hands" for undocking.

b. Sampling requirements

- o 2 four-hour samples (discharge)
- o 2 one-hour samples (hose disconnect)
- o $\frac{3}{7}$ blanks (3 remaining cargos)

c. Pump requirements

- o No additional pumps are needed.

IX.6 Ballast Leg (108 hours)

- a. On the ballast voyage, the A/B stands navigation watches on the same schedule as Laden 1 and Laden 2.

- b. Assume that the 12 chemical tanks are cleaned during the first 36 hours at sea.

- c. Sampling during navigation and off-watch periods performed as previously outlined.

d. Vapor sampling requirements

- o 16 one-hour samples (tank washing)
- o 12 short-term samples (tank entry with cleanup)
- o 7 blanks
- o 2 one-hour samples (hose connect) plus one blank
- 38 tubes

e. Low-flow pump requirements

- o 4 pumps at 4 hours/pump + 1 pump at 2 hours/pump
- o Pumps included in previous requirements; no additional pumps needed.

f. Dust sampling requirements

- o Assume sandblasting during first 2 deck work periods.
- o 2 six-hour filter samples
- o 1 filter blank

g. Pump requirements

- o High-flow requirements satisfied by previously identified need.

IX.7 Able-Bodied Seaman Summary

Number of pumps for voyage

- o 9 low-flow vapor samplers
- o 3 high-flow dust samplers

<u>Leg</u>	<u>No. Tubes</u>	<u>No. Tube Blanks</u>	<u>No. Filters</u>	<u>No. Filter Blanks</u>
Loading	30	7	-	-
Laden 1	6	5	3	1
Discharge 1	18	4	-	-
Laden 2	2	3	1	1
Discharge 2	4	3	-	-
Ballast/cleaning	28	7	-	-
Ballast/remainder	<u>2</u>	<u>1</u>	<u>2</u>	<u>1</u>
	90	30	6	3
	120 tubes		9 filters	

X. REVIEW - DECK DEPARTMENT

The subjects of documentation of dermal exposures and documentation of work activities are an integral part of the Crew Exposure study and would be performed in parallel with the occupational exposure monitoring:

a. Dermal exposure documentation requirements

- o Identity of contaminant in contact with skin
- o State of contaminant (bulk liquid, atomized spray, etc.)
- o Anatomical location of contact site
- o Approximate contact area
- o Duration of contact
- o Intervening clothing and duration worn after contact
- o Personal hygiene (clothing changes, washing, etc.)

b. Work activity documentation requirements

- o Nature of work activity
- o Duration of work activity
- o Proximity to sources of airborne contaminants
- o Protective equipment used

The sampling plan outlined earlier for the C/M and A/B were constructed without prior knowledge of the cargos to be transported. As such, the indicated variations in sample duration are intended to reflect probability of exposure during various phases of the voyage, e.g., longer term-lower probability, short-term high probability. When the loading plan becomes known in advance of docking, the sampling durations in the plan would be adjusted accordingly to reflect NIOSH sampling procedures (NIOSH Manual of Analytical Methods, Volumes 1 through 6). Consequently, the number of samples (tubes) could increase by as much as 50% if a 30-minute sample duration is recommended instead of 60 minutes.

The sampling plan for the Deck Department is based on monitoring the C/M and an A/B. Depending upon the vessel, another Mate could be monitored instead of the C/M. Likewise, an O/S or Q/M could replace the A/B. In the total number of voyages that are planned, all levels of licensed and unlicensed personnel should be monitored so that the results are representative of that Department. Therefore, two members of the Deck Department would be monitored each voyage, but the makeup of this group would be varied according to the work schedule inputs by the C/M.

XI. INTERPRETATION OF EXPOSURE DATA

All samples would be analyzed for the range of compounds that were present during each sampling interval. A concentration-time histogram may then be constructed for each compound over the duration of the voyage. A time-dependence of the exposure concentration is anticipated. These histograms may also be superimposed on a common time scale so that the extent of exposure to multiple contaminants can be qualitatively observed.

It is recognized that current exposure standards or PELs are based on a continuous 8-hour work day and a 40-hour work week. The work schedules in the marine industry do not generally conform to this definition.

It is also recognized that current (nonregulatory) attempts to calculate adjusted TWA-TLVs for the unusual work schedule are based on a highly repetitive work schedule and a constant exposure level during each work period.

At a minimum, the data should be interpreted within the context of the USCG MOA with OSHA, i.e., apply OSHA compliance criteria to exposures.

- a. OSHA Compliance Criteria (OSHA Industrial Hygiene Field Operation Manual CPL2-2.20). This method treats only single chemical exposures and does not include exposure to vapor mixtures.

- (i) For a given chemical, identify the current PEL, work category, and health code from Chapter II of OSHA IHFOM. The work category establishes in Chapter XIII what mathematical adjustments in PEL are permitted for extended work schedules. The health code identifies health effects resulting from overexposure.
- (ii) Refer to exposure C(t) histogram for a given chemical on the voyage. Select an extended work period for one individual's exposure to the selected chemical.
- (iii) Calculate the permitted PEL adjustment under (i).
- (iv) Use the following procedure from Chapter II of the FOM to assess compliance.
- (v) Calculate the TWA exposure concentration during extended work period

$$C_{TWA} = \frac{\sum C_i t_i}{\sum t_i}$$

- (vi) Calculate

$$Y = \frac{C_{TWA}}{PEL}$$

- (vii) Identify the sampling and analysis error (SAE) for the chemical from Chapter IX of FOM.
- (viii) Calculate Upper and Lower Confidence Limits (UCL and LCL) on the measured C_{TWA} .

$$\left| \frac{UCL}{LCL} \right| = Y \{ \pm \} \left(\frac{SAE}{PEL} \right) \sqrt{\frac{\sum C_i^2 t_i^2}{\sum t_i}}$$

(ix) Assess compliance

$LCL \geq 1$; noncompliance

$LCL \leq 1$ and $UCL \geq 1$; possible overexposure

$UCL \leq 1$; compliance

(x) The above procedure may be repeated for different durations of extended work schedule.

b. The ACGIH methodology can be applied only to 8-hour work segments because the TWA-TLVs cannot be altered for unusual work schedules. Therefore, it can be used as a tool for screening potential overexposure situations.

(i) Single chemical vapor exposure, is

$$\bar{C}_j = \frac{\sum C_i t_i}{8} \geq \text{TWA-TLV} ;$$

where j = single chemical index.

(ii) Vapor mixture exposures, is

$$\sum \frac{C_j}{TLV_j} \geq 1$$

where C_j is as defined in (i).

To apply the mixture relationship, the vapors that are represented in the summation are assumed to act on the same organ system.

XII. ADDITIONAL TEST PLAN CONSIDERATIONS

The test plan that has been presented is correctly based on occupational exposure monitoring as the primary sampling method. Area monitoring uses similar equipment and is another form of sampling that can provide useful information. Consider the placement of area monitors in high traffic routes, general work areas, above drip trays, or adjacent to open slop tanks. By analyzing the area samples before the personal samples, the following types of information may become evident:

- o Identification of vapor components that may interfere with the chromatographic analysis of the personal samples. Knowledge of these interferences may suggest methods of circumventing the interference without compromising the primary samples.
- o Identification of multiple vapor levels in a general work area. This information would be useful in terms of the anticipated levels that may exist on the personal samples.
- o Open slop tanks may contain products that differ from the products to be loaded. The vapors from these additional liquids would contribute to the overall exposure, but would go undetected unless the area sample were collected and analyzed first. The same argument applies to drip trays.

Area monitoring may prove to be a primary monitoring technique for engine and pumproom operations.

The Organic Vapor Analyzer (OVA) is another instrument that can be used to identify the presence of multiple chemical vapors. As such, it would be a useful tool for general work area surveys as well as surveys in shielded or wake regions near deckhouses.

It is recommended that area sampling and OVA/GC surveys be used in those situations that are likely to provide useful, additional information.

APPENDIX H

TASK IV VOYAGE REPORT

I. VESSEL DESCRIPTION

I.1 Dimensions

- o Length Overall - 580 ft (approximate)
- o Length Between Perpendiculars - 560 ft (approximate)
- o Breadth (mid) - 90 ft (approximate)
- o Depth (mid) - 50 ft

I.2 Tonnage - 31,000 LT (summer mark), (approximate)

I.3 Propulsion - 17,000 hp diesel (approximate)

I.4 Cargo Tanks - 46 double-bottomed tanks of varying capacities

I.5 Cargo Pumps - independent deepwell pump and cargo transfer system on each tank

I.6 Cargo Loading Method - open drop, open loading, shore stop, short loading

I.7 Cargo Gauging Method - Each tank was fitted with a closed tape gauging system that was used on selected cargos. For other cargos, tanks were gauged with a Lufkin tape through open ullage ports.

I.8 Vapor Venting System - During cargo transfer, the majority of the vapors were vented through open ullage ports. For selected cargos, the vapors were vented to shore through a vapor return system.

I.9 Expansion Trunk Layout - symmetric about the ship's longitudinal axis with each trunk located at the aft end of the tank

I.10 Deckhouse - single aft house for crew accommodations, communications systems, and navigation

II. CARGO DESCRIPTION

Several grades of bulk liquid cargos were either loaded or discharged during a seven-day period that included docking at eight terminals. The cargos are summarized in Table I.

Prior to the loading of Tank 7S, diethylamine was indicated as the cargo to be transferred. In fact, diethanolamine was loaded into that tank. However, this change became known only after loading had commenced.

TABLE I
Cargo Distribution Plan

<u>Commodity</u> [†]	<u>Tank No.</u>	<u>Quantity (mT)</u>	<u>Terminal No.</u>
1,1,1-Trichloroethane (TCE)*	11P	300	1
Methylene chloride (DCM)*	9CS	250	1
Epoxy resin	12P	200	1
Carbon tetrachloride (CBT)*	9CP	400	1
Polyether polyol	3S	300	1
Polyether polyol	4CP	250	1
Caustic soda	12S	700	1
Ethyl acrylate (EAC)*	9S	300	2
Diethanolamine (DEA)*	7S	400	2
Vinyl acetate (monomer) (VAM)	9P	350	2
Diethylene glycol	4CS	200	2
Toluene diisocyanate (TDI)	8CP	500	3
Polyol	3P	300	3
Chloroform (discharge) (CRF)*	5C	2600	4
Propylene oxide (POX)*	5P,S	1140	6
n-Propyl acetate (PAT)*	8CF	200	6
o,p Dichlorobenzene (DOB,DBP)*	13S	500	5
Caustic soda	12C	3000	7
Methyl methacrylate (MMM)*	10S	450	8
Butyl acrylate (BTC)*	7P	450	8
Ethyl acrylate (EAC)*	8P	275	8
Vinyl acetate (monomer) (VAM)	1S	500	8
Toluene (TOL)*	1P	350	8
Xylene (XLO,M,P)*	5C	500	8

* - These chemicals included in sampling plan.

† - Abbreviations in parentheses correspond to USCG CHRIS.

III. WATCH COMPOSITION AND WORK SCHEDULES

Excluding the Master, the Deck Department consisted of four licensed Mates and ten unlicensed personnel. Of the four Mates, the Chief Mate did not stand a cargo transfer watch on deck. The three remaining Mates stood deck watch and served as cargo transfer officers; these Mates worked a fairly consistent 4-on, 8-off rotating shift schedule.

