

AD-A041 267

COAST GUARD WASHINGTON D C OFFICE OF RESEARCH AND DE--ETC F/G 13/2
OIL-IN-WATER CONTENT MONITOR DEVELOPMENTAL PROGRAM SUMMARY.(U)

UNCLASSIFIED

USCG-D-28-77

NL

1 OF 1
AD
A041267



REPORT NO. CG-D-28-77

TASK NO. 4305.6.2

J
12

AD A 041 267

OIL-IN-WATER CONTENT MONITOR
DEVELOPMENTAL PROGRAM SUMMARY

LTjg ROBERT L. SKEWES



FINAL REPORT
MAY 1977

Document is available to the U. S. public through the
National Technical Information Service,
Springfield, Virginia 22161

PREPARED FOR
U.S. DEPARTMENT OF TRANSPORTATION
UNITED STATES COAST GUARD
OFFICE OF RESEARCH AND DEVELOPMENT
WASHINGTON, D.C. 20590

AD No. _____
DDC FILE COPY,

at D D C
RECEIVED
JUL 2 1977
R
D

NOTICE

This document is disseminated under the sponsorship of the Department of Transportation in the interest of information exchange. The United States Government assumes no liability for its contents or use thereof.

The United States Government does not endorse products or manufacturers. Trade or manufacturers' names appear herein solely because they are considered essential to the object of this report.

The contents of this report do not necessarily reflect the official view or policy of the U. S. Coast Guard and do not constitute a standard, specification, or regulation.

1. Report No. U.S. CG-D-28-77	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle OIL-IN-WATER CONTENT MONITOR DEVELOPMENTAL PROGRAM SUMMARY	5. Report Date May 1977	6. Performing Organization Code	
7. Author(s) LTJG ROBERT L. SKEWES / USCG	8. Performing Organization Report No.	9. Report Price	
9. Performing Organization Name and Address U. S. COAST GUARD, G-DOE-1 OFFICE OF RESEARCH AND DEVELOPMENT WASHINGTON, D. C. 20590	10. Work Unit No. (TRAIS) 4305.5/6.2	11. Contract or Grant No. IN-HOUSE	
12. Sponsoring Agency Name and Address DEPARTMENT OF TRANSPORTATION U. S. COAST GUARD, G-DOE-1 OFFICE OF RESEARCH AND DEVELOPMENT WASHINGTON, D. C. 20590	13. Type of Report and Period Covered FINAL REPORT.		14. Sponsoring Agency Code
15. Supplementary Notes This report supersedes report No. CG-D-188.75 (December 1975) entitled "Oil-in-Water Content Monitor Developmental Program Summary".			
16. Abstract A summary of the feasibility studies of three concepts for oil-in-water content monitors, developed under separate Coast Guard contracts, is presented. The three concepts described - 1) oil fluorescence total luminescence scanning, - 2) small angle forward light scattering and 3) light scattering at 45°, 90° and 135° and turbidity at 0° - are followed through a two phase developmental program. The breadboard devices described are capable of linear monitor response to known oil mixtures over the range of 0-400 ppm with a maximum error of +15% (excluding Bunker "C"). Original monitor designs & phase II design modifications are presented. Individual contractor test program results of a USCG developed test matrix are summarized.			
17. Key Words BREADBOARD, MONITORS, OIL-IN-WATER, OIL FLUORESCENCE, LIGHT SCATTERING		18. Distribution Statement Document is available to the U. S. Public through the National Technical Information Service, Springfield, Virginia 22161	
19. Security Classif. (of this report) UNCLASSIFIED	20. Security Classif. (of this page) UNCLASSIFIED	21. No. of Pages	22. Price

408731

Handwritten signature

DDC
RECEIVED
JUL 7 1977
ALUCENT
D

6

14

1022
960

11

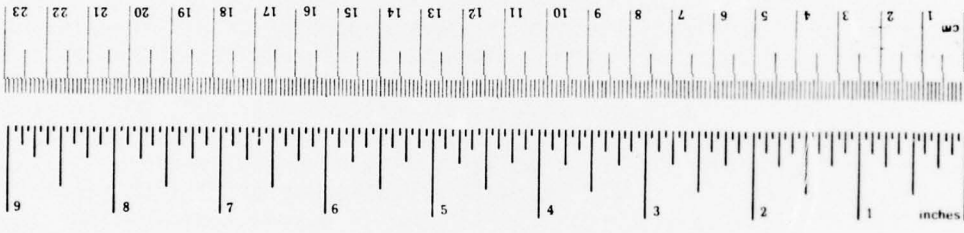
10

1271 p.

9

METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures				Approximate Conversions from Metric Measures			
Symbol	When You Know	Multiply by	To Find	Symbol	When You Know	Multiply by	To Find
LENGTH							
in	inches	*2.5	centimeters	mm	millimeters	0.04	inches
ft	feet	30	centimeters	cm	centimeters	0.4	inches
yd	yards	0.9	meters	m	meters	3.3	feet
mi	miles	1.6	kilometers	km	kilometers	0.6	miles
AREA							
in ²	square inches	6.5	square centimeters	cm ²	square centimeters	0.16	square inches
ft ²	square feet	0.09	square meters	m ²	square meters	1.2	square yards
yd ²	square yards	0.8	square meters	km ²	square kilometers	0.4	square miles
mi ²	square miles	2.6	square kilometers	ha	hectares (10,000 m ²)	2.5	acres
MASS (weight)							
oz	ounces	28	grams	g	grams	0.035	ounces
lb	pounds	0.45	kilograms	kg	kilograms	2.2	pounds
	short tons (2000 lb)	0.9	tonnes	t	tonnes (1000 kg)	1.1	short tons
VOLUME							
tsp	teaspoons	5	milliliters	ml	milliliters	0.03	fluid ounces
Tbsp	tablespoons	15	milliliters	l	liters	2.1	pints
fl oz	fluid ounces	30	milliliters	qt	quarts	1.06	gallons
c	cups	0.24	liters	l	liters	0.26	gallons
pt	pints	0.47	liters	m ³	cubic meters	35	cubic feet
qt	quarts	0.95	liters	m ³	cubic meters	1.3	cubic yards
gal	gallons	3.8	liters				
fl ³	cubic feet	0.03	cubic meters				
yd ³	cubic yards	0.76	cubic meters				
TEMPERATURE (exact)							
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature



* 1 in. = 2.54 centimeters. For other exact conversions and more data, see Tables and Tables, see NBS Special Publication 280, Units of Weights and Measures, Price \$2.25, 30 Cardinal Ave., Gaithersburg, MD 20878.

ACKNOWLEDGEMENTS

The author wishes to acknowledge and thank the following personnel for their cooperation and support in the monitor development program, and the preparation of this report:

LT. R. W. Montfort (USCG) - Author of report CG-D-188-75, the interim report on this program. Section 2.0 and portions of section 3.0 of this report are exact reprints of report CG-D-188-75.

LT J. A. Magiera (USCG) - former project officer.

Mr. E. Batutis and Mr. F. Callelo, Jr. (General Electric, Co.); Dr. J. Bochinski and Dr. A. Hadermann (Enviro Control, Inc.); and, Dr. A. W. Hornig, Dr. J. T. Brownrigg, Dr. L. P. Giering and Mr. B. R. Chisolm (Baird Atomic, Inc.) - Participating contractors. Portions of the contractors's final reports are utilized in this report to facilitate program summarization.

ACCESSION for	
DTIC	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION.....	
.....	
BY	
DESTRUCTION/AVAILABILITY CODES	
.....	
..... SPECIAL	

A

DDC
REGISTRATION
JUL 7 1977
REGISTRATION
D

CONTENTS

	<u>PAGE</u>
ABBREVIATIONS.....	iv
FIGURES.....	v
TABLES.....	vii
1.0 PROGRAM SUMMARY.....	1
2.0 PHASE I FEASIBILITY.....	4
2.1 Concepts and Developmental Status.....	4
2.1.1 Light Scattering - Enviro Control.....	4
2.1.2 Light Scattering - General Electric.....	8
2.1.3 Fluorescence - Baird Atomic.....	14
2.2 Test Program - Phase I.....	22
2.3 Conclusions - Phase I.....	28
3.0 PHASE II FEASIBILITY.....	28
3.1 Concept Modifications.....	30
3.1.1 Light Scattering - Enviro Control.....	30
3.1.2 Light Scattering - General Electric.....	38
3.1.3 Fluorescence - Baird Atomic.....	43
3.2 Test Program Results - Phase II.....	45
3.2.1 Linearity of Response.....	48
3.2.2 Homogenization and Particile Size Distribution Studies.....	50
3.2.3 Response to Oil Mixtures.....	51
3.2.4 Effects of pH.....	51
3.2.5 Monitor Response Time.....	51
3.2.6 Effects of Salinity.....	53
3.2.7 Effects of Temperature.....	53

	<u>PAGE</u>
3.2.8 Effects of Detergents.....	52
3.2.9 Effects of Particulates.....	56
3.3 Conclusions - Phase II	58
4.0 PROTOTYPE MONITOR DEVELOPMENT PROGRAM	59
5.0 REFERENCES	61

LIST OF ABBREVIATIONS

GE	- General Electric, Co.
ECI	- Enviro Control, Inc.
BA	- Baird Atomic, Inc.
TLS	- Total Luminescence Scanning
SS	- Synchronous Scanning
IMCO	- Inter-Governmental Maritime Consultative Organization
ppm	- parts per million
gpm	- gallons per minute
Δ	- fixed wavelength interval
nm	- nanometers
He/Ne	- Helium/Neon
l/m	- liters per minute
rpm	- rotations per minute
mv	- Millivolts
LED	- Light Emitting Diode
$(I_{135})_{4A}$	- ECI - intensity of back scattered light beam (#4 LED, Detector "A") in mv
$(I_{45})_{2A}$	- ECI - intensity of forward scattered light beam (#2 LED, Detector "A")
$I_{45} \left(\frac{7.03}{Z}\right)^2$	- particle size compensated function (where $Z = I_{45}/I_{135}$)
ootg	- parts per thousand
DOR	- Deviation of Response
mg/l	- milligrams per liter
EROA	- Energy Research and Development Administration
USN	- United States Navy
USCG	- United States Coast Guard

FIGURES

<u>FIGURE</u>	<u>TITLE</u>	<u>PAGE</u>
2-1	Oil-In-Water Monitor Diagram - Enviro Control Phase I Breadboard.....	5
2-2	Breadboard Oil-In-Water Content Monitor - Phase I.....	6-7
2-3	Flow Through Sensor Assy - Enviro Control - Phase I Breadboard.....	9
2-4	Phase I Breadboard Monitor and Lab Test Loop Design - General Electric.....	11
2-5	Laboratory Arrangement for Phase I Shipboard Oil-In-Water Content Monitor - General Electric.....	12
2-6	Optical Schematic of Forward Small - Angle Scattering Breadboard Used for Oil-In-Water Content Monitor - General Electric - Phase I.....	13
2-7	Hypothetical 3-Dimensional Spectrum Showing Intensity Contours.....	15
2-8	Possible Scan Modes.....	15
2-9	Overall View of Laboratory Setup Phase I Breadboard - Baird Atomic.....	12
2-10	Principal Components Appearing in Overall View of Laboratory Setup (Figure 2-9).....	18
2-11 (A&B)	Polychromators - Covers Removed.....	19
2-12	Excitation Polychromator (Phase I Baird Atomic).....	20
2-13	Emission Polychromator (Phase I Baird Atomic).....	21
2-14	Monitor Response - Enviro Control.....	25
2-15	Monitor Response - General Electric.....	26

<u>FIGURE</u>	<u>TITLE</u>	<u>PAGE</u>
2-16	Monitor Response - Baird Atomic.....	27
2-17	Desired Monitor Response.....	29
3-1	Typical Test System Schematic for Phase II.....	33
3-2	Enviro Control Homogenizer - Phase II.....	35
3-3	Enviro Control Sensor Head Design Schematic - Phase II.....	36
3-4	Photograph of ECI Sensor Head - Phase II.....	37
3-5	General Electric Monitor Schematic - Phase II....	41
3-6	Photograph of General Electric Monitor - Phase II.....	42
3-7	Baird Atomic Sensor Assembly Schematic - Phase II.....	46
3-8	Photograph of Baird Atomic Monitor - Phase II	47

TABLES

<u>TABLE</u>	<u>TITLE</u>	<u>PAGE</u>
2-1	Analysis of Phase I Breadboard Oil Monitor Response.....	29
3-1	Oil-In-Water Content Monitor Test Matrix - Phase II.....	31-32
3-2	Analysis of Phase II Breadboard Oil Monitor Response.....	49
3-3	Upper Limit of Linearity of Monitor Response - Phase II.....	50
3-4	Deviation of Monitor Response Due to Oil Mixtures - Phase II.....	52
3-5	Deviation of Monitor Response Due to Change In pH - Phase II.....	52
3-6	Deviation of Monitor Response Due to Change in Salinity - Phase II.....	54
3-7	Deviation of Monitor Response Due to Change in Temperature - Phase II.....	54
3-8	Deviation of Monitor Response Due to Detergents - Phase II.....	55
3-9	Deviation of Monitor Response Due to Particulates - Phase II.....	57

1.0 Program Summary

In 1973, the U. S. Coast Guard's Office of Marine Environment and Systems and the Office of Engineering requested development of an oil-in-water content monitor suitable for use with oil/water separators aboard USCG vessels. Requirements for these devices are established in the Federal Water Pollution Control Act (as amended), the ratified 1969 amendments to the International Convention for the Prevention of Pollution of the Sea by Oil in 1954, and the anticipated U. S. policy at the 1973 IMCO Conference (prohibiting the willful discharges of oil into any waters). The Office of Research and Development subsequently released a request for proposals for feasibility studies, for which twenty-six proposals were submitted. The three concepts thought to have the highest potential for success were chosen to pursue their concept of oil monitoring, as follows:

- a. Baird-Atomic - oil fluorescence synchronous scanning.
- b. Enviro Control - light scattering at ninety degrees ratioed against light transmission.
- c. General Electric - small angle forward light scattering ratioed against light transmission.

PHASE I

The purpose of the Phase I feasibility studies was to demonstrate the ability of each concept to accurately monitor a separator effluent stream containing from 0-100 ppm oil, despite the following interferences: change in oil specie, particulate matter (rust, paint chips, dirt, plankton, etc.), water conditions (pH, salinity, temperature), detergents, air bubbles, and electrical or mechanical operational characteristics.

During the course of the Phase I studies the Office of Engineering purchased off-the-shelf separating and monitoring systems for installation aboard USCG vessels, and in effect ended the requirements for the feasibility studies. However, the program manager redirected the monitor research program to include the needs of the merchant marine industry. Consequently, the feasibility studies were expanded to investigate the wide variety of oils which might be found in both bilge and cargo applications.

The Phase I feasibility studies, completed in February 1975, yielded the following results:

- a. All three techniques were able to monitor a known oil linearly over the range of 0 to 100 ppm with a maximum error of $\pm 15\%$. This error includes the error associated with the analytical technique (solvent extraction-infrared absorption) used to determine the actual oil concentration being monitored.
- b. None of the techniques were oil specie independent. Every oil and oil mixture sampled had a unique response curve.

c. All three of the breadboard devices were affected by particulate matter, changes in the water conditions (temperature, pH, salinity), and detergents.

d. A universal instrument that did not have to be calibrated for oil type was not available.

e. A monitor that could operate properly for bilge applications as well as for tanker deballasting and cleaning was not considered practical. Each operation had its own particular controlling parameters, and hence, the problems should be handled separately.

The Phase I program, including concept descriptions and test program results, is discussed in Section 2.0.

Phase II

For the above reasons prototype development was postponed and a second phase feasibility program was initiated with each of the three vendors. The decision to proceed with these concepts alone, was made for the following reasons: 1) Phase I monitor accuracy and reliability results were quite similar for all three contractors, with none of them having a distinct advantage; 2) there were significant areas of investigation under each of the techniques that showed promise for improvement in response or for reduction in the variation of response due to oil specie; 3) no new concepts were thought to have more chance for success than the original three concepts; and 4) insufficient standardization of the Phase I monitor testing program was thought to have biased performance data on the monitors. As a result, a specific test program was developed to adequately compare monitor test data. Additionally, the program was altered to address the bilge water application only, thus reducing the variety of oils tested.

The second feasibility phase was completed in February 1976, and yielded the following results:

a. Linear monitor response to a known oil mixture was demonstrated over the range of 0-400 ppm with a maximum error of $\pm 15\%$ (excluding BUNKER "C").

b. All three techniques remained oil specie dependent. However, if individual oils or oil mixtures are predictable, deviation of monitor response can be reduced (i.e., optical masking; electronic compensation techniques).

c. Interferences caused by particulates, detergents or water conditions (temperature, pH, salinity) have decreased; particulate interference may be further reduced electronically. Detergents, if predictable, may also be compensated for by means such as optical masking.

d. Design capabilities demonstrated in this phase were considered sufficient to eliminate the need to calibrate a prototype monitor for oil type.

The Phase II program, including concept modifications, test matrix, and test program results, is discussed in Section 3.0.

Section 4.0 updates the developments in the USCG monitor research program since the completion of Phase II, and discusses anticipated USN laboratory tests of the three breadboard monitors.

2. PHASE I FEASIBILITY

The main goal of this phase of the program was to demonstrate the feasibility of concepts for measuring oil dispersed in water, independent of oil type. Many problems were identified during this program which will have to be solved prior to the development of a useful shipboard instrument. Part of the goal, however, was obtained in that all three methods were able to measure oil linearly over the range of 0 to 100 ppm when oil type was known. All three showed dependency upon oil type, and methods of reducing this dependency or its effects are being investigated and are discussed later. The following sections briefly describe the concepts, the breadboard system developed, the results obtained, and the level and directions of future development.

2.1 Concepts and Developmental Status

2.1.1 Light Scattering - Enviro Control

The basic concept of Enviro Control's phase I breadboard was light scattering of oil droplets at a right angle to the incident light beam. To make a first-order correction for color and particulate matter interference, the transmitted beam was monitored and proportioned against the scattered light. During the developmental work it was shown that the ratio of scattered to transmitted light was a poor correction for particulate interference, therefore, some other method had to be employed to remove the effects of it. The most direct method was to remove the particulates prior to analyzing the sample stream for oil.

The overall layout of Enviro Control's phase I breadboard oil content monitor is shown in Figure 2-1 with an actual photograph in Figure 2-2. The breadboard consisted of a turbine pump, hydrocyclone separator, homogenizer, flow-through sensor assembly, and electronics for signal conditioning of photomultiplier outputs and auto-calibrations. The turbine sampling pump delivered an 8.2 liter per minute flow to the breadboard and provided a system pressure of 30 psi for proper operation of the hydrocyclone. The hydrocyclone was added to the breadboard in an attempt to remove particulate matter from the sample stream. The sample flow was split at this point with approximately half the sample stream (cyclone overflow-oil but no dirt) continuing to the homogenizer and the other half (cyclone underflow-dirt but no oil) being discarded. To condition the sample stream (provide an homogenous oil-water mix) prior to entering the sensor cell, an off-the-shelf Tekmar homogenizer was selected and modified for installation. The sample stream then passed through the sensor cell where light scatter at 90 degrees and light transmission was measured. These measurements were processed electronically to determine oil content.

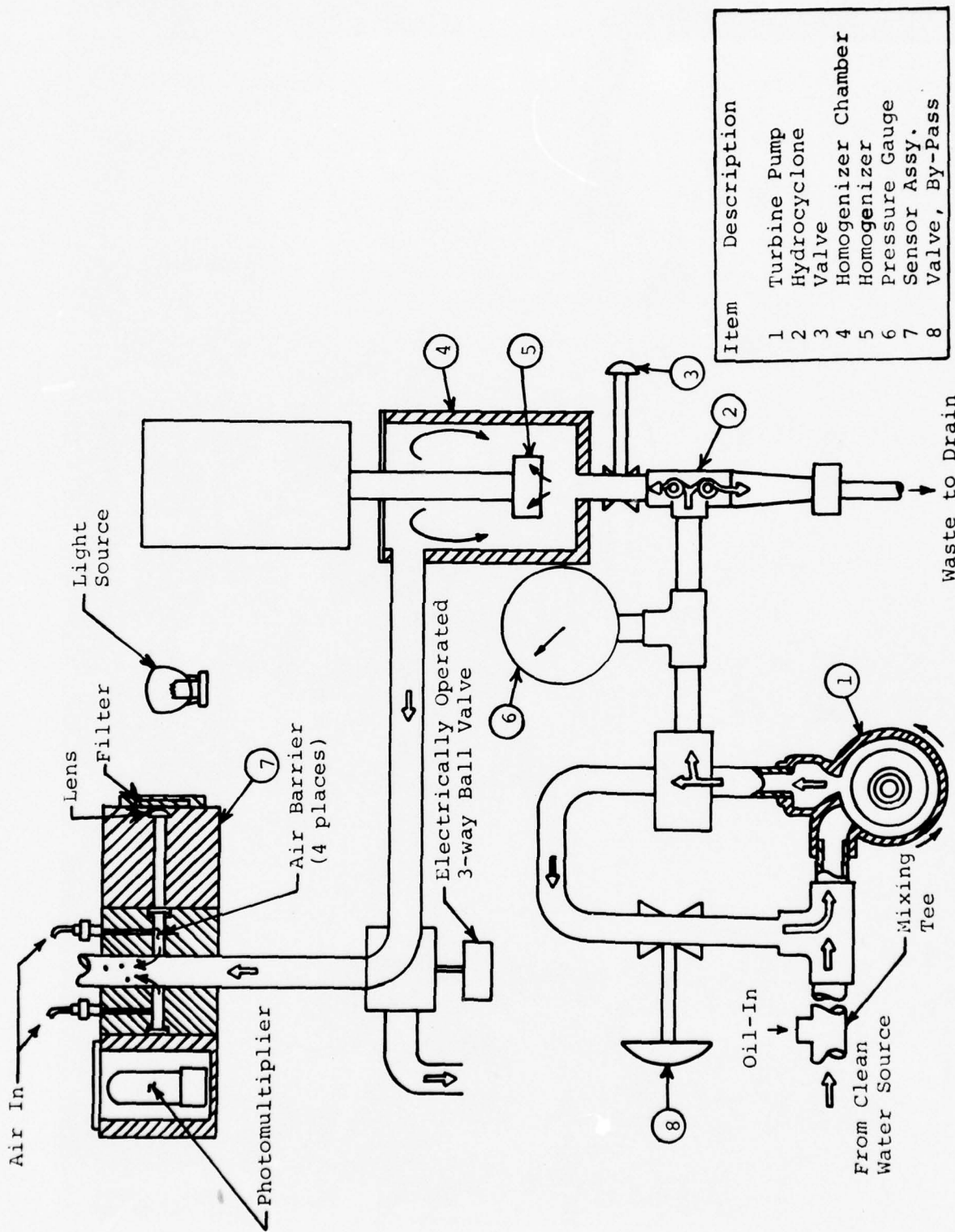


Figure 2-i Oil-in-Water Monitor Diagram - Enviro Control Phase I Breadboard

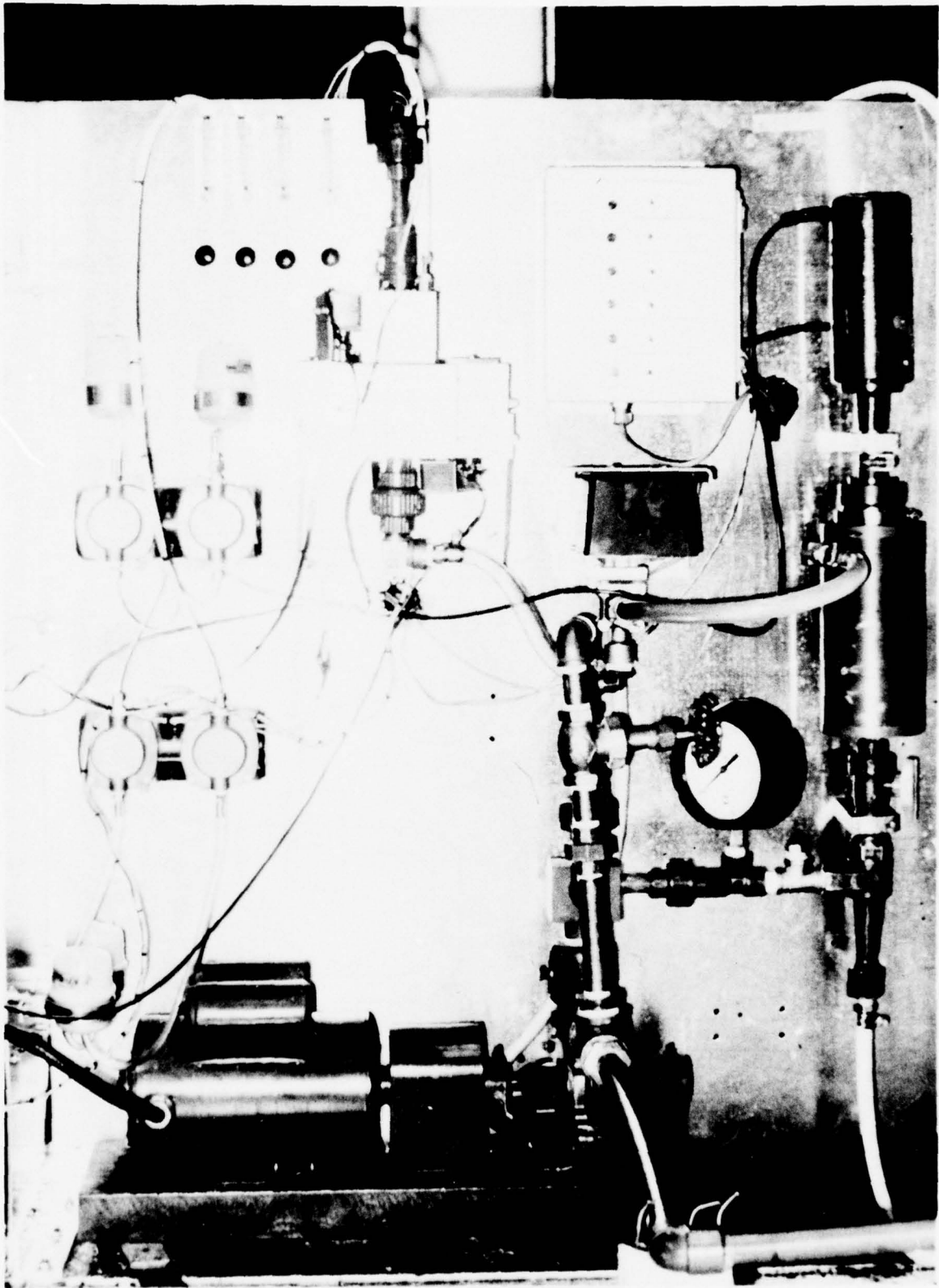


Figure 2-2 (Part 1 of 2: see part 2 for key)
Breadboard Oil-in-Water Content Monitor - Phase I

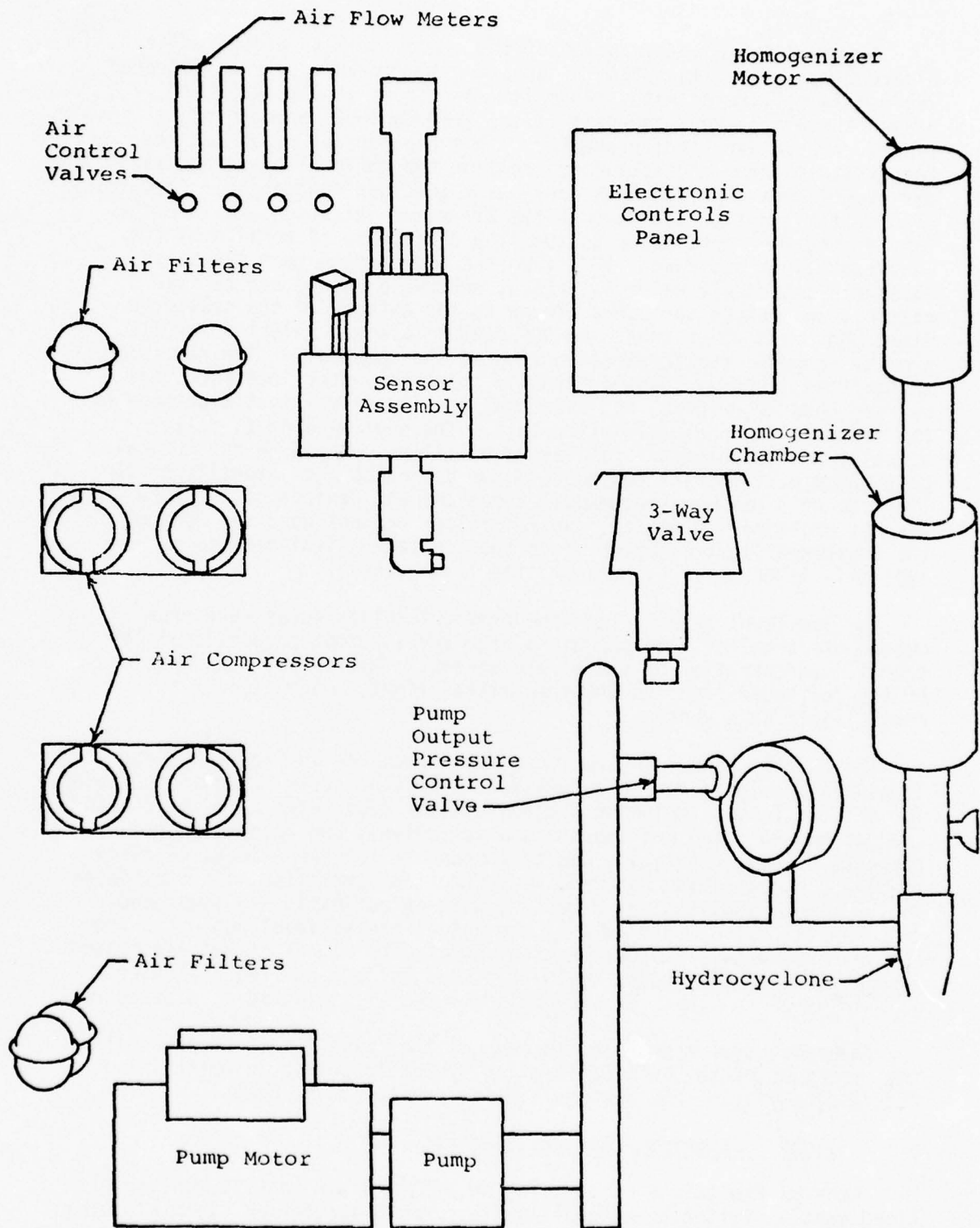


Figure 2-2 (Part 2 of 2)

Identifiers for Oil-in-Water Content Monitor

A more detailed description of the sensor cell is presented in Figure 2-3. White light from a tungsten lamp (peak energy in infrared region) is collimated with a 29 millimeter focal length lens, and passed through a long band-pass filter (780 to 1050 nanometers), a window, and an air barrier chamber. This air barrier prevented the sample stream from contacting and fouling the optic windows, and each air chamber was supplied by a constant volume air compressor. From this chamber the light passed through the air-water interface and into the sample stream perpendicular to the flow direction. A portion of the resultant light scattered (90°) from the transmitted beam was passed through a second air-water interface, entered a second air barrier chamber, and passed through a window to the cathode of the scattered light photomultiplier tube. An RCA C31004 tube was selected for its greater range in the infrared portion of the spectrum. The remaining transmitted light was passed through a third air-water interface, air barrier channel, window, and a neutral density filter to the cathode of the transmission photomultiplier tube. The neutral density filter actually consisted of several layers of filters placed in the optical path ahead of the transmission detector to reduce the intensity of the light so that maximum recommended anode current density of the tube was not exceeded. A neutral density filter was not used in front of the scattered light detector since the scattered light density is typically 1/1000th of the transmitted light density.

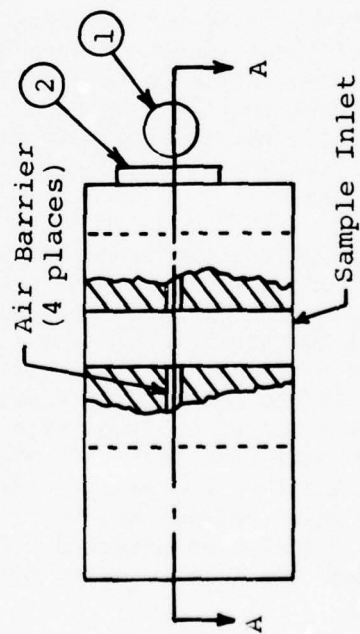
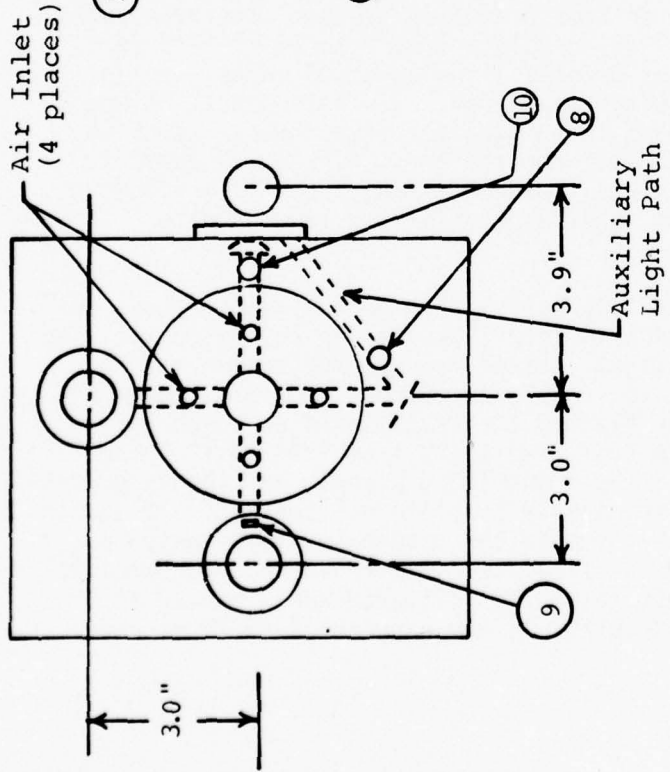
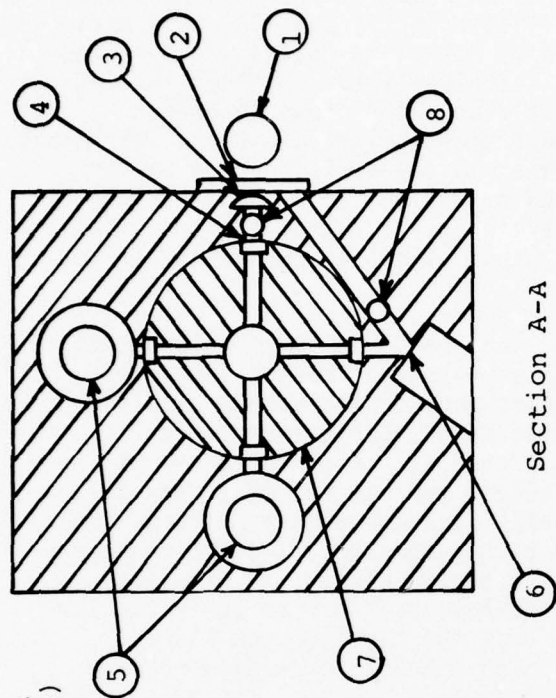
The low level signals from the photomultiplier tubes were processed electronically to produce a high level output proportional to the oil concentration of the sample stream. This output was a ratio of the scattered light to the transmitted light, multiplied by a controllable gain constant.

The fourth channel in the sensor cell pictured in Figure 2-3 was originally designed for an automatic calibration system which compensated for drift effects, including photomultiplier tube leakage (dark) current changes due to aging and temperature variations, and changes in tube response. This calibration was to compensate for the effects of dirty windows. Compensation was made by controlling amplifier gain and biases in the signal conditioning circuitry with an automatically sequenced servo system which would balance the actual signal level against a pre-set level. During auto-calibration process the signal offset associated with photomultiplier tubes would be biased to zero and the amplifier gain adjusted to a span corresponding to the oil selected as a standard.

The above system was used throughout the phase I test program with the exception of the auto-calibration system (problems in maintaining the responsivity of the photomultiplier precluded its use).

2.1.2 Light Scattering - General Electric

General Electric's concept for an oil-in-water content monitor utilized spatial filtering of small-angle forward scattering light allowing discrimination of oil droplets from other scattering material. In particular, this technique determined the ratio of the forward scattered signal



Item	Description	Quantity
1	Light Source	1
2	Filter	1
3	Lens, Collimating	1
4	Window (4 places)	4
5	Photomultiplier Tube	2
6	Mirror	1
7	Flow Cell	1
8	Shutter (Solenoid Actuated)	1
9	Neutral Density Filter	2
10	Shutter/Aperture Combination	1

Figure 2-3
Flow Through Sensor Assembly - Enviro Control
Phase I Breadboard

to the transmitted signal of a 1 milliwatt helium-neon laser. This ratio was an attempt to eliminate any window deterioration effect on monitor response. The premise in using forward scattering is that there is greater scattering in the forward direction by materials (oils) whose refractive index is close to that of water. Solid particles, however, having a refractive index appreciably different than water, tend to either absorb the exciting light or scatter more to the sides and back. With this light scattering discrimination technique and the addition of a solids separation process, normal errors caused by solids, air, and plankton were thought to be minimized. Prior to determining the ratio, the two signals themselves were compared to the laser output signal to remove any effect of laser output intensity fluctuations.

A flow diagram of the phase I test loop and breadboard oil content monitor is presented in Figure 2-4 with a photograph of the laboratory arrangement in Figure 2-5. The breadboard monitor included a sampling flow pump, hydrocyclone separator, static mixer, optical sensor cell, and all necessary electronics for proper readout. A constant volume Moyno pump was used to deliver a 1.5 gallons per minute (GPM) flow to the hydrocyclone. As with Enviro, General Electric used a hydrocyclone for particle removal prior to analysis by the monitor. The cyclone overflow (0.75 GPM) was then passed through a static mixer. It was felt that the action of the hydrocyclone actually caused oil to centrifugally coalesce out of the sample stream such that the overflow was poorly homogenized. The mixer was installed in an attempt to re-disperse the oil. There was no homogenizer in this breadboard system. The breadboard optics were designed to monitor oil droplets from 2 to 25 microns in diameter. This was the range of droplet sizes expected to be seen in the effluent stream of an oil-water separator. (In retrospect, it would have been better to have designed an homogenizer since there was no way of generating the proper mix to test the monitor. Work under phase II revealed that the heavy types of oils produced many droplets which were actually larger than 25 microns, thus accounting for lower monitor response.)

From the static mixer, the flow passed through the optical test cell. This cell was designed to provide laminar flow past the cell windows. The laser beam, 632 nanometer red light, passed through the sample stream where scattering would occur. The forward scattered light was then monitored by a spatial filter which blanked the transmitted beam and was adjusted to collect the forward scattered light from $1/2^\circ$ to 1° . The forward scattered light signal, the transmitted signal, and the laser output signal were processed electronically to yield oil content. It should be noted that the spatial filter used in the breadboard represented a compromise between sensitivity, particulate discrimination, and particle size range to be expected. This spatially filtered angle of $1/2$ to 1° allowed the monitoring of oil droplets in the range of 2 to 25 microns.

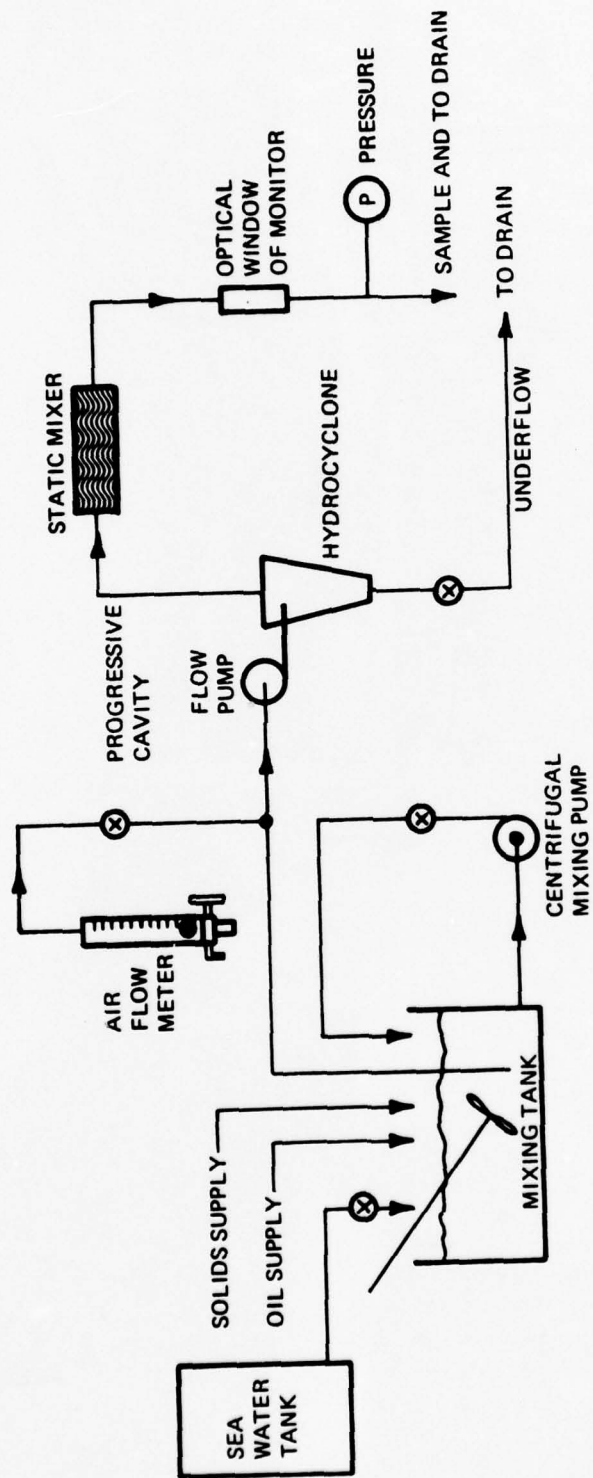


Figure 2-4 Phase I Breadboard Monitor and Lab Test Loop Design -
General Electric