For the majority of the voyage (eight terminals in seven days), the unlicensed deck personnel worked a 6-on, 6-off repeating schedule. Near the end of this observation, that schedule was changed to 4-on, 8-off.

A cargo transfer watch consisted of one Mate and two A/Bs. The Mate functioned as a supervisor, and nearly all tank gauging activities were performed by the A/Bs.

Figure 1 illustrated the work shifts that were either monitored or observed at each terminal. Time gaps between terminals represent transit times from one berth to the next.

IV. SAMPLING STRATEGY AND SAMPLE ANALYSIS

Table 1 listed the products that were loaded and discharged during the observation period as well as the compounds that were selected for occupational exposure monitoring. That selection process was governed by several factors that resulted in excluding certain products from the sampling plan. The following products were excluded for the indicated reasons.

- o Epoxy resin - no established health standard or sampling and analysis method
- o Polyether polyol - same as epoxy resin
- o Diethylene glycol - same as epoxy resin
- o Polyol - same as epoxy resin
- o TDI - The use of impingers and absorbing solutions for personal monitoring is not compatible with shipboard work activities.
- o Vinyl acetate (monomer) - unavailability of recommended thermal desorption equipment
- o Caustic soda - Primary occupational exposure is through dermal contact with bulk liquid.

Table II was then constructed and served as a guide during monitoring of vapor exposures. NIOSH was consulted regarding monitoring procedures

AD-A118 179

CG-D-22-82 A CREW EXPOSURE STUDY - PHASE I. VOLUME II - AT SEA
/ W.J. ASTLEFORD, ET AL SOUTHWEST RESEARCH INST., SAN ANTONIO, T
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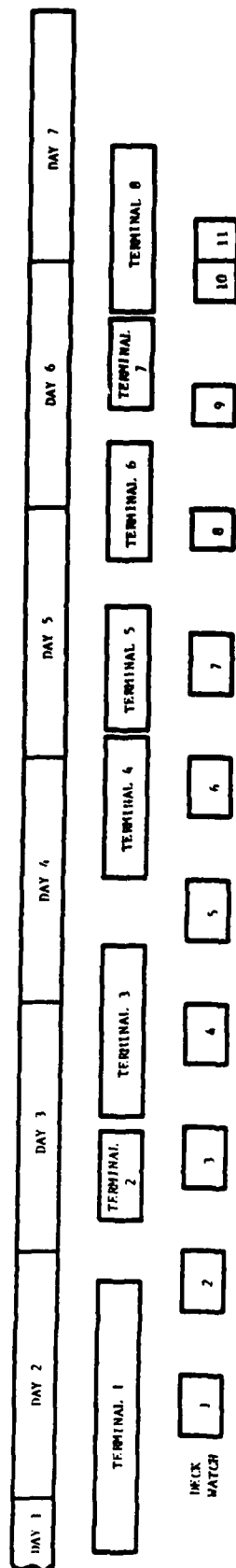


FIGURE 1. DURATION OF TERMINAL DOCKINGS
AND WORK SHIFTS

for butyl acrylate because there is no published sampling and analysis method for this compound. Based on these discussions, it was recommended that the procedures for ethyl acrylate also be applied to butyl acrylate. Table II reflects the initial indication that diethylamine was to be loaded. With the change in cargo plan, the sampling procedures for diethylamine were applied to diethanolamine.

In addition to the conventional sampling methods that employ pumps and tubes, passive dosimeters were also utilized. The badges contained two adsorption elements; one element served as a backup section. All tubes and passive dosimeters were analyzed by an AIHA Accredited Laboratory using the appropriate NIOSH- or manufacturer-recommended procedures.

The results of the sampling efforts are summarized in Tables III and IV. Table III consists of three parts:

- o Part A contains data that are pertinent to the sampling conditions.
- o Part B contains desorption efficiencies for adsorbent/analyte combinations.
- o Part C summarizes the calculated exposure concentrations.

Table IV pertains to the other Deck Department personnel who were monitored, and it contains two parts that are analogous to Parts A and C of Table III.

Ambient vapor concentrations were calculated using the following analytical expressions.

o Adsorbent Tubes

$$C \text{ (ppm)} = \frac{W_c}{\eta Q t} \left(\frac{24.45}{MW} \right) \left(\frac{T + 273}{298} \right) \left(\frac{760}{P} \right)$$

where

W_c = cumulative weight of analyte on the tube corrected for blank, μg

η = desorption efficiency as a decimal

Q = sampling flow rate, LPM

t = sample duration, min.

MW = analyte molecular weight

T = sampling temperature, $^{\circ}\text{C}$

P = sampling barometric pressure, mm Hg

TABLE II
Recommended NIOSH Sampling Procedures

Chemical	(1) TWA/Ceiling (ppm)/(ppm)	(13) NIOSH Method Number	Adsorbent		Desorp. Solution	TWA Concentration			Ceiling Concentration		
			Type	Size		Sample Volume (l.)	Sample Flow Rate (l./min.)	Sample Time (min.)	Sample Volume (l.)	Sample Flow Rate (l./min.)	Sample Time (min.)
Butyl Acrylate (12)	10/- (ACGIH)	--	(3)	(6)	(9)	Same as Ethyl Acrylate (14)			--	--	--
Carbon Tetrachloride	10/25	S314	(3)	(6)	(9)	15	0.2	75	5	1	5
O-Dichlorobenzene	-/50	S135	→		→	--	--	--	3	0.2	15
P-Dichlorobenzene	75/-	S281	→			3	0.05	60	--	--	--
Ethyl Acrylate	25/-	S35	→		(10)	10	0.20	50	--	--	--
Diethylamine	25/-	S139	(4)	(7)	(9)	50	1.0	50	--	--	--
Methylene Chloride	500/1000	S329	(3)	(8)	→	2.2	0.05	44	1	0.2	5
Methyl Methacrylate	100/-	S43	(5)	(8)		3	0.03-0.05	100-60	--	--	--
N-Propyl Acetate	200/-	S48	(3)	(6)	→	10	0.2	50	--	--	--
Propylene Oxide	100/-	S75	→			5	0.2	25	--	--	--
Toluene	200/300/500 (2)	S343	→		→	12	0.2	60	2	0.2	10
1,1,1-Trichloroethane	350/-	S328	→			6	0.2	30	--	--	--
Xylene	100/-	S318	→		→	12	0.2	60	--	--	--
Chloroform	-/50	S351	→			--	--	--	15	1.0	15

NOTES: (1) OSHA Standard
(2) Peak Concentration
(3) Activated Charcoal
(4) Silica Gel
(5) XAD-2 Resin
(6) L = 7 cm, OD/ID = 6/4 mm, 20/40 mesh, 100/50 mg
(7) L = 7 cm, OD/ID = 6/4 mm, 20/40 mesh, 150/75 mg
(8) L = 7 cm, OD/ID = 8/6 mm, 20/50 mesh, 400/200 mg
(9) Carbon Disulfide
(10) 0.2N H₂SO₄ in 10% Methanol
(11) Water
(12) No NIOSH Method Noted
(13) NIOSH Manual of Analytical Methods, Volumes 1-6
(14) Based on Discussions with NIOSH

TABLE III

A. Occupational and Area Monitoring Data
for AB1 and AB3 Deck Watches

Sample No.	Terminal No.	Pump No.	Flow Rate, LPM	Average Temp., °F	Average RH, %	Time Start, Hour(s)	Sample Duration, Min.	Blank No.	Type of Sample ⁽¹⁾
500 ⁽³⁾	1	P5	0.201	72	62	0949 ⁽²⁾	121	502	P
501	1	M6	0.048	72	62	0937	133	502	P
63821 ⁽⁴⁾	1	--	--	72	62	0953	116	62023	P
503	1	P5	0.201	67	88	1806	140	503	P
63822	1	--	--	67	88	1811	135	62023	P
504	2	P6	0.201	64	93	0402	5	506	P
505	2	P5	0.201	64	93	0344	4	506	P
507	2	P5	0.201	61	86	0610	69	509	P
508	2	G7	0.936	61	86	0613	66	510	P
511	2	P5	0.201	57	76	0803	151	509	P
512	2	G7	0.936	57	76	0803	93	510	P
63823	2	--	--	57	76	0811	143	62025	P
513	3	G6	1.038	48	60	1239	61	516	A
514	3	G6	1.038	51	40	1413	43	516	A
515	3	G6	1.038	48	40	1545	96	516	A
63824	3	--	--	48	40	1552	89	63840	A
517	5	M4	0.048	40	85	0620	63	523	P
518	5	P6	0.201	40	76	0659	16	523	P
519	5	M4	0.048	44	68	0725	70	523	P
520	5	M6	0.048	44	68	0904	69	523	A
521	5	M4	0.048	52	70	1024	60	523	P
522	5	M6	0.048	52	70	1020	69	523	A
524	5	G7	0.936	57	62	1614	15	526	P
525	5	G7	0.936	57	62	1631	15	526	P
527	5	G7	0.936	57	62	1648	7	526	P
528	8	P3	0.207	64	95	0006	73	118	P
63838	8	--	--	64	95	0012	67	62028	P
529	8	M7	0.048	64	95	0020	59	119	P
530	8	P3	0.207	64	95	0135	71	118	P
531	8	M7	0.048	64	95	0135	71	119	P
63825	8	--	--	64	95	0135	71	62028	P
532	8	P3	0.207	64	98	0303	59	119	P
533	8	M7	0.048	64	98	0303	59	119	P
63826	8	--	--	64	98	0303	59	62028	P

- NOTES: 1. P = personal; A = area
 2. 24-hour clock
 3. Three-digit sample numbers refer to tubes.
 4. Five-digit sample numbers refer to passive dosimeters with backup section.

TABLE III
B. Data for Sampling Media

PASSIVE CHARCOAL DOSIMETERS		
<u>Compound</u>	<u>n, Desorption Efficiency, %^(2,3)</u>	<u>Sampling Rate (cm³/min.)⁽¹⁾</u>
Methylene Chloride	93	37.8
Carbon Tetrachloride	100	30.3
1,1,1-Trichloroethane	101	30.2
Ethyl Acrylate	83.2	23.3
Butyl Acrylate	86.9	25.3
Chloroform	96	32.9
Toluene	97	34.7

DESORPTION EFFICIENCIES FOR SAMPLING TUBE MEDIA

<u>Compound</u>	<u>n, Desorption Efficiency, %⁽³⁾</u>	<u>Adsorbent</u>
Methyl Methacrylate	96.8	XAD-2
Diethanolamine	66.4	Silica Gel
Methylene Chloride	98.3	Charcoal
Carbon Tetrachloride	98.0	"
1,1,1-Trichloroethane	100.6	"
Xylenes	98.1	"
Ethyl Acrylate	93.6	"
Butyl Acrylate	88.2	"
Chloroform	97.8	"
o-Dichlorobenzene	91.0	"
p-Dichlorobenzene	88.2	"
Toluene	98.4	"

NOTES:

1. Manufacturer's data
2. Manufacturer's data except for EAC and BTC. The DEs for these two compounds were determined individually, as manufacturer's data were not available.
3. All desorption efficiency determinations made at two levels with three replicates per level.