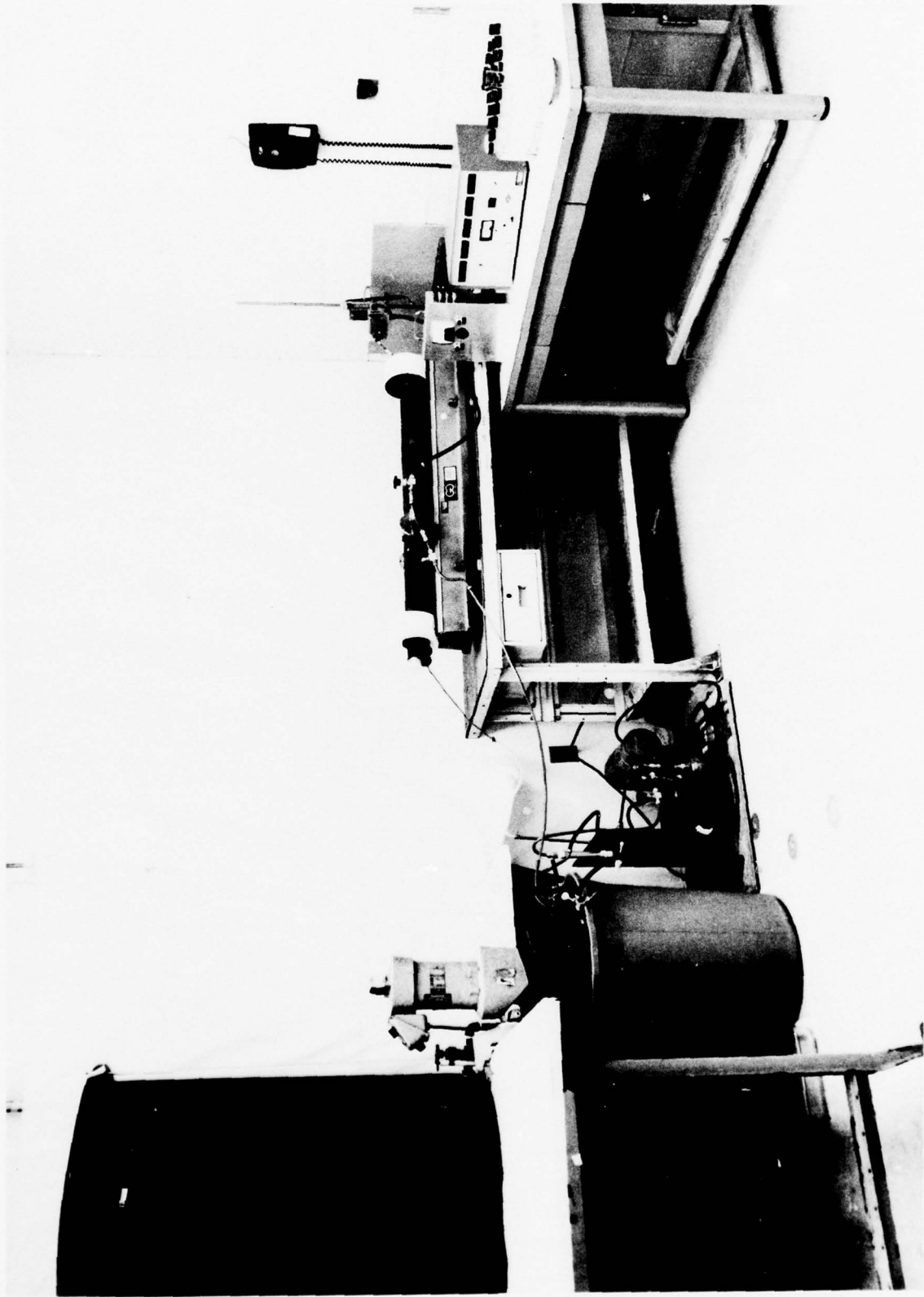


Figure 2-5 Laboratory Arrangement for Phase I Shipboard Oil-In-Water
Content Monitor - General Electric

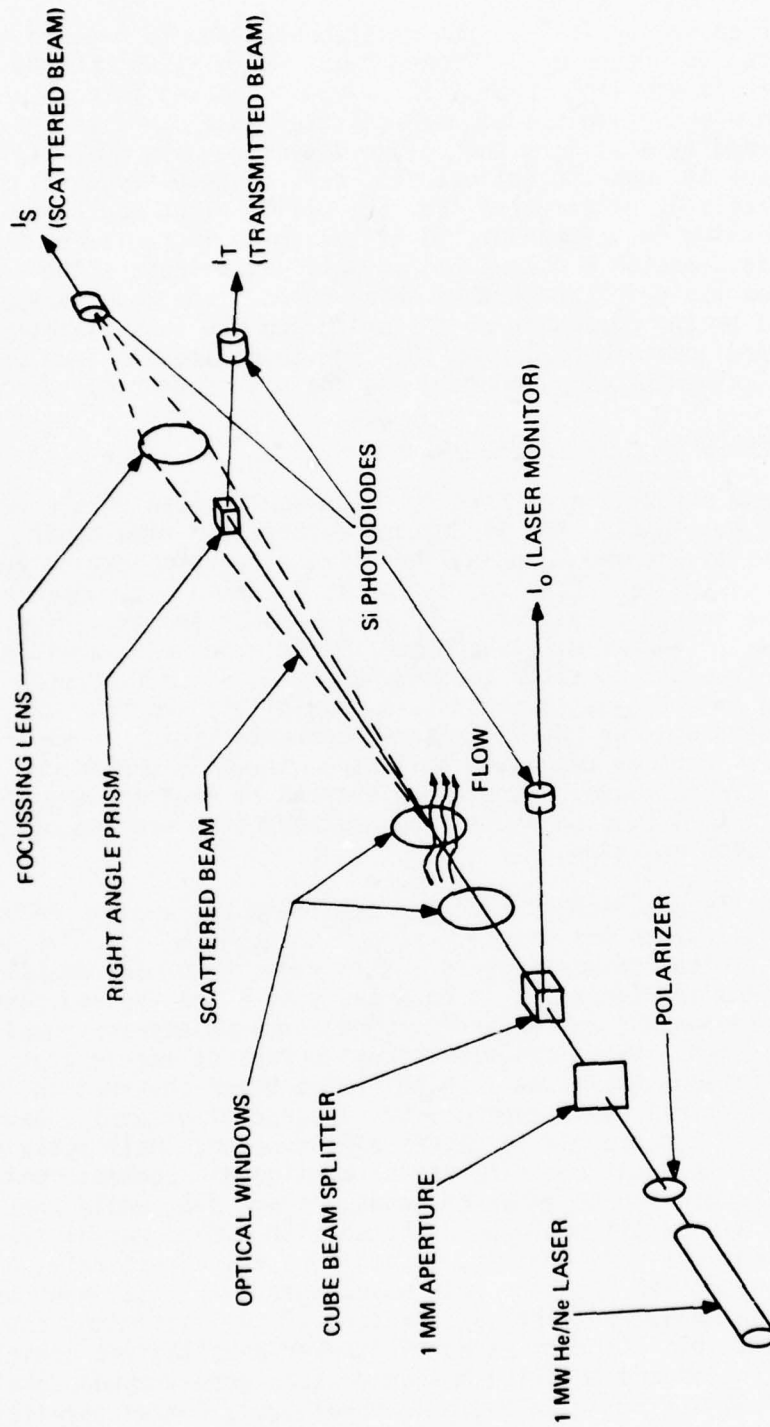


FIGURE 2-6 OPTICAL SCHEMATIC OF FORWARD SMALL-ANGLE SCATTERING BREADBOARD USED FOR OIL-IN-WATER CONTENT MONITOR - GENERAL ELECTRIC - PHASE I

A schematic of the optical detector as constructed for use in the breadboard monitor is presented in Figure 2-6. A 1 milliwatt He/Ne laser generates a visible red light beam (632 nm) which passes through a polarizer and a 1 mm aperture to a cube beam-splitter where part of the laser energy is monitored by a silicon photodiode detector. The rest of the beam energy passes through the optical test cell containing quartz windows. Approximately 40 centimeters from the cell a right angle prism removes the remaining beam (transmitted light) which is monitored by a second photodiode detector. A lens behind this prism focuses the scattered beam around the prism and onto a third diode. The annulus spatial filter is formed by the dimension of the prism and the lens diameter, giving the desired aperture of $1/2$ to 1° . The three signals from the diodes are then mathematically compared and the oil content calculated.

2.1.3 Oil Fluorescence - Baird Atomic

All petroleum products are known to fluoresce because of the presence of aromatic compounds. The fluorescence varies in wavelength, line width, and intensity, depending on oil density, geographic origin, and state of solution, and depending on whether it is mixed with other oils. The high inherent sensitivity of fluorescence methods and the universal fluorescence of all natural oils suggested that fluorescence could be made the basis of an oil-in-water content monitor. Since fluorescence varies depending on oil type, much of this feasibility program was devoted to documentation of the luminescent characteristics of various oils and mixtures in order to design an instrument which would sum fluorescence at various wavelengths (when excited at several wavelengths). It was hoped that this summing would have obviated this problem of variations in fluorescent emission.

The maximum fluorescence information available for a given oil-in-water sample would relate the emission at all wavelengths as a function of all possible excitation wavelengths. This might have been displayed as a plot presented in Figure 2-7. The x and y axes are the emission and excitation wavelengths respectively. The contours express equal intensity of emission. Since emission always occurs at wavelengths longer than excitation, there would be no fluorescence observed in the upper cross-hatched triangle. Each oil or mixtures of oils will have contours similar to the example in Figure 2-7; however, their peaks would vary in intensity and location. Therefore, a bilge oil content monitor based on normal excitation or emission scans, Figure 2-8, would not be necessary. A single oil could be detected with either normal scan; however, if another oil were present, it could be missed entirely, if its peak emission was too far from the scan wavelength. An instrument based on this type of scanning would be satisfactory if the instrument could be calibrated for each oil mix such as an oil tanker deballasting monitor. If both the excitation and emission monochromators were scanned simultaneously, separated by a fixed wavelength interval (Δ), a scan parallel to and at the Δ distance from the diagonal scatter line would be generated. This was the basis for Baird Atomic's phase I breadboard oil content meter. The rationale for the use of this synchronous scan was that small aromatic

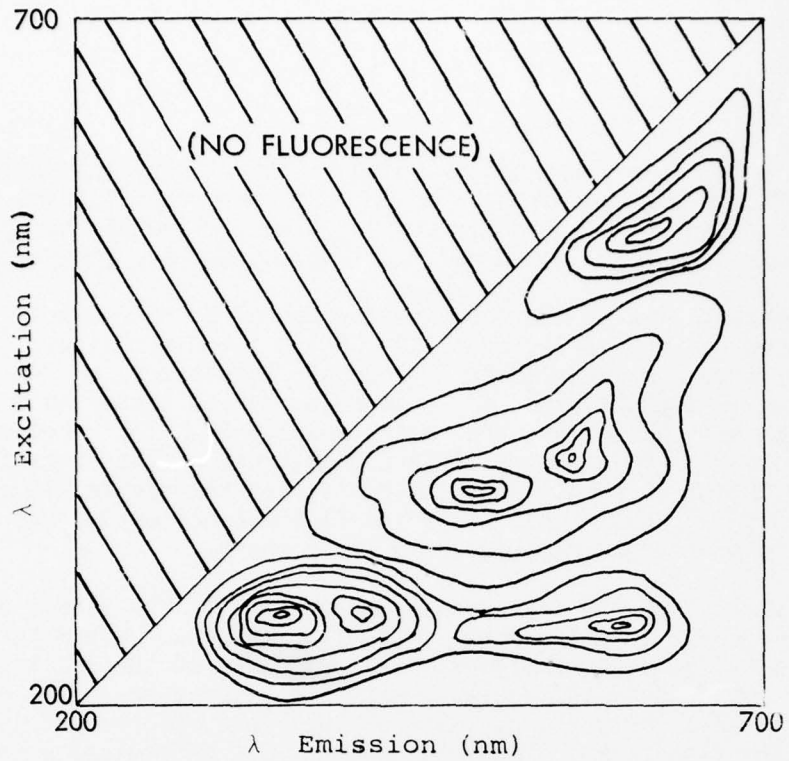


FIGURE 2-7 HYPOTHETICAL 3-DIMENSIONAL OIL SPECTRUM SHOWING INTENSITY CONTOURS

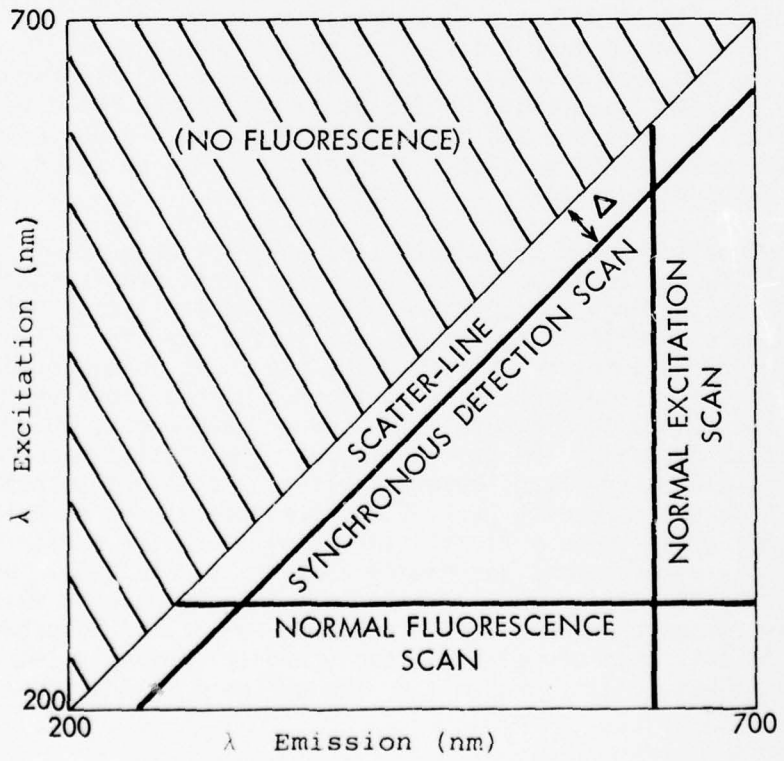


FIGURE 2-8 POSSIBLE SCAN MODES

molecules have their principal emission in the ultraviolet region, whereas larger molecule emission is shifted to much longer wavelengths. Thus, a synchronous scan with a properly chosen Δ would have picked up the emission of more components of an oil, as long as they are independent.

An overall view of the laboratory setup of Baird Atomic's breadboard is presented in Figures 2-9 and 2-10. A 1.0 liter per minute (l/m) deionized water stream was pumped through an air bubble trap to the emulsifier unit. This emulsifier was an in-house design featuring a five-stage assembly of slotted stators and rotors powered by a 1/2 horsepower motor operated at 3000 RPM. Oil was injected upstream of the emulsifier with a syringe injection pump. From the emulsifier the sample flowed straight into the optical sensor unit where the fluorescence output was monitored with a picoammeter and recorded on a strip chart.

The excitation and emission polychromators of the sensor unit are shown in Figure 2-11 A and B respectively. These polychromators were actually modified monochromators. The exit slit of the excitation monochromator was removed and replaced with a slotted mask. This mask was designed to allow only the portions of the light spectrum of interest to reach the flowstream. These bandwidths were determined with the aid of a computer from preliminary results of synchronous scans performed on each oil of interest. In this case, three (3) slits were designed into the mask to allow excitation at 295, 475, and 505 nanometers. As for the emission monochromator, the entrance slit was replaced with an identical mask. This allowed only the fluorescent emissions of interest to be collected. From preliminary tests, it appeared that a Δ of 75 nanometers would yield the best results. Thus, the excitation polychromator was tuned to a center wavelength of 385 nm which allowed the three excitation wavelengths to penetrate the flow cell. The emission polychromator, however, was tuned to 460 nm (385 + 75) which allowed emissions of 370, 550, and 580 nm to be monitored.

A schematic of the light path through this sensor assembly is presented in Figures 2-12 and 2-13. The white light from a focused xenon source passes through the entrance slit of the excitation polychromator and onto a collimating mirror. The collimated beam is reflected off a plane mirror and onto the grating where the light is dispersed. The first order dispersed light is then focused onto a short vertical section of the quartz sample tube. The center wavelength, 385 nm, is adjusted by a control governing the grating angle. The slotted mask in front of the sample allows only the proper wavelengths of light to reach the sample. The corresponding part of the breadboard used to collect and measure oil emission is optically very similar to the excitation side. An identical slotted mask positioned near the sample tube and at a right angle to the excitation mask permits only the fluorescent emission from the water volume being excited to reach the detection polychromator. The grating in this polychromator is then tuned to pass only the fluorescent emission at wavelengths greater, by the amount Δ , than the corresponding

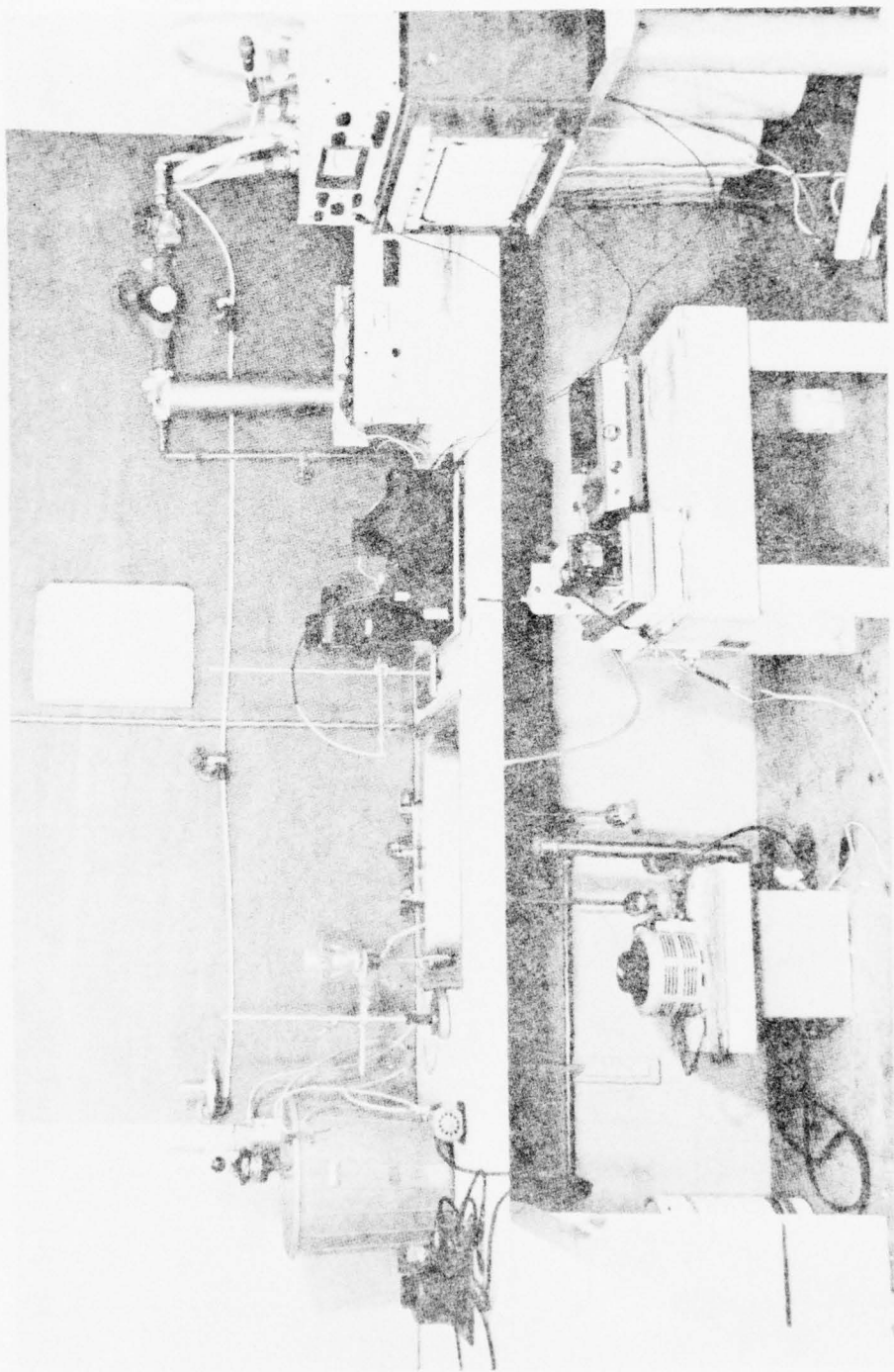


FIGURE 2-9 OVERALL VIEW OF LABORATORY SETUP.
Phase I Breadboard - Baird Atomic

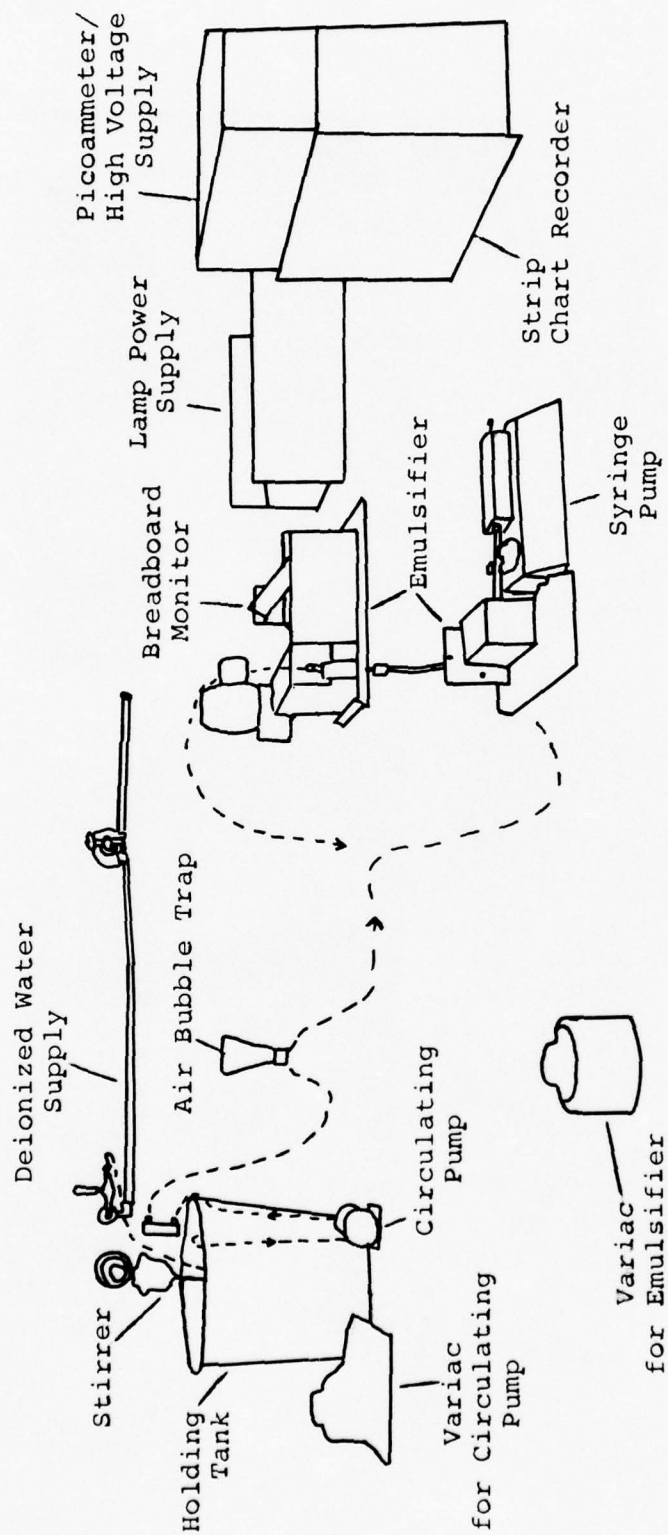


FIGURE 2-10 PRINCIPAL COMPONENTS APPEARING IN OVERALL VIEW OF LABORATORY SETUP (FIGURE 2-9).

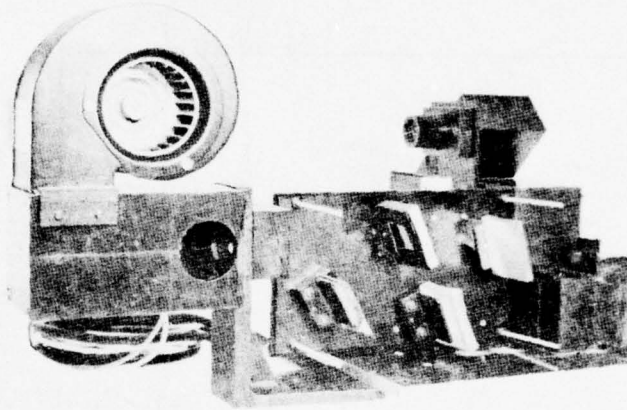


FIGURE 2-11A EXCITATION POLYCHROMATOR (COVER REMOVED).

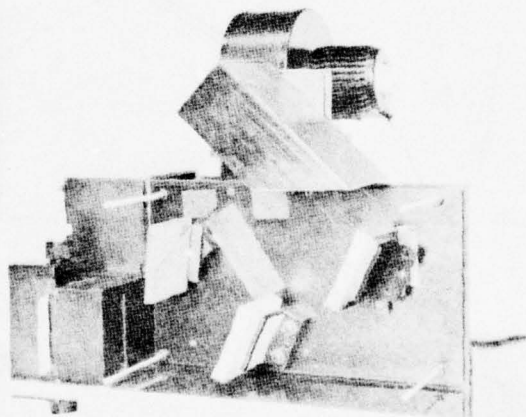


FIGURE 2-11B EMISSION POLYCHROMATOR (COVER REMOVED).

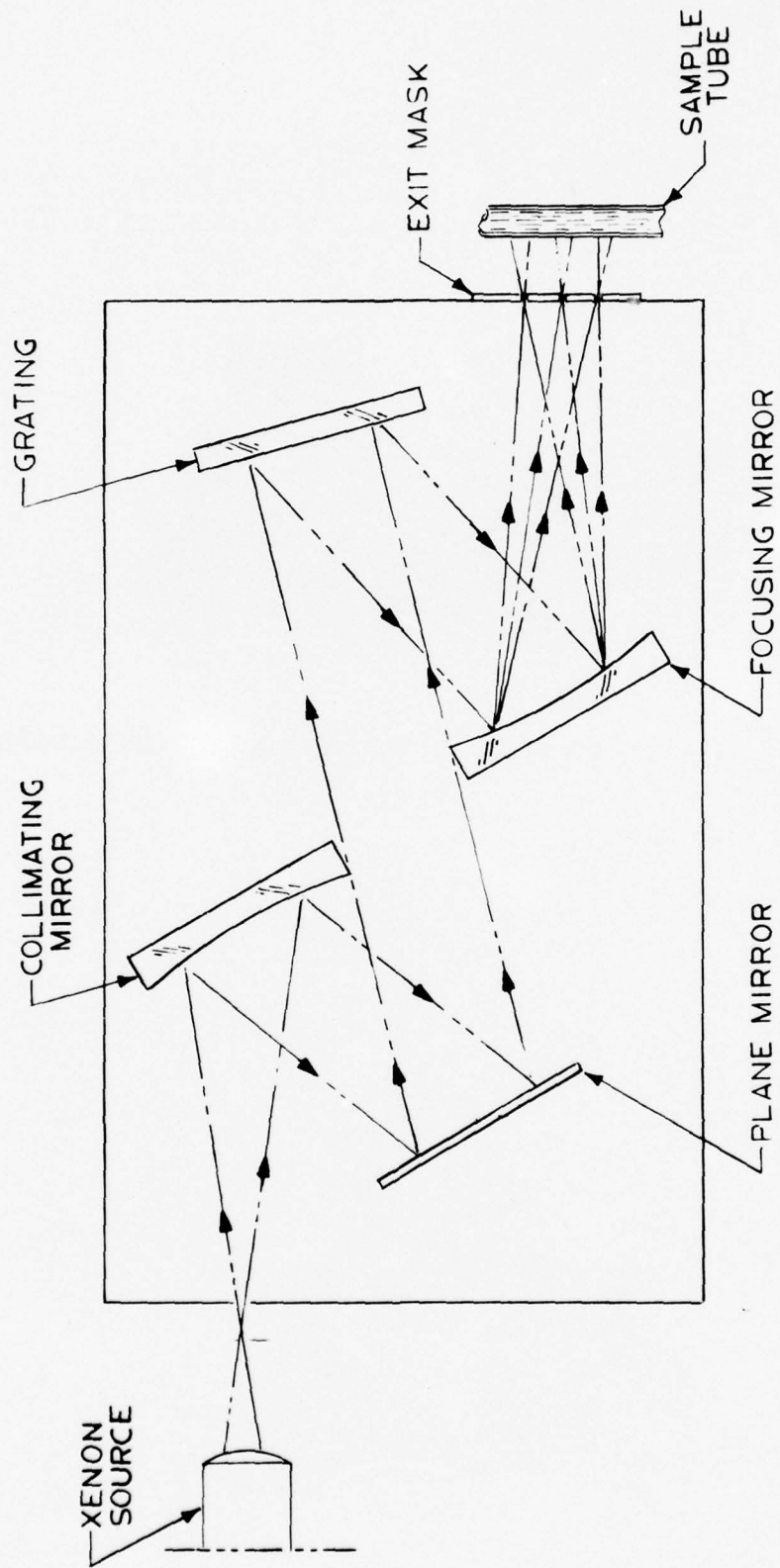


FIGURE 2-12 EXCITATION POLYCHROMATOR

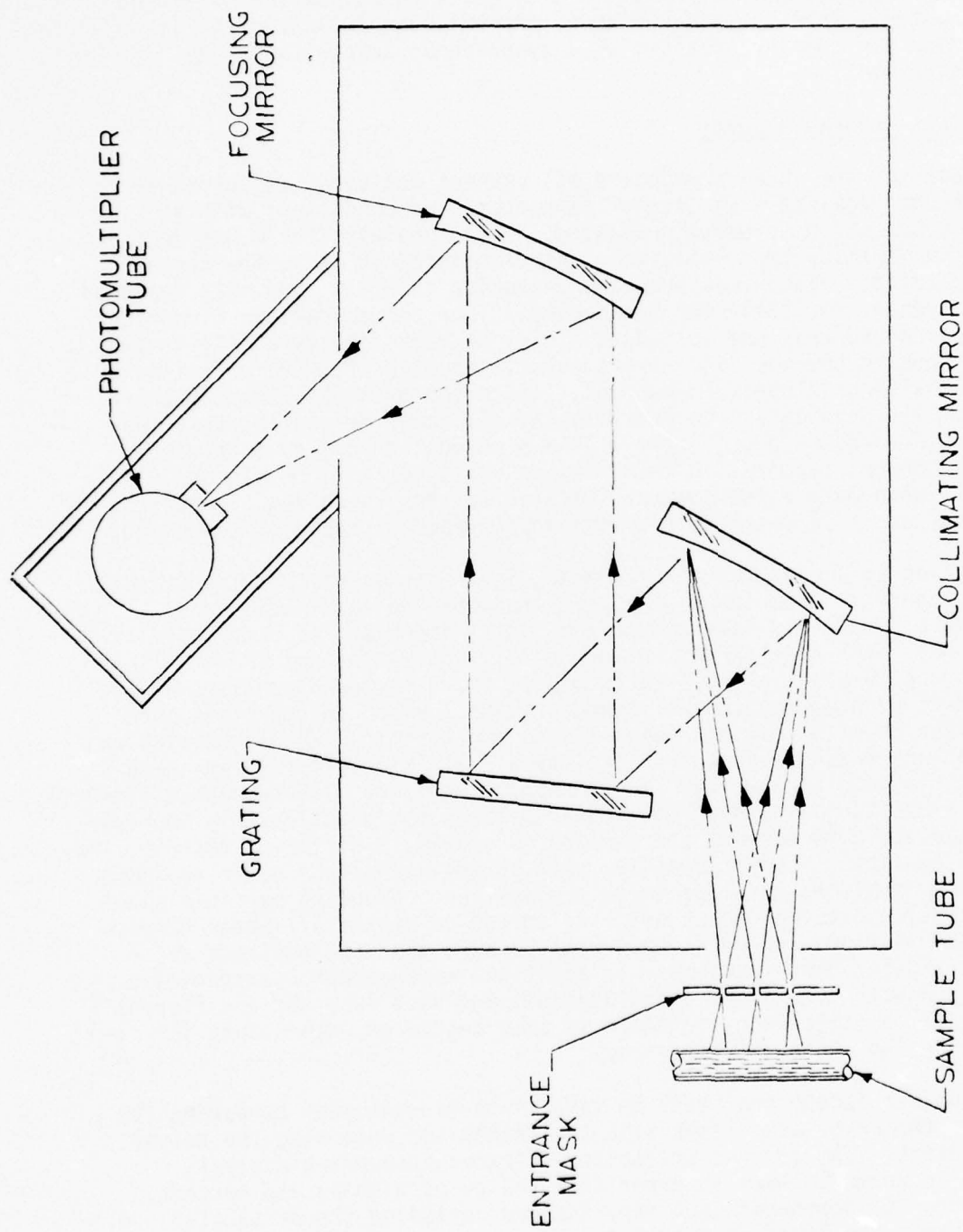


FIGURE 2-13 EMISSION POLYCHROMATOR

excitation wavelengths. The emission wavelengths are then collected and focused onto a RCA 1P28 photomultiplier tube, producing a photocurrent proportional to the combined spectral energy of the different wavelengths. This summing action of the emission polychromator is equivalent to summing sections of a synchronous scan without any mechanical motion.

2.2 Test Program Results

Each of the three breadboard oil content monitors was tested by the vendors against a variety of parameters and conditions with a large volume of data being generated. Unfortunately, there was very little uniformity or statistical control maintained among the three test matrices. Each test program, including the test loop, was designed by the vendor for their own breadboard. Thus the comparison of monitor response based upon the test data had to be made very carefully so that variations in testing, and errors associated with it, were not mistaken for variations in monitor response. Since the main objective of these feasibility studies was to determine if oil could be continuously measured (independent of oil type with ± 5 percent error) in a flowing sample stream, the monitor responses to oil types will be discussed in detail, with only a few comments offered for the remaining parameters. If more detail is desired, the individual reports should be consulted.

Prior to discussing oil response, it is important that the effects of the vendors' test loops on monitor response be examined. In order to make a completely fair comparison, it is important to understand exactly what each monitor was subjected to: The purpose of the test loop was to supply a uniform oil-water mix to the breadboard monitors with a method of controlling the oil concentration. Also, the particle size distribution of an oil mix generated in one test loop should be similar to that generated by another. If they are strikingly different, then there is a good chance that the breadboard monitors will respond differently. Thus, a monitor's response may appear better, but actually this improved response could be because the monitor is viewing a different distribution of oil particles. Unfortunately, part of the variations observed among the three monitors were due to this condition. Since no particle size distribution data was taken prior to injection of the oil-water samples into the monitors, there is no way to be sure that the monitors are seeing similar distributions. In addition, each vendor constructed a test loop with no uniform specifications and each loop had a different method of oil injection, so there is some degree of uncertainty in comparing the monitors' responses.

Another factor that must be taken into account when comparing the data is the error associated with the method for determining the actual oil content. The solvent extraction-infrared absorption analysis method is known to have an error that can be as high as ± 10 percent. This error is dependent upon many factors including the particular procedures used, the level of training, etc.

For comparison, the 9250 Lube Oil used by Baird Atomic was assumed to be similar to that used by G. E. and Enviro. At this point in development, it would have been better if all three breadboards were tested with oils from the same batch to eliminate any variation in product.

Table 2-1 gives an analysis of the data from the oils tested while Figures 2-14, 2-15, and 2-16 present the visual plots of the oil response curves for each breadboard. Linear regression analysis was performed on the data of each oil with a corresponding correlation coefficient calculated. An additional regression analysis and correlation coefficient was calculated using the data point from all the oils listed in Table 2-1 to determine an average response independent of oil type for each monitor. All calculations were made utilizing a Texas Instrument SR51 calculator.

As can be seen from Table 2-1, all three of the monitors were able to measure oil linearly. This is evidenced by comparing the equations generated to the correlation coefficients. A correlation coefficient of one (1) would mean that the data was a perfect fit to the regression line. With this data, all of the monitor responses for the individual oils gave a correlation coefficient of .99 or higher. This indicated that there was a very strong relationship between the data points and the generated curves or that the monitor readings versus the oil content correlated extremely well when the oil type was known. This indicates that part of our goal, i.e. to measure oil linearly over the range of 0 to 100 ppm, was obtained. The problem of the variation in response to oil types, however, still persists. Each of the three regression curves generated from all oils seen by a particular monitor has a much poorer fit. This is indicated by the lower correlation coefficients which do not exceed .87. Thus, the relationship between monitor response versus oil content, independent of oil type, was not as strong for any of the three units.

The problem of variation in response due to oil type can be further analyzed by considering the slopes of the different curves for different oil types for each monitor. This is also presented in Table 2-1. The absolute values of the slopes and intercepts can not be compared from one monitor to another since each monitor has an arbitrary response scale. The important thing to consider is the relative changes that occur in one monitor's response compared to another. The percent change of the upper and lower slope limits relative to the mean slope ranges from 40 to 88 percent for all three breadboards. Also, the standard deviations as a percentage of the mean slope range from 29 to 53 percent. These figures support the lower correlation coefficients calculated for each of the breadboard monitors when determining oil type dependency.

Information is also presented concerning the intercepts of the curves in Table 2-1; however, very poor control of the bias point was exercised in the test programs making the data inconclusive. For example, the bias level was not corrected to zero during Enviro Control's test program. Most of the bias level was caused by the dark current of the photomultiplier and could have been subtracted from the data by the use of the auto-calibrate system; however, this system was not used during the test program.

TABLE 2-1 ANALYSIS OF BREADBOARD OIL MONITOR RESPONSE

OIL	BAIRD ATOMIC		GENERAL ELECTRIC		ENVIRO	
	LINEAR REGRESSION $y = mx + b$ (12 PTS)	COR. COEF. r	LINEAR REGRESSION $y = mx + b$ (5 PTS)	COR. COEF. r	LINEAR REGRESSION $y = mx + b$ (4 PTS)	COR. COEF. r
MARINE DIESEL	$y = 2.58x + 4.52$	0.9985			$y = 0.792x + 58.86$	0.9998
2190 TEP LUBE OIL	$y = 1.76x + 1.86$	0.9854	$y = 0.0158x + 0.000385$	0.9983	$y = 0.503x + 45.94$	0.9981
9250 LUBE OIL	$y = 2.02x + 6.63$	0.9952	$y = 0.0173x + 0.0179$	0.9940	$y = 0.510x + 39.85$	0.9993
NAVY SPECIAL	$y = 0.21x + 1.05$	0.9930	$y = 0.0121x - 0.0113$	0.9983		
#2 (NAPHTHENIC)	$y = 1.86x + 4.85$	0.9881	AROMATIC $y = 0.0226x + 0.0511$	0.9919		
#4 (NAPHTHENIC)	$y = 3.21x + 3.17$	0.9986				
#4 (PARAFFINIC)	$y = 2.50x + 9.12$	0.9916				
#6 (NAPHTHENIC)	$y = 0.46x - 0.25$	0.9955				
BUNKER "C"			$y = 0.00927x + 0.00637$	0.9953	$y = 0.314x + 48.29$	0.9989
ALL OILS	$y = 1.60x + 7.54$	0.6982	$y = 0.0112x + 0.0665$	0.8710	$y = 0.496x + 48.29$	0.844
	SLOPE (m)	INTERCEPT (b)	SLOPE (m)	INTERCEPT (b)	SLOPE (m)	INTERCEPT (b)
MEAN (AVE.)	1.825	3.874	0.0154	0.0129	0.5298	48.16
UPPER LIMIT	3.21	9.12	0.0226	0.0511	0.792	58.86
Δ% ABOVE MEAN	75.89%	135.4%	46.75%	296.12%	49.49%	22.22%
LOWER LIMIT	0.21	-0.25	0.00927	-0.0113	0.314	39.55
Δ% BELOW MEAN	88.49%	106.45%	39.81%	187.6%	40.73%	17.88%
VARIANCE (n)	0.932	8.21	0.0000208	0.000454	0.0291	48.39
STD. DEV. (n)	0.966	2.866	0.00456	0.0213	0.1706	6.956
(STD. DEV./MEAN) % (n)	52.93%		29.61%		32.2%	

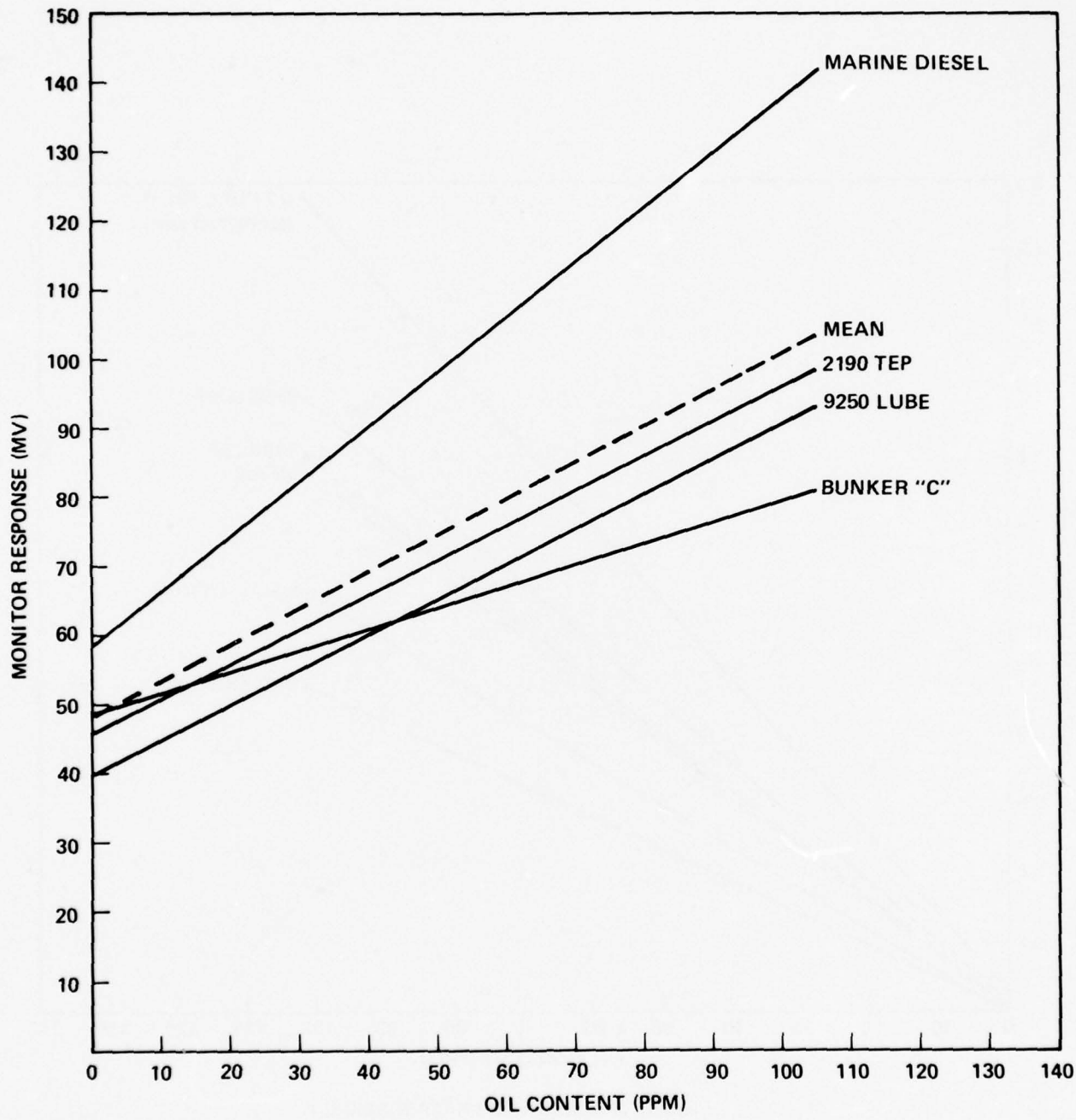


FIGURE 2-14 MONITOR RESPONSE(ENVIRO CONTROL)