TABLE IV

A. Occupational and Area Monitoring Data for AB2 and AB4 Deck Watches

Sample No.	Terminal No.	Pump No.	Flow Rate, LPM	Average Temp., °F	Average RH, %	Time Start, Hour(s)	Sample Duration, Min.	Blank No.	Sample (1)
100 (3)	1	H1	0.0489	71.8	62	0942 (2)	126	502	P
101	1	4A	0.201	71.8	62	0951	117	502	P
62021 (6)	1	--	--	71.8	62	0942	126	62023	P
102	1	4A	0.201	66.7	88	1811	134	103	P
62022	1	--	--	66.7	88	1814	131	62023	P
104	2	G5	1.01	61	87	0614	107	510	P
105	2	4A	0.201	61	87	0619	102	509	P
106	2	4A	0.201	57.3	77	0847	110	509	P
62024	2	--	--	57.3	77	0851	106	62025	P
107	5	G5	1.067	57	61	1613	15	526	P
108	5	G5	1.067	57	61	1629	15	526	P
109	5	G5	1.067	57	61	1645	10	526	P
113	5	5A	0.149	60.5	54	1129	6	122	P
110	6	G5	1.067	60.5	54	1101	15	111	P
112	5	G5	1.067	60.5	54	1119	26	111	P
114	8	5A	0.149	64	94	0006	68	118	P
115	8	M2	0.0488	64	94	0000	54	119	P
62026	8	--	--	64	94	0020	54	62028	P
116	8	5A	0.149	64	94	0112	82	118	P
117	8	M2	0.0488	64	94	0132	82	119	P
62027	8	--	--	64	94	0112	82	62028	P
120	8	5A	0.149	64	94	0113	54	118	P
121	8	M2	0.0488	64	94	0113	54	119	P
62029	8	--	--	64	94	0120	57	62028	P

NOTES: 1. P = personal; A = area

2. 24-hour clock

3. Three-digit sample numbers refer to tubes.

4. Five-digit sample numbers refer to preservative desiccators with backup section.

TABLE IV
B. Calculated Ambient Vapor Concentrations, ppm

Sample No.	CBT*	DCM	TCE	DEA	EAC	CRF	XLP (1)	TOL	BTC	MMM
100	10.4	<0.9	2.1							
101	9.2	<0.25	2.3							
62021	5.7	<1.3	<0.7							
102	0.5	<0.2	0.5							
62022	<1.6	<1.2	<0.7							
104				<0.3						
105					<0.07					
106					<0.07					
62024					<0.70					
107						31.7				
108						22.4				
109						14.0				
110						30.4				
112						28.6				
113							2.6			
114								15.4	2.6	
62026					2.4			30.6	5.5	<2.1
115					7.0					
116					<0.1			3.2	1.5	
62027					1.5			3.1	5.1	<1.4
117										
120					1.1			5.7	0.3	
62029					2.9			14.1	<0.9	
121										<2.1

* See Table I for abbreviations of chemicals noted.

(1) XLP = paraxylene

o Passive Dosimeters

$$C \text{ (ppm)} = \frac{[W_{CF} + 2.2 W_{CB}]}{n(SR) t} \left(\frac{24.45}{MW} \right) \left(\frac{T + 273}{298} \right) \left(\frac{760}{P} \right)$$

where

W_{CF} = weight of analyte on exposed front strip corrected for blank, ng

W_{CB} = weight of analyte on backup strip corrected for blank, ng

SR = passive sampling rate, cm^3/min .

Other quantities are as defined for the adsorbent tubes.

Barometric pressure readings were not available on the ship. As an acceptable alternative, the barometric pressure at 2400 hours of each day was obtained from the U. S. Weather Service Station nearest to the various terminals. The average pressure and its variation over each 24-hour period are summarized below:

<u>Day</u>	<u>Average B.P., mm Hg</u>
2	765 $\pm$ 0
3	768 $\pm$ 3
4	772 $\pm$ 1
5	771 $\pm$ 2
6	766 $\pm$ 3
7	762 $\pm$ 0

Day 1 is not represented in these data because sampling was initiated on Day 2 after docking at Terminal No. 1. Based upon the low level analyte weights on the adsorbent materials and the barometric pressures relative to standard atmospheric pressure, it was judged that correction of concentrations for pressure was unnecessary. Temperature variations were broader; therefore, ambient concentrations were corrected for sampling temperature.

The following comments are relevant to Table III.C and the analogous part of Table IV.

- o Two types of concentration data are presented. The first type is definitive and corresponds to sampling conditions where the weight of adsorbed analyte exceeded the detection limit of the analytical instrumentation, e.g., DCM concentration for Sample No. 500. The second type corresponds to conditions that produced adsorbed analyte weights that were less than the detection limit of the analytical chemistry instrumentation. These

concentrations are preceded by "<," the less than symbol, e.g., CBT concentration for Sample No. 500. In these latter cases, the concentrations were based on the instrument detection limit by chemical and the actual sampling conditions.

- o Several of the samples indicate the presence of multiple chemical vapors. In some cases, all of these vapors could be designated as "primary" because of the commonality of sampling rates and adsorbents. In other instances, there was a "primary" target vapor, and the potential presence of other fugitive vapors not associated with a work task of interest was documented as being "secondary" in nature. These primary and secondary vapors have a common adsorbent material, but the secondary vapors were sampled at the primary rate. Concentrations of secondary vapors were thus calculated at the sampling rate for the primary chemical vapor. These primary and secondary concentrations are identified in the documentation of deck watch activities.

V. SUMMARY OF DECK WATCH ACTIVITIES AND OCCUPATIONAL EXPOSURES

According to plan, two Deck Department employees were identified, and their work activities and occupational exposures were monitored during Deck Watch Period Nos. 1 through 10 (see Figure 1). Both employees were A/Bs, worked the same watch schedule, and were primarily involved with cargo transfer operations. These individuals are identified as AB1 and AB2 in the following discussions of the work shifts.

Observation of the selected Deck Department personnel was terminated at the conclusion of Deck Watch Period No. 10 and was not resumed at the end of the succeeding 8-hour-off watch period because there would have been insufficient time to remove project equipment from the ship before it sailed. Alternatively, a second pair of A/Bs was monitored during the 4-hour Deck Watch Period No. 11. This decision permitted the loading of all chemicals, except xylene, to be observed in Terminal No. 8.

V.1 Deck Watch Period No. 1

Methylene chloride (DCM) and carbon tetrachloride (CBT) were loaded during the six-hour watch period from 0600 to 1200 on Day 2. During this loading and all succeeding loadings, a tank ullage record board was maintained at a work station that was located on an elevated catwalk approximately midway between the deckhouse and the bow.

The loading hoses for these products were hooked up during the previous shift. At approximately 0611, a 1-ft heel of each product was loaded into the respective tanks. Loading of DCM and CBT resumed at 0930 and 0940, respectively, and was completed by shore stop at 1103 and 1110, respectively. During the period from 0611 to 0930, neither AB1 nor AB2 worked in proximity to Tanks 9CS or 9CP. Their work was performed primarily on the catwalk and included general housekeeping and stowing of fittings and flanges in a midship storeroom.

Work Scenario - AB1

On this shift, AB1 had primary responsibility for gauging these two product tanks. Gauging was performed roughly each half hour beginning at 1000. The general work pattern consisted of remaining at the ullage board on the catwalk between gauging rounds. AB1 descended from the catwalk to an expansion trunk only as necessary to measure ullage. Tanks were gauged manually with a Lufkin tape through the open ullage ports. Because many of the expansion trunks were relatively inaccessible due to deck piping and the fact that the lips of the ullage ports were approximately 50 in. above deck level, gauging was performed while standing on the hatch cover. From this position, the liquid surfaces were sounded with the worker's breathing zone directly over the ullage port at a distance ranging from 3 to 5 ft. The majority of the ullage measurements were made with the body positioned crosswind to the ambient wind direction, which was from starboard to port. In only one instance was the body positioned downwind of the ullage port.

AB1's activities relative to the DCM and CBT tanks are summarized below:

<u>Time</u>	<u>Activity</u>	<u>Duration (sec)</u>
1000	Gauge DCM tank	96
1003	Gauge CBT tank	60
1032	Gauge CBT tank	70
1034	Gauge DCM tank	80
1100	Gauge DCM tank	56
1102	Gauge CBT tank	25
1108	At DCM ullage port for line blow	240
1115	Above CBT tank on catwalk for line blow	144

During the period from 0930 (resumption of loading on the DCM tank) to 1117:24 (completion of line blowing on CBT tank), nearly 12% of AB1's time was devoted to activities that were directly related to these two tanks. Excluding a one-half hour breakfast break and a 15-minute coffee break, the remainder of the work shift was spent at the ullage record board on the catwalk.

AB1's occupational exposures to DCM and CBT were monitored during product loading through the end of the shift. The results are summarized in Table V, where three-digit sample numbers reflect samples collected with pump-tube methods, and five-digit sample numbers refer to passive dosimeters. Note the P-S indicators on vapor concentrations which, for the tube samples, are dictated by the appropriate NIOSH method. For completeness, the tubes were also analyzed for the S vapors. The sampling time exceeded the minimum duration for TWA sampling with tubes in order to reflect the fact that during the majority of the loading time, AB1 was physically located in an area that was judged to have low exposure potential, i.e., on the catwalk. The sampling time was not terminated at the

completion of loading because of the potential for vapor discharge through ullage ports that remained open after loading was completed.

Loading of 1,1,1-Trichloroethane (TCE) into Tank 11P began at 1115 and finished at 1210 after AB1's shift had been completed. His samples were not analyzed for TCE because there was no direct or indirect contact with the area surrounding 11P.

The time preceding 0930 was judged to have negligible potential for exposure and was, therefore, not monitored.

TABLE V
AB1 Occupational Exposures -
Deck Watch Period No. 1

Sample No.	Sample Duration, Min.	C(CBT), ppm	C(DCM), ppm
500	121	<0.3 (P) *	2.3 (S) **
501 } +	133	<0.1 (S)	2.1 (P)
63821 }	116	<1.8 (P)	3.1 (P)

* P = primary compound on adsorbent

** S = secondary compound on adsorbent

+ = parallel samples

Work Scenario - AB2

A large portion of the activities performed by AB2 during his first work shift were in areas where exposure to the chemicals of interest (CBT, DCM, and TCE) were either minimal or nonexistent. As with AB1, actual work documentation and personal sampling of AB2 commenced at approximately 0940 hours. This time coincided with the resumption of loading of tanks 9CS (DCM) and 9CP (CBT). A majority of AB2's responsibilities were concerned with other tanks (12C and 3S) that were being loaded concurrently. It was not until 9CS and 9CP had finished loading that AB2 became involved in activities around these two tanks.

The chemicals loaded into 12S and 3S were caustic soda and polyether polyol, respectively. The work tasks performed by AB2 around 12S were dedicated to ensuring that the 12S product line was clean and free of caustic residue. To facilitate his efforts, the 12S product line was purged with nitrogen supplied by the dock. While purging was in progress, AB2 would open and shut the 12S product valve located near the tank expansion trunk, and also tapped the line with a wrench periodically to jar loose any caustic that had adhered to the inside of the pipe. This

activity commenced at 1000 hours and lasted approximately 35 minutes. Following a 20-minute break period, AB2 was then observed gauging 3S on two separate occasions.