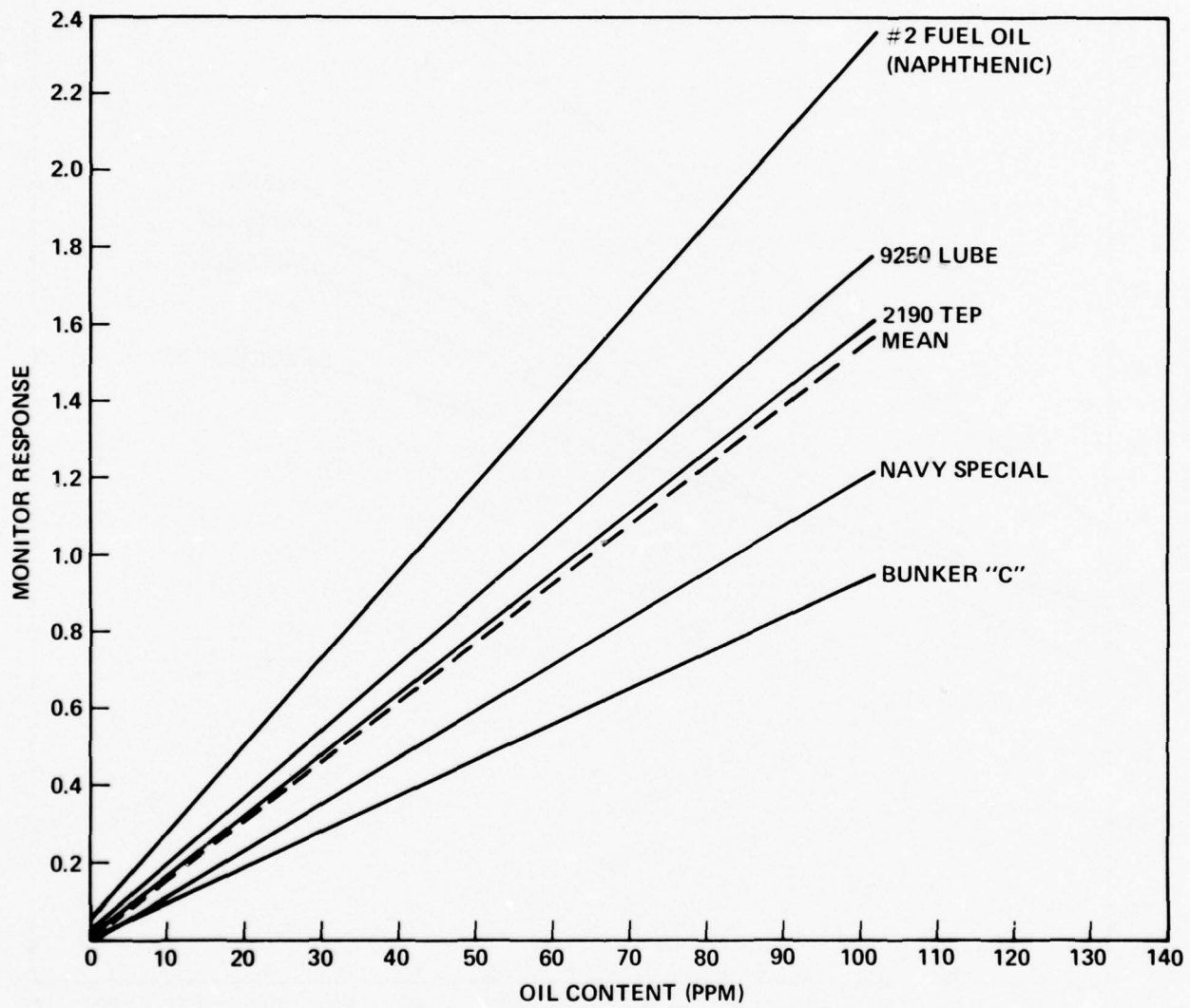


FIGURE 2-15 MONITOR RESPONSE(G.E.)

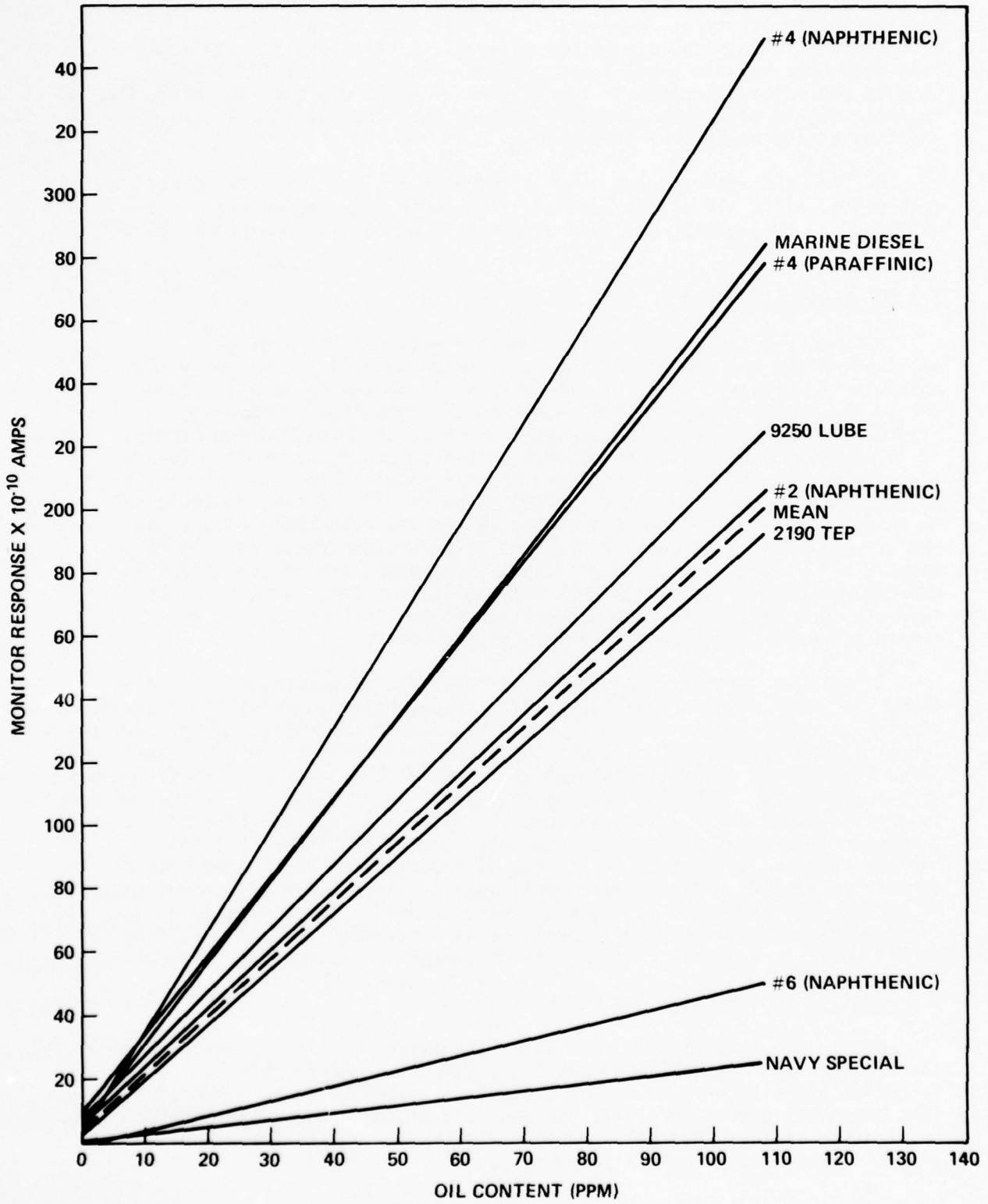


FIGURE 2-16 MONITOR RESPONSE(BAIRD ATOMIC)

From the data presented it has been shown that none of the monitors at this stage of development could serve as a universal instrument independent of oil type. However, if the oil type is known then each of these instruments could possibly be used. A bilge application would fall somewhere between these two extremes. Since there would normally be only two major oil types in the bilgewater (fuel oil and lube oil), the response should also fall somewhere between the response of a single oil and that of the group presented here.

As for other parameters, such as temperature, pH, salinity, dirt, detergents, etc., all effect monitor response to some degree and will have to be investigated further before a useful instrument can be developed.

2.3 Conclusions - Phase I

Figure 2-17 shows the desired monitor response for a bilge application and the proposed Coast Guard error band of ± 5 ppm or $\pm 10\%$, whichever is greater. This single curve would be the calibration curve set by the manufacturer into an installed bilge monitor. Comparing Figure 2-17 with the response curves from the three breadboard monitors, it is apparent that they did not meet this accuracy requirement. Nevertheless, because of the inconclusive Phase I results, the non-uniformity of contractor testing, and the limited range of oils tested, it could not be assumed that these three techniques lacked the potential to function satisfactorily as a bilge monitor. The three breadboards were able to measure oil linearly when the oil types were known, however variation in monitor response between oil types was a problem. Phase I test results indicate that insufficient homogenization of the influent oil/water sample was primarily responsible for this variation.

It was the goal of this program to enter into a prototype development stage upon completion of the feasibility stage; Unfortunately, the feasibility studies were not conclusive enough to warrant selection of any single device for prototype development. It was therefore decided to conduct a second phase feasibility program with each of the three contractors. The follow-on work conducted by the three vendors included: 1) modification of the monitors to improve their sensitivity and selectivity to oil, 2) reduction of the envelope of curves (monitor response data) caused by different linear monitor response to various oil types, 3) reduction of background bias due to particulates or varying water conditions, 4) resolution of various areas of uncertainty that came to light in Phase I, and 5) demonstration of each instrument's capabilities and limitations in monitoring the effluent from an oil water separator. This work is discussed in Section 3.0.

3.0 PHASE II FEASIBILITY

Due to the inconclusive results of the first feasibility phase, and the possibility that modifications might improve monitor operation, a second feasibility program was contracted with each of three vendors. This phase was geared solely to the solution of the bilge water monitor application in that only oils and conditions relating to bilge conditions were utilized as test matrix parameters.

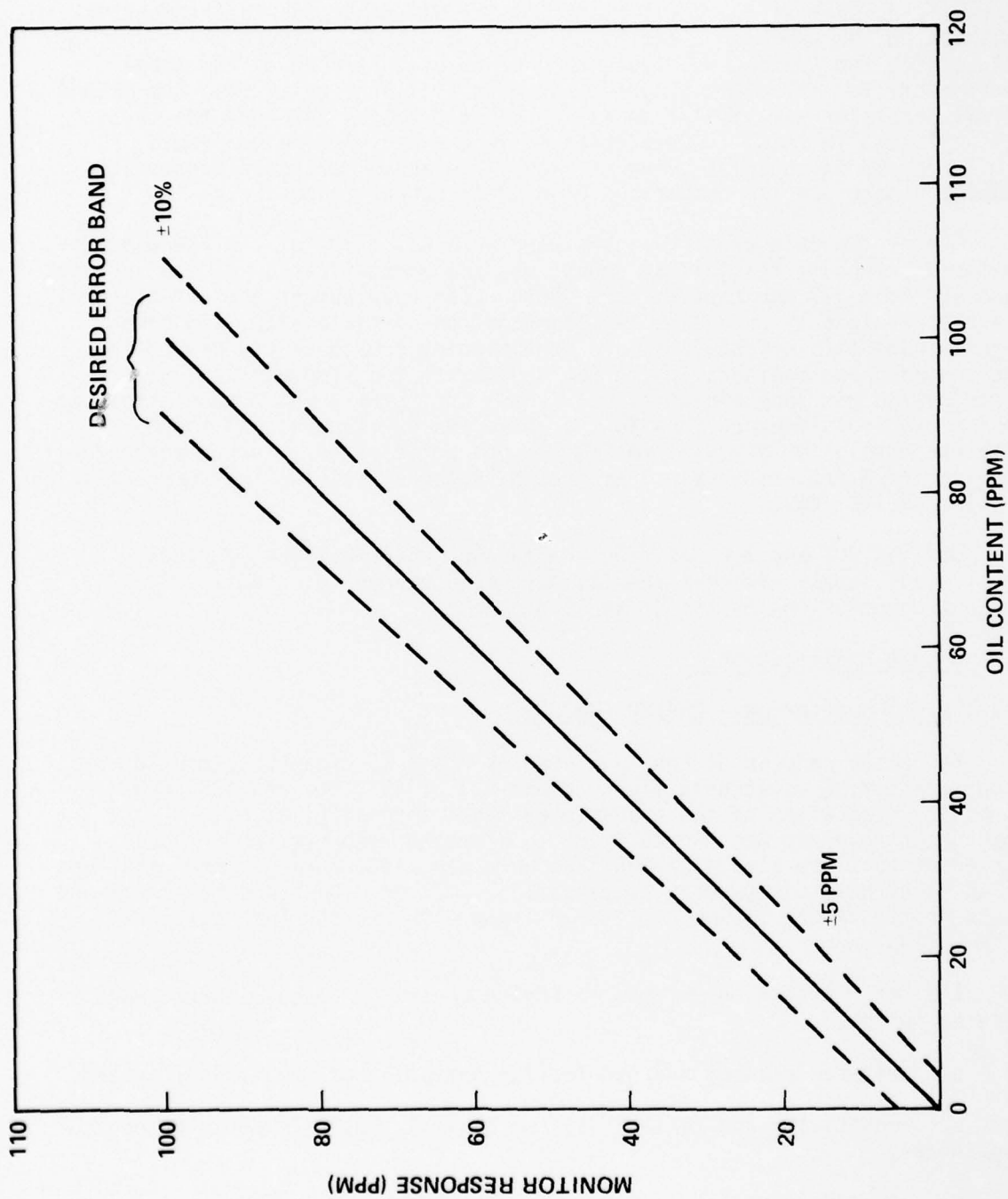


FIGURE 2-17 DESIRED MONITOR RESPONSE BILGE APPLICATION

In an attempt to reduce any variation in the test parameters among the monitors, a uniform test matrix, shown in Table 3-1, was developed. Consequently, monitor response to identical oil mixtures, detergents, particulate matter and water conditions could be obtained. Additionally, attempts were made to ensure that the three test loops were as similar as possible, so that input oil particle size distributions to the monitor would be in the same range and of the same magnitude. Figure 3-1 illustrates the typical test loop components used by each of the three contractors for this test program. It should also be noted that the method of oil injection was similar in all three test loops, and that the test oils utilized in Phase II were obtained from a Navy source to ensure similarity of oil species being sampled. The above mentioned constraints enabled a more concise comparison of monitor output responses.

One of the main problems associated with all three of the breadboards in the first phase feasibility study, was the homogenization of the influent sample. Most all monitors to date, both under development and off-the-shelf, are either directly or indirectly dependent on particle size. In order to eliminate this effect, a sample conditioning component was needed in the second phase monitors, which would generate the same particle size distribution mix independent of oil type. The three vendors thus attempted to improve emulsifier designs in the phase two development, although complete resolution of this problem was not anticipated. Future approaches may require a private research project directed at solving the homogenization problem exclusively.

Section 3.1 and 3.2 describe the concept modifications, current development levels and test results of the second phase. Section 3.3 presents conclusions on the Phase II program.

3.1 Concept Modifications

3.1.1 Light Scattering - ENVIRO CONTROL

The basic concept of Enviro Control's Phase II breadboard monitor was light scattering (scattered light intensity) at 45°, 90° and 135° and turbidity (logarithm of the transmitted-light intensity) at 0°. Instrument response was "normalized" to standard response, even though different particle size distributions were generated during homogenization, by an electronic dissymmetry compensation function. (Dissymmetry is defined as the ratio of the forward scattered light, I45, to the back scattered light, I135).

The major design objectives of Enviro Control's Phase II breadboard were as follows:

- a. Self-calibrating and non-fouling operation of the optical system.
- b. Sensitivity and reliability; mechanical, optical, and electronic ruggedness.
- c. Low sample residence time.
- d. Low shock and flammability risks or hazards.

TABLE 3-1 OIL-IN-WATER CONTENT MONITOR TEST MATRIX - PHASE II

TEST NO.	OIL MIX.	OIL RATIOS	OIL MIX. CONCENTRATION (PPM)	pH	TEMP. (°F)	PARTICULATES (mg/l)	SALINITY (ppt)	DETERGENTS (PPM)	NO. DATA POINTS	REP. (X)	TOTAL	REMARKS
1	FB	1:1, 1:2, 3:1	10, 20, 50, 125	T	T	0	0	0	12	2	24	STANDARD TESTS FOR LINEARITY AND DEVIATION OF RESPONSE. OIL CONTENT BY IR ANALYSIS
2	FEB	1:1:1, 3:1:1, 1:3:1, 1:1:2	10, 20, 50, 125	T	T	0	0	0	16	2	32	
3	PEC	1:1:1, 3:1:1, 1:3:1, 1:1:2	10, 20, 50, 125	T	T	0	0	0	16	2	32	
4	FC	1:1, 1:2, 2:1	10, 20, 50, 125	T	T	0	0	0	12	2	24	
5	Fj	1:1, 1:2, 2:1	10, 20, 50, 125	T	T	0	0	0	12	2	24	
6	FB	3:1	10, 20, 50, 125	T	35, 100	0	0	0	8	2	16	EFFECTS OF TEMPERATURE
7	FB	3:1	10, 20, 50, 125	4, 10	T	0	0	0	8	2	16	EFFECTS OF PH
8	FB	3:1	10, 20, 50, 125	T	T	0	15, 30	0	8	2	16	EFFECTS OF SALINITY
9	FB	2:1	0	T	T	10, 20, 40, 60	0	0	4	2	8	EFFECTS OF PARTICULATES
10	FB	3:1	10, 20, 50, 125	T	T	10, 40 WATER WETTED	0	0	8	2	16	
11	FB	3:1	10, 20, 50, 125	T	T	10, 40 OIL WETTED	0	0	8	2	16	
12	FB	3:1	0 to limit	T	T	0	0	0	5	2	10	UPPER LIMIT OF OIL LINEARITY

TABLE 3-1 OIL-IN-WATER CONTENT MONITOR TEST MATRIX - PHASE II (con't)

TEST NO.	OIL MIX.	OIL RATIOS	OIL MIX. CONCENTRATION (PPM)	pH	TEMP. (°F)	PARTICULATES (mg/l)	SALINITY (ppt)	DETERGENTS (PPM)	NO. DATA POINTS	REP. (X)	TOTAL	REMARKS
13	FB	3:1	0	T	T	0	0	10, 20, 50, 100 MIL-C 2230A	4	2	8	EFFECTS TO DETERGENTS
14	FB	3:1	10, 20, 50, 125	T	T	0	0	10, 50 MIL-C 2230A	8	2	16	
15	FB	3:1	0	T	T	0	0	10, 20, 50, 100 ZIF	4	2	8	
16	FB	3:1	10, 20, 50, 125	T	T	0	0	10, 50 ZIF	8	2	16	
17	FB	3:1	20, 100	T	T	0 to limit	0	0	2	2	4	UPPER LIMITATION OF PARTICULATES

286 TOTAL

NOTES

1. Oils coded as follows:

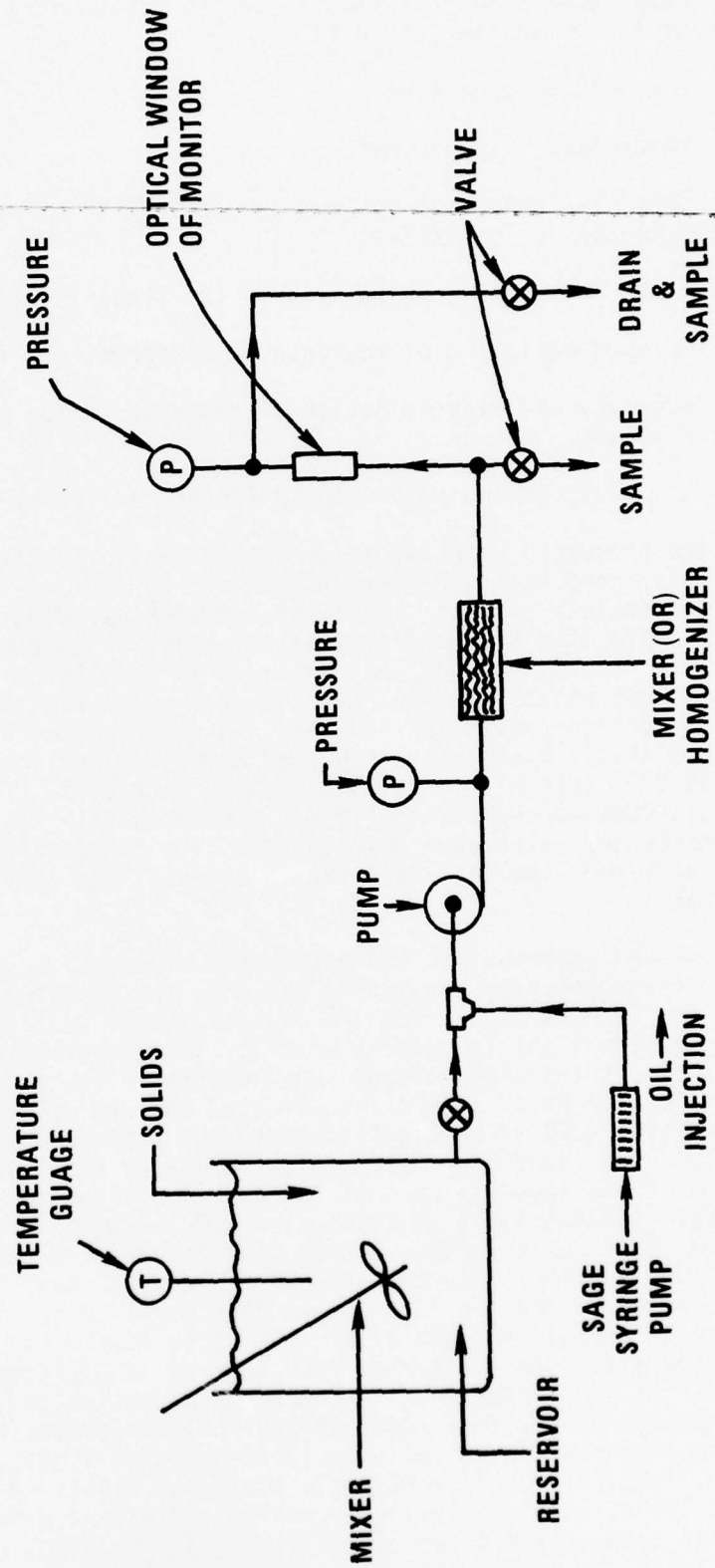
- B MARINE DIESEL
- C NAVY DISTILLATE
- E TURBINE LUBE
- F LUBE OIL
- J BUNKER C

2. T - Tap Conditions pH 5-6
TEMP 64-71°F

3. Particulate mixture will consist of the following:
40% Fe₂O₃
40% Fe₃O₄
20% Air Cleaner Dust

4. Salinity will be adjusted by the use of artificial sea salt - Instant Ocean

FIGURE 3-1 TYPICAL TEST SYSTEM SCHEMATIC FOR PHASE II



- e. Easy conversion from right angle to dissymmetry modes of operation (scatter at 45° to scatter at 135°).
- f. Low voltage operation.
- g. Homogenizer improvement.
- h. Long wavelength for optimum sensitivity to oil particles in a background of smaller particles.

The major operational objectives of the Phase II effort were:

- a. Reduced deviation of response to different oil types.
- b. Accuracy and discrimination of response in the presence of background solids.
- c. Stability of indication for different environmental conditions.

Enviro proceeded with two major approaches in an attempt to reduce the variations of response to different oils and to improve the discrimination against particulate matter. The first approach was directed toward designing a low residence time homogenizer assembly which would produce more uniform oil particle size dispersions at optimized oil-scattered light to non-oil-scattered light ratios. Early Phase II efforts with a two-stage, low-speed homogenizer design proved ineffective, and troublesome in operation. Tests utilizing a static mixer were abandoned when this design was unable to homogenize 9250 lube oil to colloidal-sized particles. Finally, an industrial grade Waring Blender TM was used to obtain design information for an improved flow-through homogenizer. The homogenizer shown in Figure 3-2, was designed from this information and utilized in the Phase II breadboard.

The second approach was the processing of additional size and shape dependent information by monitoring not only the Rayleigh scattering at 90° , but also the forward scattering (45°), back scattering (135°) and the transmission level (turbidity at 0°). To reduce voltage requirements and to eliminate the high voltage requirements of the photomultiplier tubes utilized in Phase I, ECI investigated the use of pulsating light emitting diodes (LED's) as light sources, and photodiodes as detectors. Figure 3-3 shows the sensor head design schematic and Figure 3-4 is a photograph of the sensor. Each of the four identical source assemblies (an infrared (900nm) light emitting diode (ME-5) passed at 1.0 ampere using a 50% duty cycle factor, a heat sink and triplet collimating lens) and the four identical detector assemblies (double (achromat) lens focusing a collimated beam onto a silicon photodiode operated in a photovoltaic mode, matched to an operational amplifier in a single 10-pin can) and positioned at 45° intervals. The cluster of four sources is positioned opposite the cluster of four detectors. As each source was pulsed, a reading was taken from each of the four EG&G-HAV-100A silicon photodiode detectors, and the information stored, as follows: 1) transmitted light, 10° , 2) forward - scattered light, 145° , 3) right-angle scattered light, 190° and 4) back-scattered light, 1135° . Electronic design and signal processing circuits record this data on the order of milliseconds. Fouling, responsivity and emissivity are compensated for electronically. After one cycle (4 pulses),

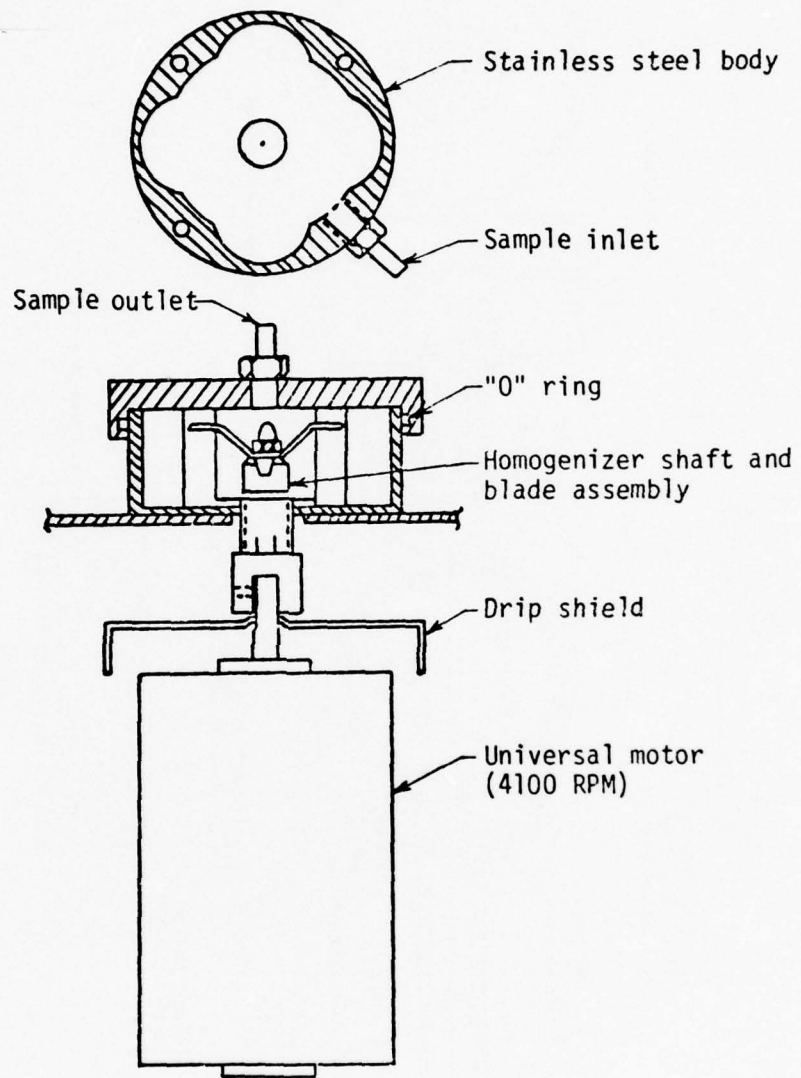


FIGURE 3-2 ENVIRO CONTROL HOMOGENIZER - PHASE II

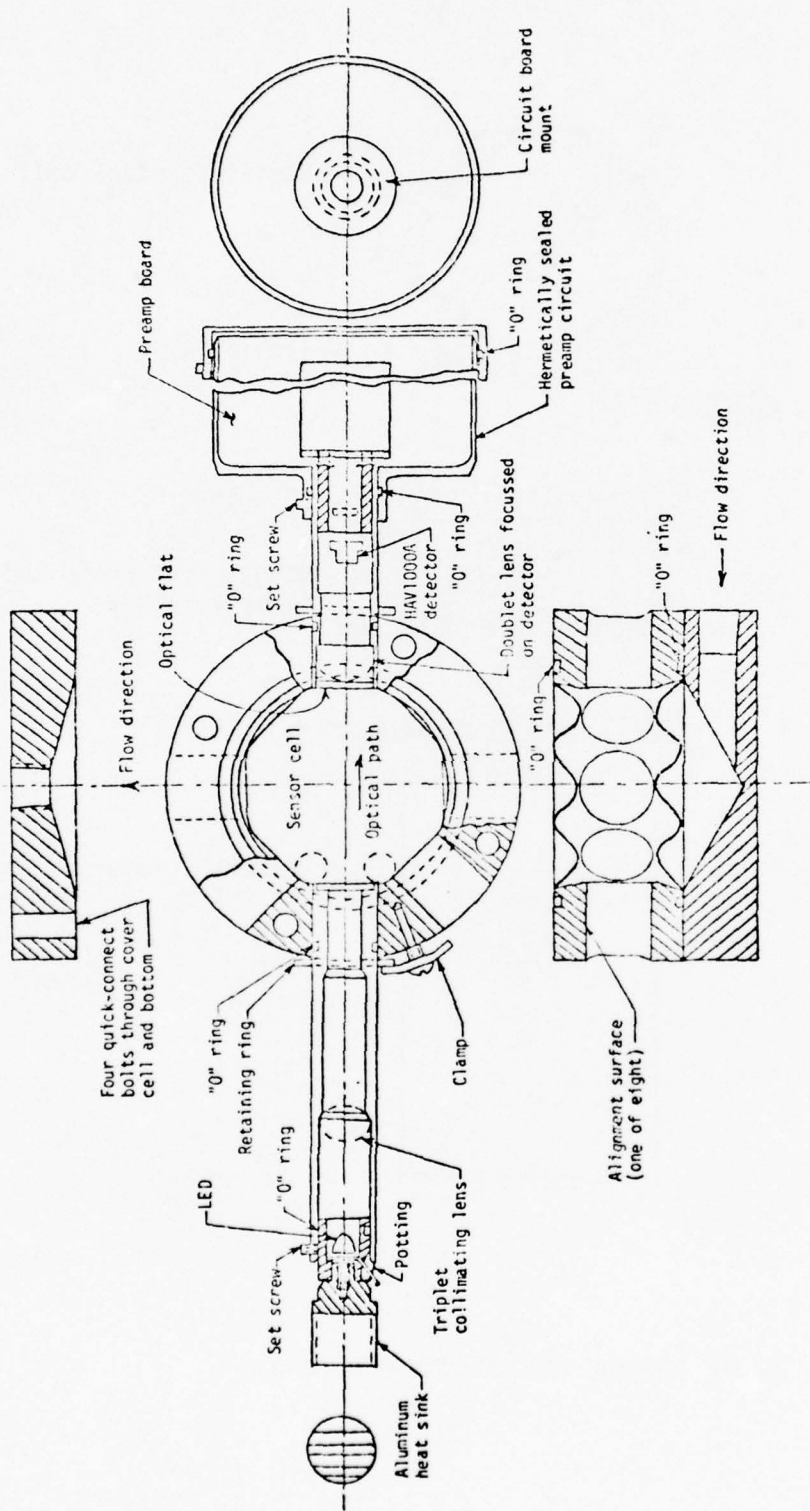


FIGURE 3-3 ENVIRO CONTROL SENSOR HEAD: DESIGN SCHEMATIC - PHASE II

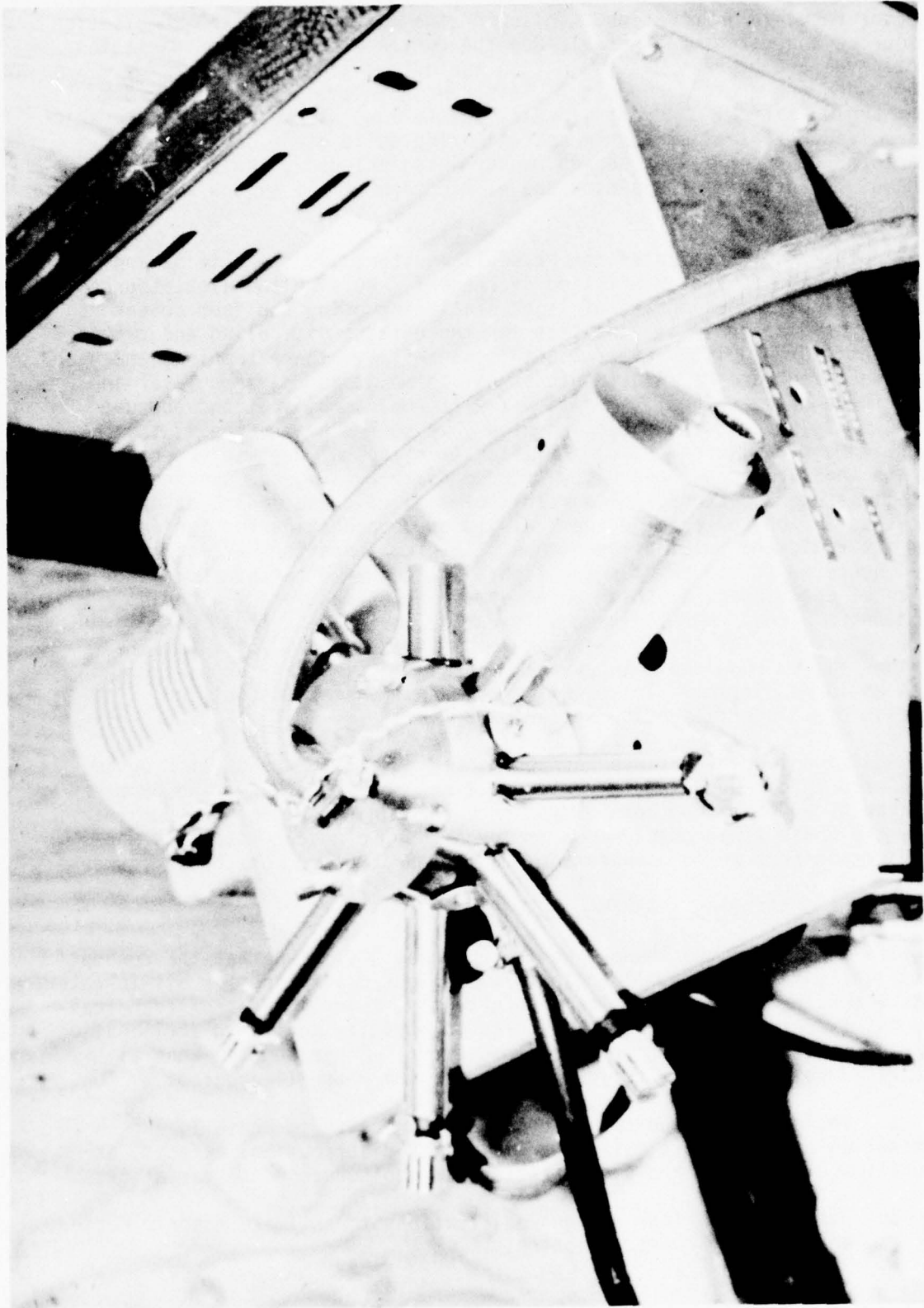


FIGURE 3-4 PHOTOGRAPH OF ECI SENSOR HEAD - PHASE II

the stored information (16 light level signals) was processed, generating 3 or 4 response curves. Each curve provided some different combination of detector response information. Following the test program, the combination of sources and detectors that yielded the curves with the least deviation to oil type and highest discrimination against particulate matter, were recommended for prototype design. This sensor assembly design, for the right angle scattering and dissymmetry scattering, was desired for operation in a pulsed, self-calibrating mode, utilizing solid state sources and detectors. Further sensor design constraints included optimization of light distribution of the sensor and elimination of all window condensation (sealed optics).

Another modification of the Phase II monitor, was the elimination of the auto-calibrate system utilized in Phase I. Pulsing the light sources, and measuring various angles of light scattering using the four detectors, allowed for electronic compensation for the effects of fouling and detector and light source drift. Even with this capability, there remained the need for some fixed internal electronic signal to maintain the zero level and gain of the output signal. Additional electronic modifications pursued in Phase II included the selection of a lamp source power supply, the selection and design of the preamplifiers for the solid state detectors, and the modification of circuitry to accommodate pulsing and synchronizing of solid state detectors. As a result of some of these modifications, the Phase II monitor provided optical window compensation for fouling from its ratio and pulsing techniques. This compensation was shown to be adequate up to the point where light is attenuated beyond the detection limits of the diodes, at which point some form of mechanical cleaning would be required. Nonetheless, this was an improvement from Phase I, where an air barrier system was used to eliminate window fouling. The previous system required maintenance, and also a clean air supply, which would be difficult in an engine room environment without the addition of an air filtration system.

Additional modifications were performed during the Phase II program. In an effort to reduce sample residence time, the Phase I turbine pump was replaced by a MOYNO constant volume, once-through, high pressure pump. Also, the Phase I hydrocyclone was removed, due to poor reliability and an adverse effect on homogenization, to further improve monitor performance.

3.1.2 Light Scattering - GENERAL ELECTRIC

The results of the Phase I monitor program indicated that the concept of spatially-filtered, small angle forward light scattering for oil-in-water content monitoring was feasible. Concurrently, several areas of technical uncertainty were discovered, and efforts to optimize monitor discrimination revealed the potential for further improvement. Consequently, General Electric investigated the following areas in the Phase II program:

- a. Validation of monitor response and linearity in Phase I, and, examination of oil droplet size (particle size distribution) effects, as a function of oil type and concentration, on monitor response variations.
- b. Breadboard monitor design modifications to optimize discrimination, response and accuracy characteristics.

- c. Homogenization techniques.
- d. Optimized spatial filter optics.
- e. Modification of the monitor laboratory verification test loop and program to assure known and controllable conditions.
- f. Optical hardening of the breadboard to eliminate interference of outside parameters on monitor response
- g. Determination of the effects of low temperature on monitor response (eliminate condensation if required).
- h. Improvement of monitor oil sensitivity, reduction of response variations to oil types, sensitivity, reduction of response variations and reduction of background light caused by particulate matter and water conditions.
- i. Determination of the effect of cell orientation (horizontal or vertical flow and gravity effects) on monitor response.

The first task of the Phase II program was to conduct verification tests on the Phase I data to determine the cause of the variation in monitor response. Phase I program results had indicated that the breadboard monitor was capable of measuring oil linearly, however, variation due to oil specie was a problem. In the original design of the breadboard, the spatial filter optics were set to read oil particles between 2-25 microns. Theoretically, monitor response to any oil mixture within this size distribution, should be oil specie dependent, excluding some variation due to the differences in refractive indices among the oils. Phase II verification tests, however, revealed that droplets greater than 25 microns were present in the sample stream (as determined by HIAC TM particle counter). Thus, the problem of variation of response appeared to be partially caused by homogenization. Consequently, Phase II efforts included an investigation of techniques designed to provide an influent oil sample droplet size distribution of between 2-25 microns, for the operational oil types and concentrations being tested.

Initial Phase II homogenization studies concentrated on "active" homogenization devices (mixers) which produced better dispersion, but also introduced undesirable response lag times. Additionally, passive, low-volume devices were investigated. Among those concepts and devices tested were 1) high velocity turbulent flow, 2) a high-shear micro-pump, 3) a high-shear, high-volume centrifugal pump and 4) a small bore static mixer. The static mixing approach was considered the most successful and was utilized for the test programs following the homogenization evaluation. The hydrocyclone utilized in the Phase I monitor was eliminated since solids removal was considered inadequate and homogenization capabilities were poor.

The interface of the selected homogenizer with the spatial filter optics was considered a critical point, since selection of an optimized homogenizer,

capable of producing 2-25 micron sized droplets for "viewing" in the sensor cell, would eliminate the need for adjustments to the spatial filter. The spatial filter optimization task required that consideration not only be given to the homogenizer utilized, but also to air/solids discrimination constraints. Addition of the homogenizer was considered a realistic approach, however, if the homogenizer produced droplets in excess of 25 microns, the spatial filter would have to be opened to include larger droplets. This would have resulted in a trade-off between homogenization and solid particle discrimination (increasing the optics angle by opening the spatial filter, results in a decrease in sensitivity to oil and an increase in particulate matter interference.) As a result of these tasks, a 3mm spatial filter was used, in conjunction with the small bore static mixer.

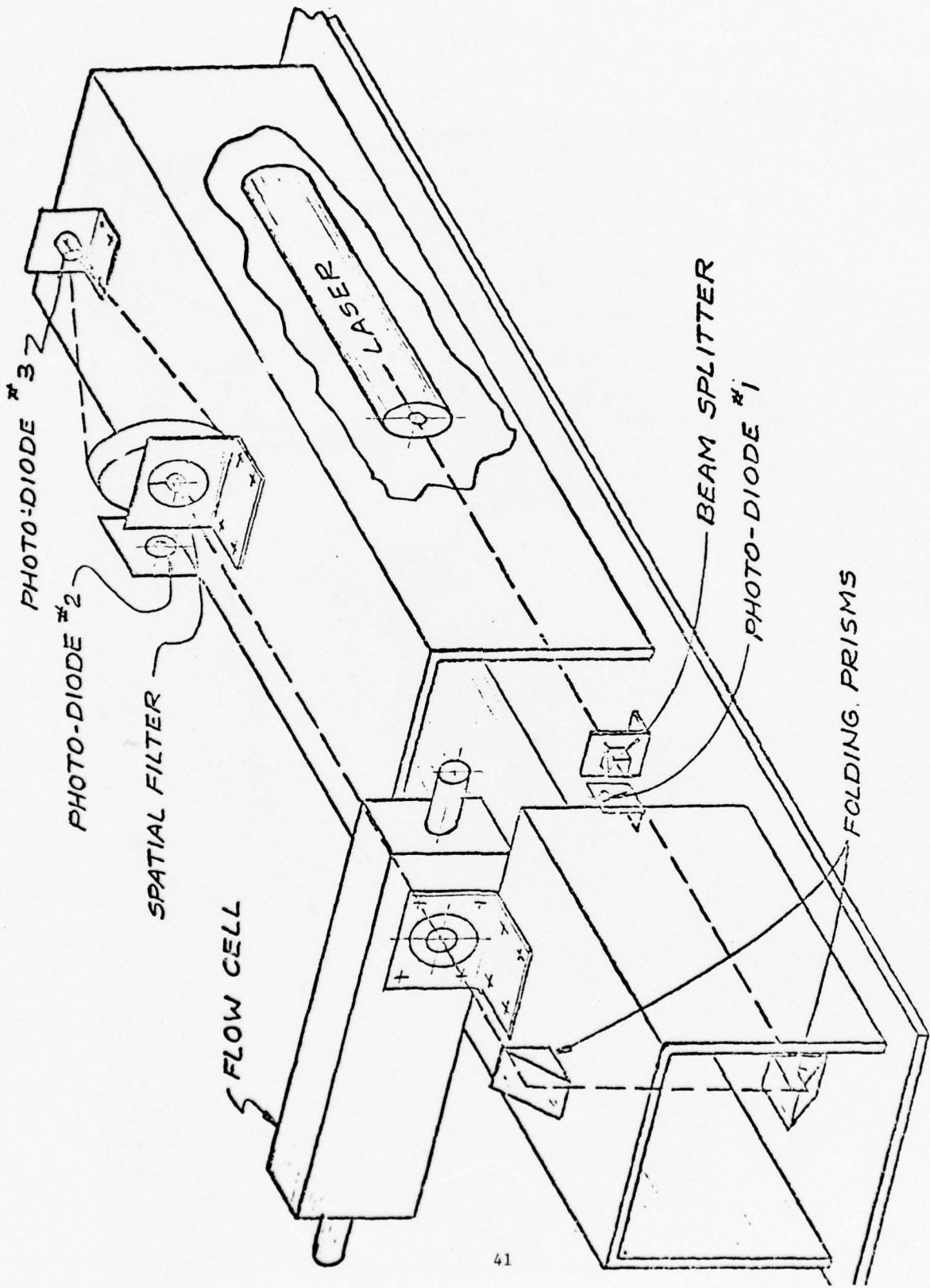
Efforts to optically harden the device for resistance to shock and vibration continued parallel to the homogenization studies. Appropriate mounts for all optics were fabricated, and steel channels were used to stiffen the monitor's aluminum structure. Further modifications included optical window redesign, installation of flow distributors, addition of a new laser source and flow rate adjustment. Figure 3-5 shows a schematic of the monitor, and Figure 3-6 is a photograph of the device. The redesigned monitor featured two folding prisms, designed to fold the optical path into two levels to reduce overall monitor size. Light from a laser source was first focused upon a beam splitter. At 90° to the beam splitter, part of the laser energy was monitored by a silicon photodiode detector (I_o). The remaining energy from the laser was then folded, utilizing two folding prisms, such that the upper light path was 180° from the original laser beam. The laser beam was then directed into the sample cell. Light exiting the sample cell passed through a spatial filter, and the remaining beam was removed by a right angle prism and monitored by a second silicon photodiode (I_t). A lens behind the prism focused the scattered beam around the prism, onto a third silicon photodiode detector (I_s). The laser intensity (I_o), transmitted signal (I_t) and scattered signal (I_s) were ratioed electronically.