At 1115 hours, the Second Mate on watch instructed AB2 to obtain postloading samples from Tanks 9CS and 9CP. The method for retrieving liquid cargo samples consisted of standing atop the tank hatch (similar to tank gauging) and lowering a glass sample bottle placed in a metal basket through the ullage port opening. AB2 stood both upwind and downwind of the open ullage port during this activity. While waiting for the Second Mate's order, AB2 rested on a horizontal pipe located approximately 5 ft downwind and on the starboard side of 9CS.

The first potential exposure to TCE occurred at approximately 0952 when AB2 retrieved a heel sample from Tank 11P. The preloading sample is taken after a 1-ft "heel" of product has been pumped into the tank. A product inspector takes a parallel sample and sends it to the laboratory for verification of product specification. While the analysis is being performed, loading is stopped and does not resume until approval is received from the laboratory.

Another method for securing the ship's cargo samples was also observed at Terminal 1. This method consisted of collecting a bottle sample of the cargo from the drain valve located at the product loading manifold while cargo is being loaded. This type of sample is known as a line sample. A higher potential for skin contact usually results when line samples are taken because the drain valve opening is usually larger than the opening in the sample bottle. AB2 obtained line samples of DCM and TCE during this first watch period.

A summary of AB2 activities involving possible exposure to DCM, CBT, and TCE during the first watch period is listed below.

<u>Time</u>	<u>Activity</u>	<u>Duration (sec)</u>
0942	Line sample at loading manifold (CBT)	180
0952	Preloading tank sample at 11P (TCE)	120
1108	On standby and retrieving post-loading tank sample at 9CP (CBT)	390
1120	On standby and retrieving post-loading tank sample at 9CS (DCM)	195
1138	Line sample at loading manifold (TCE)	60

AB2's occupational exposures to the three chemicals were monitored using both active (pump and tube) and passive (dosimeters) sampling equipment. A total of three exposure samples were collected simultaneously

during the latter half of AB2's watch (0942-1148 hours). Two of the samples were obtained by the pump-tube method and are noted by the three-digit sample numbers. The five-digit number refers to the passive dosimeter. The calculated vapor concentrations, based on chemical analyses of these samples, are shown in Table VI.

TABLE VI
AB2 Occupational Exposures -
Deck Watch Period No. 1

Sample No.	Sample Duration	C(CBT), ppm	C(DCM), ppm	C(TCE), ppm
100	126	10.4 (S) **	<0.9 (P) *	2.1 (S)
101	117	9.2 (P)	<0.25 (S)	2.3 (P)
62021	126	5.7 (P)	<1.3 (P)	<0.70 (P)

P* - primary chemical of interest based on
NIOSH sampling procedure

S** - secondary chemical of interest

V.2 Deck Watch Period No. 2

This watch period included the hours between 1800 and 2400 on Day 2. As of 1800 hours, the loading of all products had been completed with the exception of the epoxy resin. The ullage ports and expansion trunks for tanks 9CP, 9CS and 11P, which contained the chemicals of interest for Terminal No. 1, had been dogged down on the previous 6-hour watch. Just prior to sailing from this terminal and all other terminals, a quick-setting caulking compound was manually applied to seal the ullage ports and expansion trunks of the tanks that had been loaded in a given port. The purpose of this material was to prevent product vapor loss during transit, and it was applied by crew members other than the A/Bs on cargo transfer watch.

Work Scenario - AB1

AB1 worked on deck from 1800 to 2026. At that time, he left the deck to perform navigation watch duties on the bridge for the remainder of the 6-hour watch. The epoxy resin was loaded into tank 12P, and AB1 performed the following activities in conjunction with that product loading.

<u>Time</u>	<u>Activity</u>	<u>Duration (min.)</u>
1819	Confer with 2/M after coming on watch	7
1830	Gauge 12P	1
1847	Gauge 12P and stand on expansion trunk to monitor line blow	3
1859	Assist dock inspector in collecting epoxy resin sample through Butterworth opening	4
1908	Dog down 12P Butterworth opening	1

The gauging procedure was the same as during the previous watch period. There were no discernible product odors emitted from Tank 12P. During his time on deck, AB1 had no direct work contact with Tanks 9CS, 9CP, or 11P. However, because (1) the ambient wind was from starboard to port and (2) his activities associated with Tank 12P necessitated walking downwind past 9CS, 9CP and 11P to get to 12P, his potential exposures to DCM, CBT, and TCE were monitored. The results of that monitoring are summarized in Table VII. Excluding the time devoted to Tank 12P, the remainder of the deck time was spent either at the ullage board on the catwalk or in performing general housekeeping tasks on the catwalk.

TABLE VII
AB1 Occupational Exposures -
Deck Watch Period No. 2

<u>Sample No.</u>	<u>Sample Duration, Min.</u>	<u>C(CBT), ppm</u>	<u>C(TCE), ppm</u>	<u>C(DCM), ppm</u>
503	140	<0.2 (P)*	<0.1 (P)	<0.2 (S)**
63822 [†]	135	<1.5 (P)	<0.6 (P)	<1.2 (P)

* P = primary compound on adsorbent

** S = secondary compound on adsorbent

† = parallel samples

Work Scenario - AB2

The work activities of AB2 during his second deck watch (1800 - 2400 hours) were divided between various deck duties in preparation for leaving Terminal 1 and standing a navigation watch in the deck house while the ship was in transit to Terminal 2. His deck duties consisted of deck cleanup and assisting in the loading of the epoxy resin (Tank 12P). A summary of specific duties performed by AB2 while on the deck is shown below.

<u>Time</u>	<u>Activity</u>	<u>Duration (min.)</u>
1811	Deck cleanup near port loading manifold	19
1837	Inside deckhouse (actual activity within unknown)	18
1900	Collecting product sample from tank 12P through Butterworth opening	7
1907	Stowage of sample bottle at containment house near midship	10
1920	Bolting blind flanges to loading manifold valves, securing tank openings on products that were loaded at Terminal 1	40

AB2's occupational exposure to DCM, CBT, and TCE was also monitored during his second deck watch, even though the tanks containing these chemicals had been closed during the previous watch (1200 - 1600 hours). As compared to the concentrations obtained during Deck Watch Period No. 1, lower ambient vapor concentrations would be expected during Watch Period No. 2. The vapor levels noted in Table VIII confirm this trend.

TABLE VIII
AB2 Occupational Exposure -
Deck Watch Period No. 2

<u>Sample No.</u>	<u>Sample Duration (min.)</u>	<u>C(CBT), ppm</u>	<u>C(DCM), ppm</u>	<u>C(TCE), ppm</u>
102	134	0.5 (P)	<0.2 (S)	0.5 (P)
62022	131	<1.6 (P)	<1.2 (S)	<0.7 (P)

V.3 Deck Watch Period No. 3

Four products were loaded at Terminal No. 2: Diethylene glycol (DEG), Vinyl acetate (VAM), Diethanolamine (DEA), and Ethyl acrylate (EAC). Deck Watch Period No. 3 encompassed the last six hours of dock time. All products were open loaded and open gauged with the exception of EAC, which was close loaded with vapor return to shore and close gauged through the tank's remote, tape system.

Throughout the loading, the odor of EAC was evident at the starboard manifold, near the expansion trunk, and on the central portion of the catwalk that included the ullage gauging board. The EAC expansion

trunk and ullage board were located aft of the starboard loading manifold. Prevailing winds were from stern to bow. The presence of EAC odors suggests that the vapor return system was operated under slight positive pressure, thus permitting fugitive emissions through expansion trunk and ullage port seals as well as at on-deck flange couplings on the return line.

Normally, product samples are collected for quality control purposes. These samples may be collected either through the ullage port or at the slip stream valve on the manifold. The DEA samples were collected at the manifold by a Mate that wore (1) a full-face respirator with an organic vapor cartridge and (2) rubber gloves. While standing on the drip pan grating, approximately two liters of DEA were discharged into the drip pan from a height of roughly 3 ft. Rubber boots were not worn, and the DEA splashed onto his work boots and pants.

Work Scenario - AB1

AB1 worked on deck from 0600 to 1035. He then went to the bridge on navigation watch to prepare for the departure to the next terminal. There were two work breaks--30 minutes for breakfast at 0720 and a 15-minute rest break at 1005. Therefore, total deck time during cargo transfer was 230 minutes on this shift. AB1's activities that pertain to cargo transfer are summarized below.

<u>Time</u>	<u>Activity</u>	<u>Duration (sec)</u>
0633	Gauge DEG tank	104
0642	Gauge DEA tank	180
0649	Observe second A/B collecting VAM sample at 9P	60
0830	Gauge VAM tank	102
0929	Gauge VAM tank	38
1023	Gauge EAC tank	600
1031	Gauge EAC tank	240

With the exception of the EAC tank, all gauging was performed while standing on the expansion trunk hatch. Consistently, AB1's breathing zone was roughly 4 ft directly above the open ullage port. The length of time needed to gauge the DEA tank was longer than the time to open gauge the other tanks because of difficulty in maintaining visual contact with the liquid surface. This difficulty resulted from the fact that the warm DEA vapors aerosolized upon contact with the ambient temperatures that were roughly 12 to 15°C below the freezing point of DEA, thus giving the appearance of a "smoke" discharge from the tank.

AB1 remained at the ullage board on the elevated catwalk during periods when he was not involved with the indicated tank monitoring

activities. As mentioned earlier, this procedure was followed quite consistently during the entire observation.

Occupational exposures to DEA and EAC were monitored in two stages-- from the beginning of the shift until breakfast and then after breakfast until AB1 left the deck for the bridge. The results are summarized in Table IX. The passive dosimeter served as a parallel monitor for Sample No. 511. Sample Nos. 507 and 511 represent consecutive samples for EAC before and after mealtime. Sample Nos. 508 and 512 are also consecutive samples but for DEA.

TABLE IX
AB1 Occupational Exposures -
Deck Watch Period No. 3

Sample No.	Sample Duration, Min.	C(DEA), ppm	C(EAC), ppm
507	69	--	<0.1
511	151	--	<0.1
63823 } [†]	143	--	<0.5
508	66	<0.6	--
512	93	<0.4	--

[†] = parallel samples

Work Scenario - AB2

During AB2's third 6-hour watch, approximately 4.5 hours (0600-1035) were spent on deck performing various cargo transfer duties. He was stationed in the wheelhouse on navigation watch for the remaining 1.5 hours while the ship moved to Terminal 3. Work breaks during his deck watch activities for breakfast and coffee totaled 51 minutes. Consequently, a total of more than 3.5 hours of work activities relating to EAC and DEA were observed and documented. Occupational exposures were also monitored during this time period.

Some of AB2's work activities consisted of tank gauging and collecting cargo samples from the tanks. With the exception of Tank 9S (EAC), all tanks were gauged through an open ullage port. The 9S tank was closed and gauged using the ship's tape gauging system. Vented vapors from 9S were returned to shore by means of flexible tubing connected to the tank's vapor return connection. AB2 wore a full-face mask with an A-200 Draeger cartridge during his initial gauging rounds. However, for the bulk of his watch time, he gauged without this safety equipment.

AB2 also spent a considerable amount of time at two other locations not related to the activities mentioned above. One of the locations was at the center walkway where a total of 46 minutes was consumed recording tank ullage readings on the ullage board. The other predominate location was near the starboard loading manifold, which was located downwind of both 7S (DEA) and 9S (EAC). The majority of the time spent at the manifold was at deck level. His primary activity was devoted to assisting the Second Mate in collecting a line sample of EAC from the 9S product line drain valve. When not at deck level, AB2 was observed on the elevated walkway above the loading manifold. This walkway was approximately 12 ft above deck and extended over the entire (length of the product) manifold piping. A summary of activities during this watch period between 0600 and 1035 hours is shown in Table X.

TABLE X
AB2 Work Activities -
Deck Watch Period No. 3

<u>Activity</u>	<u>Frequency</u>	<u>Duration (Min.)</u>
Near starboard loading manifold (at deck level)	4	4, 2, 20, 5
On starboard loading manifold top platform	2	5, 12
9P (VAM) tank sample through ullage port	1	8
Gauging 9P (VAM) tank	8	Approx. 1 min. each
Gauging 4CS (DEG) tank	2	3, 1.5
4CS (DEG) tank sample through ullage port	1	3
Gauging 7S (DEA) tank	4	2, 1, 2.5, 0.5
Closed gauging of 9S (EAC) tank	3	Approx. 0.75 min. each
Standing atop 9S tank hatch up- wind of open ullage port to confirm product flow	1	6
At ullage board at center cat- walk	10	4, 2, 2, 13, 2, 5, 1, 2, 10, 4

AB2's cargo transfer activities lasted for a longer period of time on this watch as compared to similar activities noted during the preceding two deck watches. As a result, two consecutive sets of personal exposure samples were collected and are noted in Table XI. The first set includes samples 104 and 105 and represents AB2's exposure concentration to DEA and EAC, respectively. These samples were collected before his

breakfast break. When he returned back on deck, the loading of 7S had finished. Consequently, AB2 was monitored only for EAC exposure during the second period. The two samples obtained during this period consisted of a parallel measurement using both active and passive sampling equipment.

TABLE XI
AB2 Occupational Exposures -
Deck Watch Period No. 3

Sample No.	Sample Duration, min.	C(DEA), ppm	C(EAC), ppm
104	107	<0.3 (P)	--
105	102	--	<0.07 (P)
106	110	--	<0.07 (P)
60624	106	--	0.70 (P)

V.4 Deck Watch Period No. 4

This 6-hour watch occurred in the middle of the dock time at Terminal No. 3. Toluene diisocyanate (TDI) was loaded during this watch. Originally this product was to have been loaded on the previous shift, but a decision had been made to delay the loading to the 1800 to 2400 hour watch so that food stores and nitrogen cylinders could be taken aboard first. While these items were being transferred, the 8CS tank was being prepared to receive the TDI by purging it with nitrogen from a dock supply source. TDI was listed in the cargo log book as the previous product that had been carried in this tank. The transfer hose for TDI was connected by the personnel on the previous watch; no special procedures or equipment was observed when this connection was made.

At approximately 1730, the cargo officer and an A/B put on full-body protective suits and self-contained breathing apparatus (SCBA) with full-face masks. They were assisted by a second A/B, who then left the deck. Loading began, and shortly thereafter, the A/B went to the stern end of the deck where he removed his suit and SCBA because it was heavy and cumbersome. He did not return to the deck. As a safety precaution, no one was to be permitted on deck while the TDI was transferred unless he had a product-related responsibility and then only if the proper protective equipment were being worn. The crew quarters and mess were alerted to this requirement.

The cargo transfer officer was then the only crew member on deck. At the beginning of loading, the Mate monitored the transfer visually through the open ullage port until he was satisfied that the product was being delivered to the proper tank. At that point, he dogged down the ullage port and ascended to the catwalk, where he removed the SCBA at

its connection to the face mask and replaced it with an organic vapor cartridge. As the TDI was now being close loaded with vapor return to shore, all subsequent gauging was based on the remote tape system on the tank.

The Mate did not remain on deck throughout the loading; the weight of the suit and the environmental temperature of nearly 40°F necessitated rest breaks that were taken in the ship's office.

While the safety precautions with respect to protective equipment and personnel on deck were uniformly applied at the initial stages of loading, these precautions were not consistently applied throughout the loading. At one point during the loading, two other individuals were on deck without protective equipment. One was a Mate who worked forward of the TDI tank. The other was a day worker who was relocating nitrogen cylinders on the forward starboard deck. From the dockside, the transfer of TDI was monitored by one individual who was not equipped with any protective clothing or respirator.

AB1 did not work on deck during this shift. Prior to completing the TDI loading at 2145, AB2 put on the protective suit and full-face mask with adsorbent cartridge. He then assisted the dock workers in disconnecting and blinding the loading hose and manifold flange. A special blind was used on the hose, and it permitted methylene chloride (MEC) to be injected into the line by a portable pump. The loading hose is then backflushed to shore against the closed valve on the ship's manifold. The MEC serves as a solvent that removes TDI residue from the hose so that it does not polymerize.

V.5 Deck Watch Period No. 5

The scheduled departure from Terminal No. 3 was delayed six hours because the Polyol was loaded at a low rate from a series of tank trucks. Consequently, the six-hour Watch Period No. 5 took place while the ship was underway from Terminal No. 3 to Terminal No. 4. With the exception of a 45-minute period during which AB2 assisted the Bosun in securing the ship's bow line, both AB1 and AB2 were on navigation watch for the entire shift.

Because Chloroform (CRF) was to be discharged at Terminal No. 4, the decision was made to extend the project observation time on deck and obtain information relative to this operation.

At 1235, the starboard manifold flange to the CRF tank was removed, and hose hookup proceeded. During this operation, the wake from a passing vessel caused a stern spring line to snap and the ship to move away from the dock. As the ship recoiled toward the dock, the discharge hose was damaged when it became trapped between the hull and the dock bumper. The damaged hose was removed from the ship's manifold at 1340. During this period of time, an area sample (Sample No. 513) was collected by taping the pump and sampling medium to the manifold flange for Tank 4S, which was located directly adjacent to the CRF flange. The separation

distance between flanges was approximately 2 ft. This sampler was placed in that work location because of the presence of CRF odor from the exposed manifold ball valve and the presence of EAC odor from Tank 9S. A new hose was then delivered to the dock; reconnect was resumed at 1413, and the discharge began at roughly 1500. Sample No. 514 was collected during this 43-minute period and at the same location as Sample No. 513. Between 1239 and 1500, a Mate and an A/B were present in that work area for a majority of their time.

After the discharge began, active and passive area samplers were placed in parallel at the ullage board on the catwalk. This location was selected because (1) it was the established work station between tank gaugings and (2) because of the increased amount of foot traffic on the catwalk in support of bringing stores onto the ship. Since the wind was from starboard to port, Sample No. 515 was set up primarily for CRF. Passive Sample No. 63824 was intended for CRF and EAC; the odor of the latter product was apparent on the catwalk.

The results of these area samples are presented in Table XII.

TABLE XII
Area Samples in Terminal No. 4

Sample No.	Sample Duration, min.	C(CRF), ppm	C(EAC), ppm
513	61	<0.08 (P)*	<0.02 (S)*
514	43	<0.1 (P)	<0.03 (S)
515 } 63824 } [†]	96	0.4 (P)	<0.01 (S)
	89	<1.7 (P)	<0.8 (P)

* P = primary compound on adsorbent

** S = secondary compound on adsorbent

† = parallel samples

V.6 Deck Watch Period No. 6

This watch period in Terminal 4 encompassed the hours of 1800 to 2400 on Day 4. Chloroform discharge proceeded throughout this shift. ABl's product transfer responsibilities were assumed by the second Mate on duty. Throughout this shift, ABl transferred ship's stores from trucks on the levee road over a distance of roughly 100 yards to the dock on the starboard side of the ship. He participated in loading these stores into nets; the stores were then taken aboard by crane. ABl did not board the ship until the end of his shift.

Occupational exposure monitoring was not performed on this shift. This decision was justified on the basis that:

- o the discharge proceeded without interruption, and, under these conditions, prior experience indicates that vapor emissions are virtually nondetectable because air is ingested into the tank, and
- o the prevailing winds were from starboard to port.

These two factors combined to produce an extremely low probability of exposure during those stated hours.

The cargo transfer officer in charge of discharge gauged the CRF tank on an hourly basis, and the gauging time was nominally one minute in each case. The stores were transported from shore to the deckhouse entrance by a traveling crane. The crane operator's (AB2) work station was estimated to be 15 ft above the elevated catwalk. His exposure potential was likewise judged to be negligible.

V.7 Deck Watch Period No. 7

Deck watch period No. 7 took place between the hours of 0600 and 1200 on Day 5 in Terminal No. 5. The only product loaded at this terminal was mixed isomers (o, p) of dichlorobenzene (DBO and DBP). Loading began into Tank 13S at 0600 and finished at 1250 on the next shift. This product was open loaded and close gauged through the tank's remote tape system.

Each of these isomers has a distinctly different freezing point and odor property. DBO freezes at 0.3°F, while DBP freezes at 130°F. DBO has a pleasant, aromatic odor, and the odor of DBP is similar to mothballs.

The product was loaded at a temperature in excess of the freezing point of DBP. As the vapor space above the liquid was discharged from the tank, the vapor was cooled below the freezing point of DBP, and crystals of that isomer grew on the flame screen and the lip of the ullage port. The odor of DBP was apparent at several points on deck, which suggests that the DBP was subliming. The odor of DBP masked the odor of the DBO isomer since the threshold odor concentration for DBP is lower than that of DBO. This analysis also suggests that the vapors of both isomers were present in the work environment.

Work Scenario - AB1

The initial plan was that AB1 would manually gauge the DBO/DBP tank (Tank 13S) every 30 minutes using a Lufkin tape. This plan was subsequently modified in two respects.

- o The tank was not manually gauged through the open ullage port. Rather, the remote system was used.

- o ABl gauged the tank only once.

The expansion trunk for Tank 13S was approximately 10 ft from the entrance to an equipment storeroom that was located on the starboard side of the deckhouse on the main deck level. The majority of ABl's work time was spent between the dock, midship, and the bow. However, his work activities necessitated several trips aft to the storeroom to retrieve equipment that was needed forward.

There were only two times when ABl was directly involved with Tank 13S.

- o The time occurred at 0615, and for approximately two minutes, he was dogging down the Butterworth covers on the DBO/DBP tank.
- o At 0858, ABl gauged Tank 13S using the remote system, which was located roughly 17 ft toward the bow from the expansion trunk. The duration of this activity was three minutes, which was longer than usual because the low ambient temperature had caused the viscosity of the tape lubricant to increase with a corresponding increase in system response time.

As Tank 5C (CRF) was to be cleaned, ABl was involved with dockside hookup of the washwater line and its on-deck connection. Prior to the hose hookup, he had made two round trips from Tank 5C to the storeroom past Tank 13S to bring blowers back to the CRF tank. His time in proximity to Tank 13S was minimal and was limited to the time to walk past the tank, pick up the blower, and walk back past the tank. Other midship activities included a 12-minute period to assist in removing the starboard manifold flange for the CRF tank, a 20-minute effort to repair a diaphragm stripping pump on the catwalk above Tank 5C, and a 4-minute period that was spent in conversation at the starboard manifold.

At approximately 1015, a bow mooring line broke. ABl was one of several crew members that were involved in replacing the line, and as a part of this activity he made three trips to the storeroom near Tank 13S to get needed equipment and supplies. His total cumulative time in proximity to the DBO/DBT tank was 12.5 minutes for this operation.