Monitor performance verification concluded that response characteristics were comparable to the original bench model. Particle size distribution studies confirmed the monitor's dependency on sample size (2-25 microns) for acceptable response.

Additional studies undertaken in Phase II revealed the following results:

1) Gravity Effects Study - Highly emulsified oil is unaffected by gravity. However, oil droplets larger than 25 microns in size contributed a 15% deviation in monitor response between horizontal and vertical sample cell positions.

2) Low Temperature Effect Study - No significant effects were attributed to sample temperature changes. Condensation effects caused significant interference in monitor response, but were successfully eliminated using desiccants.



41

FIGURE 3-5 GENERAL ELECTRIC MONITOR SCHEMATIC - PHASE II

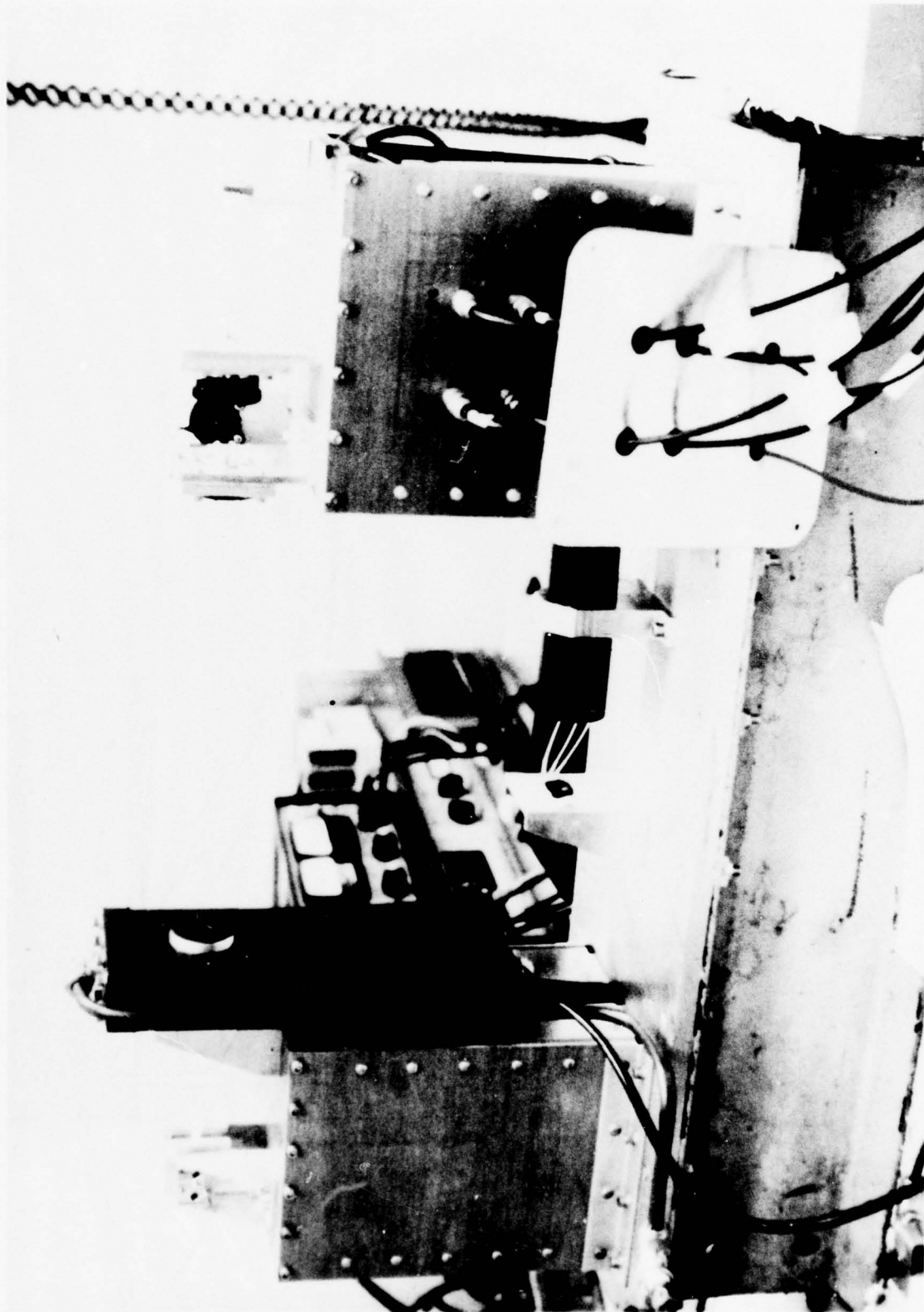


FIGURE 3-6 PHOTOGRAPH OF GENERAL ELECTRIC MONITOR - PHASE II

3.1.3 FLUORESCENCE - BAIRD ATOMIC

Results of the Phase I test program confirmed expectations that the Baird Atomic breadboard monitor would exhibit the widest variation in response between the oil types tested, because of the differences between the fluorescent components of these oils. The device was however, the least effected by other parameters such as pH, salinity and particulate matter.

The monitor performance in Phase I and subsequently, in Phase II, was predictable because of the nature of the concept of oil fluorescence, itself. The level of fluorescence of particulate matter was low as compared to monitor signal recovered, due to the light scattering characteristics of the particulate matter. On the other hand, the addition of detergents to the sample stream, and the increase in influent sample temperature increased the fluorescent signal, because those variables increased the level of emulsification of the influent sample. Increased emulsification resulted in a greater number of smaller oil droplets, each with a reduced optical density to the excitation light. The reduction in optical density allowed a greater proportional volume of those oil droplets to fluoresce, and resulted in an increased monitor output signal. Obviously, emulsification of the influent sample had to be optimized in Phase II to improve monitor performance.

Another problem encountered during Phase I had been the problem of energy transfer. It had been possible to satisfactorily measure both a heavy oil (Bunker "C") and a light oil (Marine Diesel) separately, however mixing the two oils resulted in a transfer of the energy of the light oil to the wavelengths of the heavy oil. Fluorescence was no longer observed at the lower wavelengths for the lighter oil, and the fluorescence level at the higher wavelengths increased, yet the energy transfer and fluorescence levels of the two wavelengths were not additive. Part of this non-linear increase in signal was thought to be caused by quenching - the lighter oil cutting the heavier oil - allowing better homogenization and a decrease in optical density.

Baird Atomic approached the problems of emulsification, energy transfer and quenching in the Phase II effort by investigating the following:

- a. Improved emulsifier design.
- b. Synchronous scan mask optimization.
- c. Total luminescence modification.
- d. Transmission and right angle scatter channels.

By increasing emulsification, Baird Atomic hoped to reduce the variations in monitor response caused by temperature, detergents (non-fluorescent) and optical density. The improved emulsifier design was a high-speed (10,000 rpm), motor-driven Tekmar Model 456 generator. The emulsifier was redesigned as a two-stage device, with stainless steel ball

bearings. Although emulsification was not considered optimum, significant improvement was noted over Phase I results. In addition, by USCG request, a FLOTEC Model R251-1104V circulating pump was added at the influent end of the breadboard monitor to make the device independent of the positive pressures which might exist in the oil/water sample.

The Phase I breadboard mask design was optimized with the aid of a computer, for 30 oils and mixtures which included oil types (crudes) not applicable to the bilge environment. Phase II synchronous scan mask optimization utilized only oil mixtures that were specified by the final test program, which were representative of bilge environments (marine diesel, 9250 lube oil, 2190 TEP lube oil, Navy distillate and Bunker "C"). As before, this optimization was done with the aid of a computer program, however it was more refined and included mask slit height information.

The purpose of the transmission and scatter channel task was to investigate a first-order correction to changes in instrument response due to deterioration of the light source, fouling of the flow cell, and scattering due to air bubbles and particulates. The transmission channel, operated at a long wavelength where most oils do not absorb appreciably, was designed to ratio the oil fluorescence signal to the transmission signal, thus monitoring all effects related to fluorescence except scattering. Monitoring of the same wavelength at right angles to the transmission channel, allowed a first-order correction for scatter. Plastic fiber light pipes, photomultiplier tubes and filters were the significant components utilized in this design effort. Sequential recording of fluorescence, transmission and scatter signals was conducted, and the data was analyzed to derive an algorithm allowing for compensation of monitor response.

In a parallel effort, Baird Atomic investigated the use of total luminescence scanning (TLS), in lieu of synchronous scanning, for the Phase II breadboard oil content monitor. A second optical unit was constructed and tested. The unit, TLS or synchronous scan, that appeared to give the most accurate response with the least variation due to oil type was to be used in the final breadboard. The earlier instrument made use of the emission confined to a selected synchronous scan, whereas the total luminescence unit considered emission over the entire excitation/emission plane. This instrument was similar in size, complexity and cost to the previous breadboard, and used the same general components, however, it required a different configuration of the polychromators and placed a higher priority on minimizing scatter. The TLS breadboard used two high quality commercial monochromators modified for polychromatic use, which were coupled to the sample cell in a manner similar to that of Phase I. The light from the light source, passed through the excitation polychromator onto the sample tube. A lens system then imaged the luminescent sample tube onto the entrance slit of the emission polychromator. A second lens system imaged the total luminescence pattern (emission polychromator turned 90° in reference to excitation polychromator to disperse the fluorescent light into a two dimensional field) on the final mask located at the photomultiplier tube detector. A two dimensional raster-scanning accessory was fabricated to allow accumulation of the necessary basis data on the oil mixtures specified in the final test program. The basis data along with a computer program was used to determine final exit mask design.

Figure 3-7 is a schematic of the sensor assembly, while Figure 3-8 is a photograph of the monitor.

Additional efforts conducted under Phase II included 1) modification of the sample tube and 2) replacement of the light source. The sample tube modification task investigated square sample tubes to determine whether there was a significant decrease in scatter or increase in optical efficiency over the original round sample tube. Also investigated was the dependence of luminescence on mask slit height and the effect, if any, of condensation (moisture) on signal scatter. As a result of this task, the square sample tube was utilized to complete the monitor development program, and the optical mask was modified under the assumption that the slit height function was purely quadratic. Under normal conditions, moisture was not considered a problem, and no corrective measures were necessary.

The new lamp utilized in the monitor was a Varian model 6207-UV lamp (now designated as VIX-150-UV) with a 3.5 inch focal length quartz lens. This lamp utilizes an aluminized parabolic reflector which produces parallel light, subsequently focused by the lens. The original lamp, a Varian model 6242-UV, with a ellipsoidal reflector produced a focused beam without the aid of a lens, however, it is no longer in production. The new lamp was considered optically equivalent, and was therefore incorporated into the Phase II device.

3.2 Test Program Results - Phase II

Performance verification tests on the three breadboard monitors were conducted at the respective contractor's laboratories in accordance with the test matrix shown in Table 3.1. This standardized matrix was established prior to Phase II to preclude the possibility of bias in monitor test performance results due to variance in test conditions. The only noted exceptions to the matrix were as follows:

a. DETERGENTS - General Electric, Co. and Baird Atomic, Inc. used general purpose detergent, non-ionic type, MIL-D-16791EAM3 Type 1 in lieu of MIL-C-2230A, used by Enviro Control, Inc.

b. <u>TAP CONDITIONS</u> -	pH	Temp
General Electric, Co.	5-6	64-71°F
Enviro Control, Inc.	7	60-75°F
Baird Atomic, Inc.	5-6	64-71°F

c. <u>TEMPERATURE</u>	
General Electric, Co. :	35°F, 60°F, 100°F
Enviro Control, Inc. :	35°F, 60°F, 100°F
Baird Atomic, Inc. :	34°F, 56°F, 102°F

d. <u>DATA POINTS</u> -	
General Electric, Co. :	286
Baird Atomic, Inc. :	286
Enviro Control, Inc. :	398 (conducted an additional 112 test runs at the 0 ppm level)

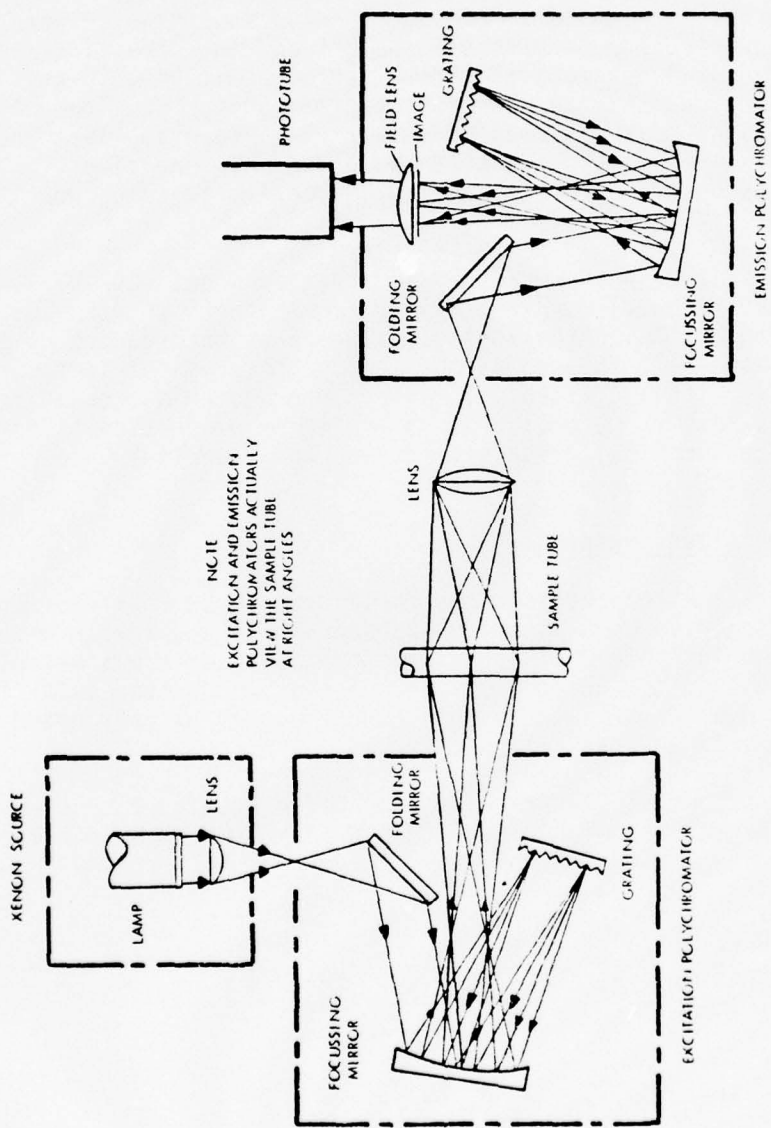


FIGURE 3-7 BAIRD-ATOMIC SENSOR ASSEMBLY SCHEMATIC - PHASE II

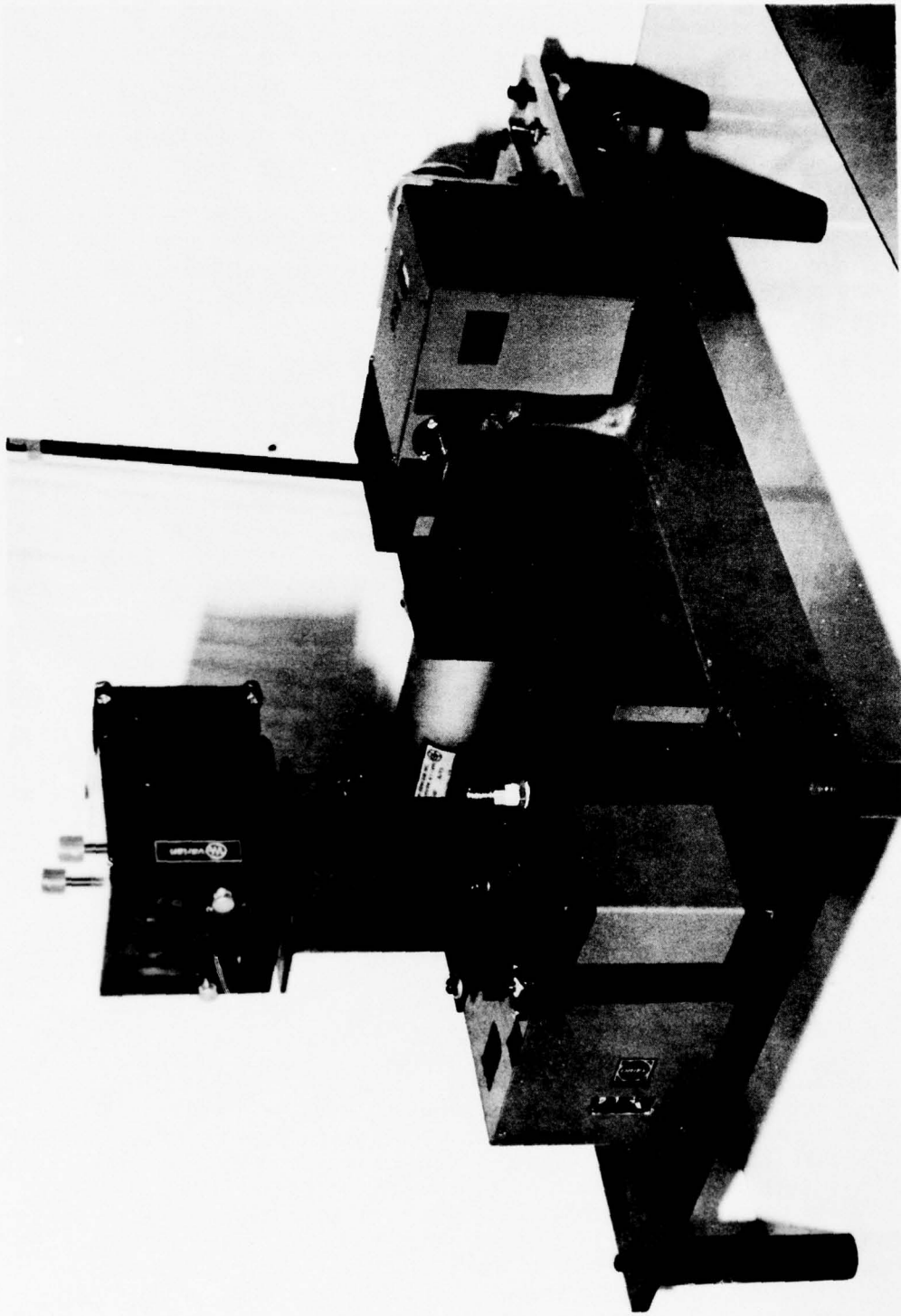


FIGURE 3-8 PHOTOGRAPH OF BAIRD ATOMIC MONITOR - PHASE II

Based on previous test results, the only exception which might be significant is the difference in detergents tested by the contractors. Additional monitor testing would be required to determine how significantly this detergent substitution effected monitor performance results.

One additional difficulty in the analysis of the Phase II performance test results was the manner of data presentation exercised by the contractors, however the degree of uniformity and control in the Phase II program was considered sufficient to allow for an adequate evaluation of the devices. As was the case in the Phase I program, the errors associated with the method for determining the actual oil content (solvent extraction - infrared analysis method) must be taken into account when analyzing the performance results of the monitors.

Section 3.2.1 - 3.2.9 summarize the results of the Phase II feasibility program. Additional details concerning either the Phase II monitor development program or the results of the test programs can be obtained by consulting the individual contractor final reports listed in the reference section of this report.

3.2.1 Linearity of Response

The primary means of analyzing Phase I monitor response data was by comparing linear regression analysis of the data, as presented in Table 2-1. A similar analysis of the Phase II monitor oil response tests is given in Table 3-2. The monitors developed during Phase II demonstrated nearly the same linearity as in Phase I, which is significant since Phase I results are for monitor response to individual oils, and Phase II results reflect monitor response to various oil mixtures, the more difficult case. The results presented in Table 3-2, specifically the "all oils w/o Bunker C" and "all oils and mixtures" linear regression curves, indicate that the Phase II breadboard monitor response was much less dependent upon oil type. The data for oil mixtures containing Bunker "C" may be somewhat biased due to handling and injection problems experienced during the test program. Insufficient mixing and the inability to adequately control concentrations of the Bunker "C" oil is believed responsible, in part, for notable decreases in correlation coefficients for these mixtures.