The wind direction was quite variable during this shift. Initially, the wind was from stern to bow, but it shifted to port to starboard at roughly 0930. Occupational exposure monitoring was conducted primarily for DBO and DBP, but the variability of the wind and presence of CRF and EAC odors admits the possibility that these latter products could appear on the sampling medium as secondary compounds. Area samples were also collected with the sampling apparatus taped to the DBO/DBP expansion trunk at breathing zone height. The area samples were intended to characterize the environment in the vicinity of foot traffic past the tank.

The results of these samples are summarized in Table XIII. Sample No. 518 was intended to be a short-term exposure sample during manual gauging of the DBO/DBP tank through an open ullage port. As mentioned earlier, this gauging procedure was changed with the result that AB1 did not gauge the tank. Nevertheless, it represents a short-term exposure measurement for DBO. The work shift included two breaks: a 30-minute break for breakfast and a 30-minute work break. AB1 did not wear a monitor during these breaks.

AB1's time on deck terminated at 1130. His sampling apparatus was removed, and the remainder of his shift was spent in the deckhouse.

TABLE XIII
AB1 Occupational Exposures -
Deck Watch Period No. 7

Sample No.	Type	Sample Duration, min.	C(DBO), ppm	C(DBP), ppm	C(CRF), ppm	C(EAC), ppm
517	Personal	63	<0.3 (S) **	<0.4 (P) *	--	--
518	Personal	16	<0.3 (P)	<0.3 (S)	--	--
519	Personal	70	<0.3 (S)	<0.3 (P)	7.9 (S)	0.4 (S)
521	Personal	60	<0.4 (S)	<0.4 (P)	<1.7 (S)	<0.5 (S)
520	Area	69	3.6 (P)	12.4 (S)	--	--
522	Area	69	2.5 (P)	8.1 (S)	--	--

* P = primary compound on adsorbent

** S = secondary compound on adsorbent

Work Scenario - AB2

Documentation of AB2 worker activity during this deck watch period was cancelled because he was not going to be involved in cargo transfer operations or work in areas where potential exposure to chemical vapors could occur. Instead, the decision was correctly made to observe and monitor the cleaning of Tank 5C, which had held chloroform and had been previously discharged at Terminal 4. AB2 was not involved in the tank cleaning activity, but did bring some tank cleaning equipment to the tank prior to the beginning of cleaning operations. The remainder of his time was spent in loading and transfer of stores onto the ship.

A detailed discussion of the cleaning observation is given in Section VI.2.

V.8 Deck Watch Period No. 8

Propylene oxide (POX) and n-propyl acetate (PAT) were loaded at Terminal No. 6. The deck watch period from 2000 to 2400 was the first 4-hour watch following the work schedule change that had been mentioned earlier. By the close of this watch period, only the loading hoses had been connected by deck personnel other than the A/B's that were being observed. Also, during this period, the double bottom and double skin around the POX tanks (5P and 5S) were purged with nitrogen from a shore supply. This operation, which included periodic measurements of oxygen and combustible gas levels in the double skin, was performed by the Mate on watch.

As there was no cargo transferred on this watch, AB1 and AB2 concentrated on maneuvering spent nitrogen cylinders on the forward portion of the deck.

Occupational exposure monitoring was not attempted on this shift because loading status, the A/B's work activities, and strong quartering winds combined to produce a negligible exposure probability.

V.9 Deck Watch Period No. 9

This 4-hour work period occurred on Day 6 from 0800 to 1200. From 0800 to 0900, the ship was underway to the next berth at Terminal No. 7. Both AB1 and AB2 were on the bridge performing their assigned navigation watch duties. Caustic soda (SHD) was to be loaded into Tank 12C after docking. This tank had previously carried 100 percent hydrogen peroxide (HPO). SHD was not included in the sampling plan; however, the cargo transfer work activities were documented.

Work Scenario - AB1

At 0900, AB1 was relieved from navigation watch and resumed his deck watch duties. During the next 40 minutes, he worked on the stern deck and assisted in the transfer of mooring lines between the tug and the ship and in the final securing and winching of all mooring lines. From 0940 to 0950, he helped set and secure the port gangway. The next several minutes were spent in general housekeeping duties on the catwalk between the ullage board and midship storeroom. His next activity consisted of assisting the 2M in removing the manifold flange for the SHD loading line. This activity took approximately 10 minutes, and both crew members wore rubber gloves and boots. The type of rubber in these items could not be determined; neoprene is the USCG-recommended material of choice.

For 20 minutes, beginning at 1035, AB1 stood on the 12C trunk hatch to view the initial stages of product loading. This activity is common practice and is used to ensure that delivery from the shore tank is underway and that the product is loaded into the proper tank. During this 20-minute period, several visual sitings were made, and the duration of each siting was 10 - 15 seconds with the breathing zone roughly four feet above

the ullage port. AB1 and all other members of the cargo handling watch wore chemical goggles and rubber gloves. Slicker gear was also worn because it was raining.

After this initial visual gauging activity, AB1 returned to the catwalk and did not gauge the tank during the remainder of the loading.

The SHD was loaded through a deck line that could deliver product to 12P, 12C, or 12S. In this case, 12P and 12S were isolated by closed ball valves on the crossover lines to these tanks. SHD leakage past these valves could potentially contaminate the products in 12P and 12S. To check on this possibility, the crossover lines to the P,S tanks have a "ring cup" attached to the bottom of the line downstream of the isolation valves. Any product leakage past these valves would accumulate in the open ring cup and be visible. AB1 made several checks of the ring cups; there was no leakage past these crossover valves.

From 1100 to 1145, AB1 worked on the catwalk carrying equipment to the forward storeroom. The loading terminated at 1145. When the loading was finished, AB1 came aft to the 12C expansion trunk to collect product samples in bottles. He wore all of the previously mentioned protective equipment; however, the sampling procedure resulted in skin contact with SHD. When the drop line, bottle cage, and the bottle were removed from the tank, they were coated with a film of SHD, and the product was transferred to the exterior surface of the protective gloves. One glove was then removed so that he could retrieve the bottle cap from his pocket. His bare hand was then partially inserted into the glove, which was then pulled into place using the thumb and index finger on the other gloved hand. To accomplish this, the thumb on the gloved hand was placed inside the cuff of the other glove. In pulling this glove into position, SHD was transferred to the skin on the wrist. This event occurred at the end of the shift, and AB1 went to the deckhouse to wash up.

Work Scenario - AB2

The first hour of this 4-hour watch period was spent in the wheelhouse while the ship was in transit to Terminal No. 7. As the ship was docking, AB2 was on the bow deck operating the starboard mooring line winch and securing the ship to the dock. Following this activity, AB2 took a 15-minute coffee break. Upon returning to the deck, he stationed himself atop the port side loading manifold top platform observing hookup of the caustic soda loading hose.

At approximately 1100, SwRI was notified that two cargo tanks were to be entered (1S and 5C) for final sponging and preparation for loading at Terminal No. 8. Since the chemicals being loaded at Terminal No. 7 (caustic soda and Niax Polyol) were not on the sampling plan and exposure to other chemicals was minimal to nonexistent, observation of the final hours of AB2's morning deck work period was cancelled. Instead, the tank entries into 1S and 5C were documented and monitored. These observations are contained in Section VI.3.

V.10 Deck Watch Period No. 10

Six products were loaded at Terminal No. 8: mixed xylenes (XLO, M, P), vinyl acetate (VAM), toluene (TOL), methyl methacrylate (MMM), ethyl acrylate (EAC), and butyl acrylate (BTC). The TOL and XLOMP were loaded from two barges through the port manifold, while the remaining products were loaded through the starboard manifold.

There were three factors that limited the work activities relative to loading these chemicals.

- o The barge did not have either the correct line reducers or sufficient lengths of loading hose to reach the port manifold.
- o The dock was understaffed, and starboard hose hookup was delayed, but was eventually accomplished by the 2M, the cargo inspector, and two dock workers.
- o Diesel oil for the electrical generators and fuel oil for the main engine were to be taken aboard. Because the loading time for these fuels (not chemical loading time) controlled total dock time, the primary emphasis was placed on initiating fuel loading as soon as possible.

The ship eventually supplied the needed reducers and loading hoses for the port manifold, and both AB1 and AB2 were involved in connecting these items. Product hose hookup was completed near the end of the shift, but loading of chemicals was not initiated. Engine room personnel were responsible for monitoring the loading of the fuels, and there was some concern regarding either the purity or correctness of the fuels. Fuel loading was terminated until this issue was resolved. In the interim, the A/Bs and other crew members were involved with disconnecting and reconnecting fuel delivery lines.

Because of these factors and the fact that it rained throughout the shift, most crew members remained under cover when they were not involved in specific activities. Given these circumstances, occupational exposure monitoring was not conducted.

The ship was scheduled to sail at about 0930 on the next day (Day 7). AB1 and AB2 were due on watch at 0800 on Day 7. This situation would have resulted in insufficient time to monitor their activities and to remove project equipment from the ship before it sailed. Therefore, the decision was made to continue the observation during the 0000 to 0400 shift. In retrospect, this decision permitted the observation of the loading of all chemicals except xylene, which was loaded on the 0400 to 0800 shift.

Two new A/Bs were observed between 0000 and 0400. Documentation for that watch is presented in Section V.11. The personnel are designated AB3 and AB4.

V.11 Deck Watch Period No. 11

The rain stopped shortly after the beginning of this work shift. Therefore, exposure monitoring was conducted, as well as work documentation. AB3 was generally responsible for gauging the starboard tanks (MMM-10S and VAM-1S) plus the fuel oil in 2C. AB4 had general responsibility for the port tanks (BTC-7P, EAC-8P, and TOL-1P). However, on occasion, there was cross gauging by both A/Bs. A very light breeze was present, and its general direction was from the bow to the stern.

Work Scenario - AB3

AB3's product and fuel oil-related activities are summarized below.

<u>Time</u>	<u>Activity</u>	<u>Duration (sec)</u>
0025	Gauge TOL tank	91
0029	Gauge fuel tank 2C	120
0038	Dogdown hatch cover on 2C	420
0051	Gauge MMM tank visually, dogdown hatch cover	130
0111	Gauge MMM tank	140
0143	Gauge MMM tank	64
0153	Dogdown Butterworth covers on MMM tank	360
0159	Gauge MMM tank	88
0202	Gauge VAM tank	73
0225	Gauge VAM tank	60
0228	Gauge fuel tank 2C	82
0232	Gauge MMM tank	50
0307	Gauge MMM tank	40
0330	Inspect underside of deck piping for leaks and randomly dogdown hatches and Butterworth covers	15 min.
0353	Assist 2M setup valves at starboard manifold in preparation for blowing VAM line	6 min.

The manual gauging was always performed with a Lufkin tape through open ullage ports, but the procedure varied with the tank. In the case of the MMM tank, the procedure did not include standing on the expansion trunk, which had been the procedure on previous shifts. Rather, AB3 stood on low-level deck piping which placed his breathing zone one to two feet directly above the open ullage port. The TOL tank was gauged in a similar fashion.

Three sequential sets of occupational exposure samples were collected during this shift. Each set consisted of (1) parallel active and passive dosimeters for EAC, BTC, and TOL and (2) active dosimetry for MMM. The resulting exposure concentrations are contained in Table XIV.

In this terminal, none of the acrylates were closed loaded with vapor return. Consequently, the odor of EAC was quite pronounced on the starboard deck aft of the manifold area and on the catwalk near midship. The intensity of the EAC odors increased significantly when the loading line was blown from the shore at approximately 0145. MMM odor was apparent at and downwind of the IOS expansion trunk. BTC odor could not be identified individually on the starboard deck and was probably masked by the EAC odor. While it is recognized that odor intensity is not a reliable indicator of exposure level, the purpose of discussing odor is to indicate that AB3's work environments contained at least low-level concentrations of multiple vapors even during excursions onto the catwalk to gauge 2C.

TABLE XIV
AB3 Occupational Exposures -
Deck Watch Period No. 11

Sample No.	Sample Duration min.	C(EAC), ppm	C(BTC), ppm	C(TOL), ppm	C(MMM), ppm
528 } ⁺	73	<0.1	<0.07	1.6	--
63838 } ⁺	67	<1.1	<0.6	<2.1	--
529	59	--	--	--	<2.0
530 } ⁺	71	1.1	<0.07	<0.05	--
63825 } ⁺	71	<1.0	<0.6	<0.30	--
531	71	--	--	--	<1.7
532 } ⁺	59	<0.1	<0.09	0.5	--
63826 } ⁺	59	<1.2	<0.7	<0.4	--
533	59	--	--	--	<2.0

+ = parallel samples

Work Scenario - AB4

The work scenario of AB4 during the final shift was an active one. During his shift, he performed activities similar to those explained previously for a product loading watch. These activities included gauging and retrieving tank samples from those tanks for which he was responsible. He also assisted in securing the toluene and xylene barges to the ship.

TABLE XV
Summary of AB2's Activities

<u>Activity</u>	<u>Frequency</u>	<u>Duration, min.</u>	<u>Time</u>
Dogging down Butterworth and tank hatch bolts for 7P (BTC) and 8P (EAC) tanks (Note: OVA reading in vicinity was 30-50 ppm as methane)	1	40	0006
Gauging 2C (fuel oil)	1	1.5	0056
Gauging 1P (TOL) tank	3	{ 1.5 1.0 1.5	0058 0137 0157
Collecting ship tank sample of 1P (TOL) through ullage port	1	1.5	0159
Gauging 1S (VAM) tank	2	{ 1 1	0100 0137
Gauging 7P (BTC) tank	3	{ 1.5 0.75 1.5	0109 0134 0205
Gauging 8P (EAC) tank	2	{ 2 0.75	0111 0134
Gauging 10S (MMM) tank	1	2	0141
Collecting line sample of (MMM) at loading manifold valve of 10S	1	6	0150
At center catwalk ullage board	2	{ 2 5	0135 0145
Coffee break	1	14	0210
Operating deck crane and assisting Second Mate patching up flange leak on 1S (VAM) product line near 1S tank hatch	1	27	0225
Futile attempt to collect line sample of 7P (BTC) at loading manifold valve	1	15	0314
Assisting Barge Tankerman in xylene barge tie-up	1	19	0335
Collecting 7P (BTC) tank sample for SwRI	1	3	0354

Since this was the final terminal prior to sailing on the laden voyage, he spent a significant amount of time securing bolts on the openings of all tanks that were being loaded. A detailed summary of AB4's activities is listed in Table XV.

AB4's occupational exposure to EAC, BTC, and TOL during his work shift was monitored using both passive and active personal sampling equipment. His potential exposure to MMM was obtained with pump and sample tube only. During the 4-hour watch, three consecutive sets of personal samples were collected. The measured exposure concentrations are shown in Table XVI.

TABLE XVI
AB4 Occupational Exposures -
Deck Watch Period No. 11

Sample No.	Sample Duration min.	C(EAC), ppm	C(BTC), ppm	C(TOL), ppm	C(MMM), ppm
114	68	2.4 (P)	2.6 (P)	15.4 (P)	--
62026	54	7.0 (P)	5.5 (P)	30.6 (P)	--
115	54	--	--	--	<2.1 (P)
116	82	<0.1 (P)	1.5 (P)	3.2 (P)	--
62027	82	1.5 (P)	5.1 (P)	3.1 (P)	--
117	82	--	--	--	<1.4 (P)
120	54	1.1 (P)	0.3 (P)	5.7 (P)	--
62029	54	2.9 (P)	<0.9 (P)	14.1 (P)	--
121	47	--	--	--	<2.1 (P)

VI. SUPPLEMENTARY TESTING ACTIVITIES

In order to maximize the productivity of this voyage observation, several additional tests were performed. These supplementary tests contribute to the overall understanding of chemical tankship operations, and they are documented in the following sections.

VI.1 Surveyor Inspection of Cargo Tanks

Before a tank is loaded with a given chemical, the usual procedure is that a cargo surveyor, who is retained by and represents the purchaser of the chemical, will enter and inspect the tank for the presence of moisture, debris, odor, or previous product residues. All of these factors can influence the product purity and its compatibility with its intended use.

Two surveyors boarded the ship at Terminal No. 2 for a pre-loading inspection of Tanks 7S and 9P, both of which had previously held m-xylene. These tanks had been cleaned prior to docking at Terminal No. 1. The inspectors tested each tank atmosphere with an O₂/combustible gas indicator before entering. These tests were made at one location in the tank with a drop line through the open dome on the expansion trunk. Vessel personnel witnessed the tests, but did not conduct an independent evaluation.

One inspector entered each tank and was accompanied by one member of the project team who monitored the atmosphere with the OVA and who wore personal dosimeters. Ventilating blowers were not operated during entry; the Second Mate and the remaining surveyor stood safety watch at the expansion trunk.

The monitoring results are given in Table XVII. The instrumental concentrations that were obtained with the OVA are believed to be more accurate than the concentrations obtained using charcoal tubes because high humidity (93 percent in-tank) is known to severely affect the adsorption of xylene, and the amount of xylene deposited on the charcoal under these sampling conditions is considerably outside the range over which the analysis method has been validated.

TABLE XVII
Summary of Xylene Concentrations
During Surveyor Tank Inspection

Tank No.	Duration, min.	Sample No.	Exposure Concentration, ppm	Instrumental Concentration, ppm
9P	5	504	4.2	12
7S	4	505	<0.3	9

VI.2 Tank Cleaning (Washing and Ventilation)

One complete tank cleaning operation was observed and documented. The tank, 5C, had previously carried chloroform and was being prepared to receive xylene at Terminal No. 8. Cleaning commenced at approximately 0900 hours and continued until 1607 hours of the same day. AB1 and AB2 moved washing and ventilation equipment to Tank 5C, but were not involved in the tank cleaning operation.

The ship's tank cleaning book contained the following cleaning procedure for a chloroform to xylene product change.

- o Tank washing with cold water (1 hour)

- o Tank washing with hot water and one percent solution of detergent, synthetic soap, or emulsifier (2 hours)
- o Tank washing with hot, fresh, or sea water (1 hour)
- o Steam cleaning
- o Draining of tank, lines, and pump
- o Gas free to dryness

The actual procedure that was used is summarized below:

- o Prewash ventilation of chemical residue in-tank (approximately 1.5 hours) (two blowers operating in supply mode)
- o Tank washing with cold water (approximately 1.0 hour) (one blower operating in supply mode)
- o Tank stripping of residual wash water/chemical (approximately 0.25 hour) (no ventilation)
- o Gas freeing to dryness
 - (one blower operating in supply mode; approximately 1.0 hour)
 - (one blower operating in supply mode and one blower in exhaust mode; approximately 0.75 hour)
 - (two blowers operating in supply mode; approximately 3.0 hours)

In the supply mode, the blower discharges fresh air into the tank. In the exhaust mode, the blower discharges vapor-laden air from the tank.

The chloroform vapor discharge concentration was measured at the expansion trunk with an OVA 108 during the entire tank cleaning process. The concentration-time history is shown in Figure 2.

The first operation in the cleaning process was a prewash ventilation for approximately 90 minutes using two air-driven, portable blowers (ATCO Marine Corp., Model PB-12). Initially, the chloroform concentration was 2950 ppm, and at the end of this period, the concentration had decreased to a nearly constant level of 800 ppm. Based on blower capacity ratings, the total ventilation flow rate was estimated to be 270 m³/min. If the tank had contained only vapor (no residual cargo), the gas-freeing process would have followed the theoretical dilution curve, which has a slope defined by the ratio of blower flow rate to tank volume. Departure from the ideal curve represents a time delay that results from evaporation of pure chemical from the tank interior surfaces.

<u>PRE-WASH VENTILATION</u>	<u>GAS FREEING</u>	<u>STRIPPING</u>	<u>GAS FREEING</u>	<u>GAS FREEING</u>
o Two blowers in operation	o One blower and one washing machine in operation	o No blowers operating	o One blower in operation o Tank stripping operation has ceased	o Two blowers in operation o Port blower in supply mode o Starboard blower in exhaust mode

TANK VOLUME = 1903 m³
corrected to 100% capacity

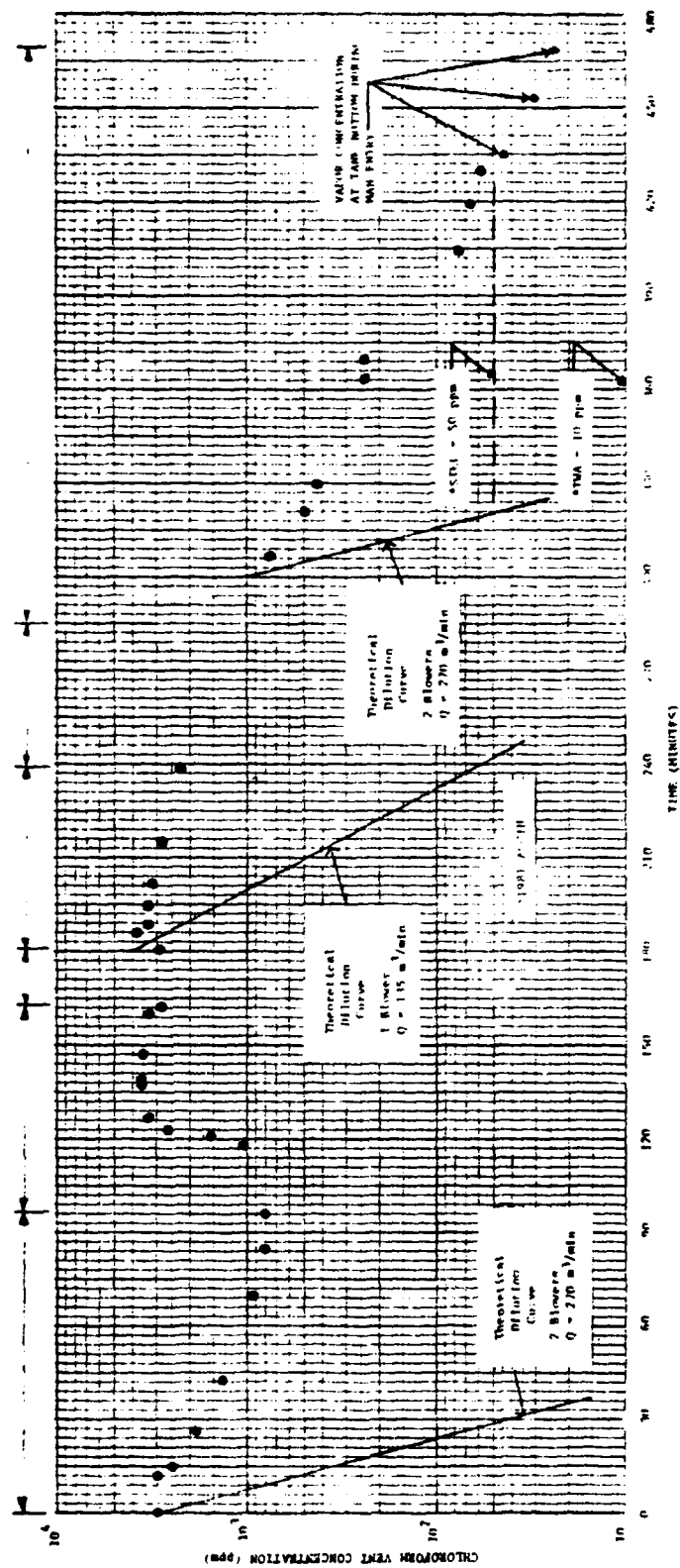


FIGURE 2. CHLOROFORM CONCENTRATION AT EXPANSION TRUNK DURING CLEANING OF TANK 5C

Following the initial ventilation operation, the tank was washed with fresh water. Portable washing machines were lowered into the tank through the same Butterworth openings that the blowers were mounted on. The blowers were propped up on one edge above the Butterworth openings to allow the washing hoses to enter the tank. One washing machine was used for a 15- to 20-minute period. During this time, the blower on the other Butterworth opening was operating. Following this first wash period, this equipment was turned off, and the washing machine and blower on the opposite Butterworth openings were activated for a similar length of time. A sharp increase in the vapor concentration from 800 ppm to a maximum concentration of 3500 ppm was measured as shown in Figure 2. The rise in concentration may have resulted from a combination of (1) an enhanced evaporation rate due to agitation of the residual chemical by the wash, and (2) the reduced rate of removal of tank vapors due to only one blower being operated. A sample of the wash slops was collected from the pump discharge at approximately 142 minutes into the test. Analysis of the sample showed that the concentration of chloroform in the water was 224 mg/liter. The solubility of chloroform in water is 8,000 mg/liter at 20°C.

After tank washing was completed, a portable stripping pump was lowered into the tank through the expansion trunk. This pump was positioned in the sump for the main product pump. To facilitate wash water and product discharge, the tank floor sloped from the port and starboard walls to the center of the tank with a fore-aft slope to promote liquid draining into the pump sump. Stripping operations proceeded for approximately 18 minutes. The blowers were off during this time. Two more liquid samples were collected from the discharge of the stripping line at 175 and 178 minutes. The chloroform concentration in these samples was 207 and 213 mg/liter, respectively.

With essentially all residual chemical/wash water removed, gas freeing commenced. Visual inspection of the tank bottom indicated only a slight wetting of the surface. Three distinct gas freeing periods were observed during the remainder of the tank cleaning process. During the first period, only one blower was in operation. The vapor concentration decreased slightly. Two blowers were then used during the second gas-freeing period. However, they were not used in the same orientation as during the initial prewash ventilation period. One of the blowers was turned over and operated in an exhaust mode by withdrawing vapors from the tank, while the other blower discharged fresh air into the tank. The blowers were operated this way to reduce the outflow of chloroform vapor through the expansion trunk so that the stripping pump could be removed. Following removal of the stripping pump, the exhausting blower was switched around to discharge fresh air into the tank. Consequently, during this last period, two blowers were used in the same manner as during the prewash ventilation. A more rapid decrease in the vapor concentration was observed.

Occupational exposure samples were not collected on the pumpman who was in charge of the tank cleaning. However, his work activities

were observed and documented. Total tank cleaning time was approximately seven hours. The pumpman spent roughly 60 to 90 minutes performing work tasks that were directly related to the cleaning operation. The majority of these tasks consisted of opening and closing the valves that regulated the utilities that were used to drive the tank cleaning equipment. During these tasks, his potential exposure appeared to be minimal because the valves were located some distance from chloroform vapor discharge points.

Toward the end of washing, the pumpman lowered the stripping pump through the tank hatch. Effective recovery of wash water/chemical residues required that this pump be positioned in the sump of the main product discharge pump. This requirement necessitated that he visually observe the relative position and location of the pump as it was being lowered into the tank, and in so doing, his breathing zone was directly above the flow of chloroform vapors that were discharged from the tank by the blower that was operating in a supply mode at the close of washing. This activity occurred in the vicinity of 150 minutes into the cleaning when the chloroform concentration was 3500 ppm. His facial expression and breathing pattern indicated a potential exposure at this level.

This situation could have been avoided by turning the blower off. In fact, he did take action to avoid a similar exposure when he removed the stripping pump after the initial gas freeing period had started. The blower mode was reversed temporarily from supply to exhaust mode. Thus, vapors were discharged from the Butterworth opening rather than the expansion trunk.

VI.3 Tank Entry

In addition to the tank entries by the cargo surveyor, crew members entered tanks on three separate occasions. Two of these entries were made into the chloroform tank (5C). The first entry into Tank 5C occurred immediately after the tank had been cleaned; the second entry into this tank occurred approximately 19 hours later. The third entry was made into Tank 1S, which had carried p-xylene prior to being cleaned approximately five days prior to docking at Terminal No. 1. The purpose for all of these entries was to clean up any solid debris and/or liquid residues on the tank floor and in the pump sump. Cleanup materials included a broom, shovel, dust pan, bucket, and rags. The crew members who entered these tanks did not participate in any of the cargo transfer activities that were documented in Section V. Environmental concentration levels were monitored during all tank entries.

Two crew members made the first entry in the chloroform tank. Both of these crew members wore full-face respirators with organic vapor cartridges, rubber boots, and cotton coveralls, but did not wear gloves. One individual was primarily concerned with sweeping dry debris on the tank bottom; the other individual concentrated on shoveling wet debris from the pump sump and mucking the remaining liquid by hand with the rags. This latter activity resulted in definite dermal contact with the liquid

residue. Despite the fact that respirators were being used, potential environmental exposure levels were monitored; the NIOSH procedure for collecting "ceiling concentration" samples was used. Deck blowers were operating during this entry.

The second entry into the chloroform tank was made by a third crew member. His clothing complement was the same as that which the previous two crew members had used with the exception that he did not use a respirator. The entry into the xylene tank was made by one of the crew members who entered the chloroform tank the first time. For this entry, he wore a respirator in addition to the other items mentioned earlier.

All tank entries were permitted without prior testing of the tank atmosphere for oxygen and combustible gas levels or potentially toxic levels. It should be noted that the combustible gas test would have been irrelevant because chloroform is not combustible.

The results of the sample analyses are shown in Table XVIII. Total entry times for these three activities were 40, 41, and 6 minutes. Crew member A cleaned the pump sump in the chloroform tank, while crew member B swept the tank bottom.

TABLE XVIII
Occupational Exposures During Tank Entry

Tank No.	Crew Member	Sample No.	Sample Duration, min.	Chemical	Concentration, ppm
5C-1	A	107	15	Chloroform	31.7
	A	108	15		22.4
	A	109	10		14.0
	B	524	15		26.9
	B	525	15		17.1
	B	526	10		10.6
5C-2	C	110	15	Xylene	30.4
5C-2	C	112	26		28.6
1S	A	113	6		2.6

VI.4 Deckhouse Environment

Vapor concentration levels were monitored in the deckhouse to assess the extent of any infiltration through access doors or the ventilation system. The site that was chosen was a crew accommodation on the

same level as the main access ways leading to the deck. Monitoring was conducted during product loading at two different terminals and product discharge at a third terminal. A strip chart recorder was connected to the OVA, which permitted continuous unattended monitoring. During unattended monitoring, total hydrocarbon concentrations (as methane) were recorded. On two occasions, the OVA was switched to gas-chromatographic (GC) mode for elemental vapor analyses.

The results of monitoring in total hydrocarbon mode are summarized in Table XIX. Deckhouse concentrations during discharging are nearly identical to those that have been recorded on previous voyages. The deckhouse concentrations during loading are consistent with the low ambient levels that were monitored on deck and which result from short loading of product tanks. The GC traces revealed no detectable peaks that corresponded to the chemicals that were being transferred. For these cases, the detector output could be characterized as essentially a constant baseline.

TABLE XIX
Total Hydrocarbon Concentrations in Deckhouse

<u>Terminal No.</u>	<u>Total Measurement Time, Hours</u>	<u>Hydrocarbon Concentration, ppm as Methane</u>	<u>Cargo Transfer Operation</u>	<u>Chemicals Transferred</u>
2	3.25	5.6-5.8	Loading	EAC, DEA, VAM, DEG
4	1.25	6.0-6.5	Discharging	CRF
8	5	5.5-7.0	Loading	MMM, BTC, EAC, VAM, TOL

VI.5 Vapor Emission Surveys on Deck

After a tank loading had been completed, the final ullage was recorded, and a product sample was collected. The ullage port and hatch cover were then dogged down, and flange blinds were bolted to any vapor return connections. Normally, during the deck watch following these activities, an epoxy resin was applied to the ullage port and hatch cover joints to provide protection for any exposed gasket material.

Vapor emission surveys were made to assess the extent of vapor leakage from these three locations on loaded tanks. These surveys included tanks that had been sealed with resin as well as tanks whose ullage ports and hatch covers were only dogged down. An Organic Vapor Analyzer, Model 108, was used during these surveys in which the entire perimeter of a mating surface was traversed with the sampling head located within one

inch of the surface. Readings were recorded as equivalent methane concentration and were later converted to chemical concentration by applying the instrument manufacturer's response factors. The results of these surveys are shown in Table XX. The data indicate that the epoxy resin effectively eliminated fugitive emissions in addition to serving its primary function, which was gasket protection. Emission levels are quite variable on the unsealed tanks. However, even at the higher emission levels, the emission rates (mass/time) would be expected to be quite low because the discharge areas are small (crack or pinhole size openings) and the pressure in the tank ullage space, which drives the discharge, should be nearly atmospheric on a recently sealed or closed tank. Therefore, these emissions will disperse quite rapidly and contribute to a low-level, multi-component background atmosphere.

TABLE XX
Vapor Emission Surveys of Loaded, Closed Tanks

Tank No.	Chemical	Chemical Concentration, ppm					
		Time = 1710 Hours on Day 4			Time = 1920 Hours on Day 4		
		Ullage Port Hatch	Tank Hatch	Vapor Return Flange	Ullage Port Hatch	Tank Hatch	Vapor Return Flange
7S	Diethanolamine	-	-	-	8-11	8-14	-
9CP	Carbon Tetrachloride	S	S	-	S	S	-
9CS	Methylene Chloride	S	S	-	S	S	-
9S	Ethyl Acrylate	250	300	100-700	2500-5000	10-75	10-13
9P	Vinyl Acetate	40-4000	40-60	-	80-120	20-80	10
10C	Methanol	-	-	-	830-4200	80-420	42
11C	Methanol	-	150-250	-	60-125	60-125	35
11P	1,1,1-Trichloroethane	95-190	45	-	5-8	5-8	190-760

- = No measurement taken.

S = Epoxy seal around joint edges, no detectable levels measured.

* = Response factor for DEA not available from instrument manufacturer.
Response factor for triethanolamine used as an approximation to DEA.