It should further be noted that the correlation coefficients for the Enviro Control, Inc. monitor response are lower in most cases than the other contractors. This may be attributed to the fact that not all of the available data provided by the monitor's output was utilized by this author to develop the linear regression curves presented in Table 3-2. (The ECI device features an electronic signal processing unit which converts the normal monitor output signal (Table 4-1 data) into a "dysymmetry compensated" signal. (see reference 5). The resulting monitor response is essentially a hybrid function of the data normally obtained, which would exhibit higher correlation coefficients and a smaller deviation of response.) In an effort to reduce the volume of data presented in the Enviro Control, Inc. final report, the computation of the linear regression curves was omitted, and only the curves were presented. The data in Table 4-1, unprocessed monitor response data, was utilized in an effort to provide some means of assessing overall monitor performance.

TABLE 3-2 ANALYSIS OF PHASE II BREADBOARD OIL MONITOR RESPONSE

OIL	BAIRD ATOMIC		GENERAL ELECTRIC		ENVIRO CONTROL *	
	LINEAR REGRESSION $y = mx + b$ (2 RUNS OF 4 PTS)	COR. COEF. r	LINEAR REGRESSION $y = mx + b$ (2 RUNS OF 4 PTS)	COR. COEF. r	LINEAR REGRESSION $y = mx + b$ (2 RUNS OF 5 PTS)	COR. COEF. r
FB	$y = 3.38x - 0.9$.995	$y = 0.0050x + 0.0037$.978	$y = .00049x - .00538$.959
FEB	$y = 4.25x - 1.2$	1.000	$y = 0.0057x - 0.0012$.982	$y = .00026x + .00045$.873
FEC	$y = 4.30x - 0.4$	1.000	$y = 0.0064x - 0.0130$.969	$y = .00020x + .00039$.958
FC	$y = 3.68x - 0.2$.995	$y = 0.0051x + 0.0710$.947		
Fr	$y = 6.39x - 4.1$.995	$y = 0.0022x + 0.0040$.995		
3FB	$y = 2.85x + 2.1$.985	$y = 0.0052x + 0.0079$.998	$y = .00028x - .00016$.979
F2B	$y = 2.69x + 1.0$.995	$y = 0.0058x + 0.0054$.985	$y = .00058x - .00094$.976
FE2C	$y = 2.67x + 3.6$.975	$y = 0.0059x + 0.0920$.979	$y = .00030x - .00017$.909
F2C	$y = 3.42x + 0.3$.990	$y = 0.0053x + 0.0586$.936		
3FEB	$y = 3.72x + 0.1$.995	$y = 0.0054x - 0.0040$.970	$y = .00018x - .00158$.950
F3EB	$y = 4.90x + 0.1$.995	$y = 0.0053x + 0.0040$.968	$y = .00018x - .00134$.969
FE2B	$y = 3.82x - 1.3$	1.000	$y = 0.0059x + 0.0090$.989	$y = .00035x - .00314$.958
3FEC	$y = 3.83x + 0.3$.995	$y = 0.0047x + 0.0210$.946	$y = .00019x - .00221$.947
F3EC	$y = 3.43x + 0.4$	1.000	$y = 0.0058x + 0.1030$.970	$y = .00017x + .00036$.973
3FC	$y = 3.08x + 1.0$.985	$y = 0.0049x + 0.0430$.930		
F2r	$y = 17.25x - 11.9$.980	$y = 0.0021x + 0.0060$.959		
3Fr	$y = 3.28x - 0.3$.995	$y = 0.0029x + 0.0290$.929		
ALL OILS w/o BUNKER C	$y = 3.31x + 1.9$.975				
ALL OILS AND MIXTURES	$y = 3.30x + 5.2$.933				

KEY: B — MARINE DIESEL MIL-F-16884
 C — NAVY DISTILLATE MIL-F-24397
 r — BUNKER "C"

F — LUBE OIL MIL-L-9000
 E — TURBINE LUBE OIL MIL-F-17331

* SEE TEXT FOR EXPLANATION OF DATA

Linearity of response tests were conducted by each of the contractors to determine the upper limit of linearity. Notable problems experienced in this test were slippage of the infusion pump mechanism at high pumping speeds and limitation of meters and electronics to the 125 ppm concentration level (the approximate scale of similar shipboard devices). Despite these problems, monitor response in all cases was demonstrated up to 400 ppm. Results for the individual contractors are presented in Table 3-3.

TABLE 3-3 UPPER LIMIT OF LINEARITY OF MONITOR RESPONSE - PHASE II

CONTRACTOR	UPPER LIMIT
ENVIRO CONTROL	400-500 ppm
GENERAL ELECTRIC	500-1000 ppm
BAIRD ATOMIC	1000 ppm

3.2.2 Homogenization & Particle Size Distribution Studies

In the Phase I feasibility studies, the problem of insufficient homogenization of the influent sample was believed to be responsible for much of the deviation of monitor response between various oils. As previously indicated, each of the contractors attempted to improve their homogenization techniques during the Phase II effort, which may explain the improved monitor performance to oil mixtures.

Additionally, General Electric undertook a particle size distribution effect study to determine the dependence of monitor response on particle size. Results of their study indicated that particles in excess of 25 microns were not being "viewed" by the monitor, and hence, were causing a deviation in monitor response due to the "undetected" oil. Furthermore, in an attempt to determine the effect of sample cell orientation on monitor response (gravity effects), General Electric compared monitor response between horizontal and vertical cell positions at identical 100 Mg/L influent oil concentrations. Results of this task indicated a 15% deviation of response between the horizontal and vertical cell positions, when particles in excess of 25 microns were present. Deviation of monitor response was insignificant for particles less than 25 microns in size.

Results of these tests reconfirmed previous determinations that adequate homogenization of influent samples is critical for optimized monitor response.

In both of the light scattering techniques, and in the fluorescence technique where increased homogenization improves fluorescence efficiency, optimization of present monitor system emulsifiers represents a potential refinement of the prototype monitoring devices, and a subsequent improvement in monitor response.

3.2.3 Response to Oil Mixtures

In addition to the linear regression analysis of monitor response presented in Table 3-2, each contractor determined the deviation of monitor response to various oil mixtures. Refinement of the Phase II test matrix, Table 3-1, was conducted in such a fashion as to select those oils mixtures which most accurately reflected the composition of naval vessel bilgewaters. With the exception of Bunker "C", which is used on only a limited number of vessels, all of the oil mixtures tested could conceivably be present in a naval vessel's bilge.

Monitor response to all oil mixtures, excluding those containing Bunker "C", was within $\pm 20\%$ of the actual oil content, as measured by the solvent extraction, infrared analysis method. This is significant in that the performance demonstrated for oil response by all three contractors was within the anticipated IMCO (Inter-Governmental Maritime Consultative Organization) and U. S. federal monitor performance specifications. When Bunker "C" oil mixtures are included, monitor response decreased noticeably, however, anticipated improvements in monitor prototype designs should reduce the degree to which the monitors are dependent upon oil specie.

Table 3-4 contains the deviation of response data for each contractor. Baird Atomic indicates in their final report that the actual monitor DOR is believed to be less (3-5% at the 50 ppm level for all oils without Bunker "C"), and attributes the difference to 1) errors in mask design and 2) statistical nonequivalence of data subsets.

Enviro Control, on the other hand, indicates that experimental errors originating in the electronic data processing unit are responsible for a portion of their deviation of response. General Electric attributes some deviation in monitor response to the inability to adequately control syringe pump oil concentrations and to minor instrument drift.

3.2.4 Effects of pH

Throughout the feasibility programs, it was commonly agreed that the effects of pH on monitor response would be insignificant. Changes in pH were not expected to effect the emulsification process of the influent oil or alter the light scattering or fluorescence phenomena in any way, hence, no appreciable effect on monitor response was expected. The results of the Phase II tests on pH, presented in Table 3-5, confirm this.

3.2.5 Monitor Response Time

All three monitors developed under the Phase II effort, exhibited response times of less than 10 seconds. (from addition of influent oil to monitor detection.) This is well within the proposed IMCO and U. S. federal specification requirement of 20 seconds.

TABLE 3- 4 DEVIATION OF MONITOR RESPONSE DUE TO OIL MIXTURES — PHASE II

	GENERAL ELECTRIC (AVERAGED)	ENVIRO CONTROL (AVERAGED)	BAIRD ATOMIC		
			@ 10ppm	@ 50ppm	@ 100ppm
SINGLE OIL TYPE	+ 10%	-----	-----	-----	-----
ALL OILS (WITH BUNKER "C")	+ 55%	+ 21%	+ 18.6%	+ 25.9%	+ 27.5%
ALL OILS (WITHOUT BUNKER "C")	+ 14%	+ 13%	+ 13.2%	+ 18.1%	+ 19.4%

TABLE 3- 5 DEVIATION OF MONITOR RESPONSE DUE TO CHANGE IN pH — PHASE II

TEST CONDITION:	GENERAL ELECTRIC	ENVIRO CONTROL			BAIRD ATOMIC			
		(1 135) 4A SIGNAL	(1 45) 2A SIGNAL	$\left[\frac{7.03}{Z} \right]^2$ SIGNAL	@ 10ppm	@ 20ppm	@ 50ppm	@ 100ppm
pH TESTED AT pH4, pH7 AND pH10 LEVELS	+ 3.8% DOR BETWEEN HIGH AND LOW LEVELS	+ 13.0%	+ 9.1%	+ 18%	+ 10.9%	+ 4.8%	+ 5.3%	+ 5.7%

3.2.6 Effects of Salinity

As in the case of the pH tests, the tests conducted to determine the effects of salinity were not expected to produce significant results. The results presented in Table 3-6 are consistent with the fact that salinity changes should not effect the emulsification process of the influent oil or alter the light scattering or fluorescence phenomena in any way. The deviations in response are in most cases less than the error associated with the solvent-extraction, infrared analysis method of determining oil content, and may be attributed, in part, to the limited amount of scattering that is characteristic of these devices.

3.2.7 Effects of Temperature

In addition to the determination of the effect of temperature changes on monitor response, studies were also conducted to determine the effect of cell window condensation.

General Electric determined that the condensation interference was significant, but that the problem could be successfully eliminated by using a desiccant and sealing the monitor housing. Baird Atomic encountered no condensation problems under normal test conditions. In all three cases, condensation on the cell windows would be expected to cause scattering of the light source, and a deviation in monitor response. Anticipated prototype designs would eliminate the presence of condensation and allow for adequate compensation of the scattered light.

Several observations were made during the temperature effects tests, the results of which are presented in Table 3-7. At higher temperatures, Baird Atomic noted some increase in monitor signal, possibly due to increased oil emulsification, since temperature increases were not expected to effect the fluorescence characteristics of the oils. Enviro Control experienced a notable difference in response at the various scattering angles being monitored, but believes that electronic compensation for this interference can be incorporated into a prototype device. General Electric noted that dramatic temperature changes resulted in thermo-physical and thermo-mechanical alterations in optical alignment, and a corresponding deviation of response. Again, proposed prototype design modifications are expected to alleviate this problem.

3.2.8 Effects of Detergents

The presence of detergents and cleaning agents aboard naval vessels dictated that a determination be made as to the effect of detergents on monitor response. Available data on separating devices indicates that, in most cases, detergents will interfere with normal separation processes by creating an emulsion that is "too tight" to separate mechanically. Initial monitor tests confirmed that detergents would also interfere with monitor performance.

Table 3-8 gives the results of the Phase II detergent interference tests. General Electric indicated that their monitor did not respond to

TABLE 3-6 DEVIATION OF MONITOR RESPONSE DUE TO CHANGE IN SALINITY — PHASE II

GENERAL ELECTRIC	ENVIRO CONTROL			BAIRD ATOMIC			
	(I ₁₃₅) 4A SIGNAL	(I ₄₅) 2A SIGNAL	I ₄₅ [$\frac{7.03}{z}$] ² SIGNAL	@ 10ppm	@ 20ppm	@ 50ppm	@ 100ppm
TEST CONDITION: SALINITY TESTED AT 15 AND 30ppt	+ 3.1% ±	+ 110% ±	+ 5.9% ±	+ 5.6% ±	+ 4.2% ±	+ 1.2% ±	+ 3.2% ±

TABLE 3-7 DEVIATION OF MONITOR RESPONSE DUE TO CHANGE IN TEMPERATURE — PHASE II

GENERAL ELECTRIC	ENVIRO CONTROL			BAIRD ATOMIC			
	(I ₁₃₅) 4A SIGNAL	(I ₄₅) 2A SIGNAL	I ₄₅ [$\frac{7.03}{z}$] ² SIGNAL	@ 10ppm	@ 20ppm	@ 50ppm	@ 100ppm
TEST CONDITION: TEMPERATURE TESTED AT 35°F, 60°F AND 100°F	+ 8.6% ±	+ 16% ±	+ 30% ±	+ 11.2% ±	+ 10.7% ±	+ 4.3% ±	+ 4.7% ±

TABLE 3-8 DEVIATION OF MONITOR RESPONSE DUE TO DETERGENTS — PHASE II

TEST CONDITIONS:	GENERAL ELECTRIC	ENVIRO CONTROL			BAIRD ATOMIC
		(I 135) 4A SIGNAL	(I 45) 2A SIGNAL	$1.45 \left[\frac{7.03}{Z} \right]^2$ SIGNAL	
A. ZIF DETERGENT TESTED AT 0ppm, 10ppm, 20ppm, 50ppm AND 100ppm LEVELS	NO EFFECT	14%	9.0%	21%	50ppm ZIF PRODUCES 10% ERROR IN MONITOR SIGNAL
B. MIL-2230A DETERGENT TESTED AT 0ppm, 10ppm, 20ppm, 50ppm AND 100ppm LEVELS	-----	34%	38%	30%*	-----
C. MIL-D-16791E AM 3 TYPE 1 DETERGENT TESTED AT 0ppm, 10ppm, 20ppm, 50ppm AND 100ppm LEVELS	0-10%	-----	-----	-----	10ppm DETERGENT EQUIVALENT TO 8ppm OIL SIGNAL

*NOTE: 1.8% DOR AT 10ppm DETERGENT CONCENTRATION

detergent MIL-D-16791E at lower concentration levels, and attributed noted monitor readings to instrument noise. However, their chemical analysis of the tested samples revealed the presence of the detergent. (Analysis indicated an amount of oil equal to 1/3 the volume of the detergent.) At the 50 ppm concentration level, the monitor detected the detergent, but the deviation of response was less than 10%. General Electric noted no monitor response to the ZIF detergent at any concentration level, and only trace amounts of "oil" (detergent) during sample analysis.

Enviro Control observed a notable deviation of response due to the presence of either detergent. At lower concentrations (10 ppm) of detergent, the deviation of response was significantly lower; the DOR for detergent MIL-C-2230A at the 10 ppm concentration level was 1.8%, whereas the DOR including the 50 ppm MIL-C-2230A data was 30%. These results indicate that reduced amounts of detergents in bilgewater might be allowable without hampering monitor performance significantly.

Baird Atomic experienced not only the scattering characteristics of the detergent indicated by the other contractors, but also the problem of the detergents fluorescing and "appearing" as oil. ZIF detergent is highly fluorescent, but did not fluoresce noticeably through the optical mask of this monitor. MIL-D-16791E detergent did fluoresce through the mask and caused significant interference. (50 ppm detergent gave a signal equivalent to 78 ppm oil.)

Recommended contractor prototype designs indicate that electronic or optical compensation should reduce the detergent interference substantially.

3.2.9 Effects of Particulates

Tests to determine the effects of particulates on monitor response were divided into studies on water-wetted particulates and oil-wetted particulates. In both cases it should be noted that some of the monitor interference observed during these tests resulted from the inability to control particulate concentrations uniformly due to inadequate mixing of influent samples and oil injection system malfunctions.

Results of the Phase II particulate interference tests are presented in Table 3-9. General Electric indicated that water-wetted particulates viewed by the monitor, (2-25 microns in size) contributed "little" to monitor interference at low concentrations (10-30 mg/l). At higher concentrations, the particulates are seen by the monitor as an oil equivalent signal. Oil-wetted particulates were considered less significant, since much of the solid particles were observed to be within the oil droplets.

Enviro Control demonstrated linear monitor response at the 10 ppm water-wetted test solids level, however the signal at 10 ppm solids corresponded to an oil signal at 100 ppm. Considerable interference was noted at all water-wetted solids concentrations. Strong interference and heavy fouling were observed during all oil-wetted solids tests.

TABLE 3-9 DEVIATION OF MONITOR RESPONSE DUE TO PARTICULATES — PHASE II

TEST CONDITIONS:	GENERAL ELECTRIC*	ENVIRO CONTROL	BAIRD ATOMIC
<p>A. WATER-WETTED PARTICULATES (WW) TESTED AT 10mg/l, 20mg/l, 40mg/l AND 60mg/l</p>	<ul style="list-style-type: none"> — LITTLE INTERFERENCE NOTED AT 10—30mg/l — AT HIGHER CONCENTRATIONS PARTICULATE INTERFERENCE IS EQUIVALENT TO OIL RESPONSE — PARTICULATE ALONE (W/O OIL) PRODUCES OIL EQUIVALENT SIGNAL 	<ul style="list-style-type: none"> — 10ppm TEST SOLIDS SIGNAL IS EQUIVALENT TO 100ppm OIL SIGNAL (RESPONSE IS LINEAR AT 10ppm TEST SOLIDS, HOWEVER) 	<ul style="list-style-type: none"> — 40mg/l of WW PARTICULATES RESULTS IN FIXED ERROR EQUAL TO 30ppm OIL — CORRECTION FORMULA RESULTS IN 6.7% CHANGE IN RESPONSE FOR ALL OIL CONCENTRATIONS
<p>B. OIL-WETTED PARTICULATES (OW) TESTED AT 10mg/l, 20mg/l, 40mg/l, AND 60mg/l</p>	<ul style="list-style-type: none"> — LESS INTERFERENCE THAN WATER-WETTED PARTICULATES 	<ul style="list-style-type: none"> — STRONG INTERFERENCE AND HEAVY FOULING AGAIN OBSERVED 	<ul style="list-style-type: none"> — AT 50ppm IN FLUENT OIL CONCENTRATION, 10mg/l PARTICULATE LOAD DECREASES MONITOR RESPONSE BY 44%; 40mg/l PARTICULATES DECREASES RESPONSE BY 73%

* AFFECTED BY PARTICULATES IN 2—25 MICRON SIZE RANGE ONLY (>25 MICRONS NOT "VIEWED" BY MONITOR)

Baird-Atomic observed that 40 mg/L of water-wetted particulates corresponded to a 32 ppm concentration of the 3FB (3 parts lube oil, 1 part marine diesel) oil mixture, and that the scattering of 1 mg/L of particulates approximated that of 13 ppm of the 3FB oil mixture. A correction formula was developed and applied to monitor response which resulted in a 6.7% change in monitor reading for all oil concentrations. Oil-wetted particulates decreased fluorescence efficiency, and increased scatter such that for a 50 ppm influent oil concentration, 10 mg/L of particulates decreased monitor response by 44%, and 40 mg/L of particulates decreased monitor response by 78%. No correction formula could be applied for oil-wetted particulates.

It is noteworthy that particulate loading of this nature (and subsequent monitor interference) would not be a significant factor downstream of a separating device featuring mechanical particulate separation (i.e., cartridges, centrifuges). In cases where the particulate loading might be a factor (i.e., gravity or parallel plate separators), the proposed prototype monitor recommendations from each contractor have allowed for some type of window cleaning feature and particulate interference compensation.

3.3 Conclusions - Phase II

In the Phase II feasibility effort, the Coast Guard had established an acceptable error band of ± 5 ppm or $\pm 10\%$ for monitor response (as determined by solvent extraction, infrared analysis method). The Phase I devices did not meet this accuracy requirement, but it was hoped that the Phase II effort would optimize monitor performance to this degree. As indicated in Table 3-4, a significant decrease in deviation of monitor response was realized, however the $\pm 10\%$ error band was not attained. Nonetheless, monitor response to oil mixtures was considered satisfactory for the following reasons:

- 1) The existing IMCO and draft U. S. monitor specifications require only ± 10 ppm or $\pm 20\%$ accuracy, whichever is greater.
- 2) The solvent extraction, infrared analysis method for oil determination has an inherent error of 5-10% itself (as a minimum).

The Phase II program results were encouraging, primarily because of the major refinements accomplished by each of the contractors. Linear monitor response for representative bilge oil mixtures were demonstrated over the range of 0-400 ppm, within a $\pm 15\%$ error band. Perhaps more important were the design capabilities demonstrated by the contractors. Although the monitors remained somewhat oil specie dependent, test results and prototype recommendations indicate that significant reductions in deviation of monitor response are possible if individual oils or oil mixtures can be predicted. Optical mask design and electronic compensation techniques demonstrated to date, can be further refined to optimize monitor response to a given environment of oil species.

Also demonstrated was the ability to reduce interferences caused by particulates, detergents and water conditions (pH, salinity and temperature).

In a given environment, i.e., a class of naval or merchant vessels, where the types of oils in a bilge can be predicted, the existing Phase II devices are believed capable of performing acceptably ($\pm 20\%$) if the particulate and detergent loadings in the bilge are kept at lower levels (approximately 10 ppm or less). Refined prototype devices should show significant improvement in performance, even at higher particulate and detergent levels.

Another factor to be considered in evaluating these devices is the potential for additional monitor response optimization due to homogenizer refinements. Increased emulsification and the corresponding reduction of scatter and optical density of the oil droplets, would result in decreased variations in monitor response and less dependency of the devices on oil specie.

4.0 PROTOTYPE MONITOR DEVELOPMENT PROGRAM

Upon completion of the second feasibility phase, an evaluation was scheduled to determine the suitability for prototype development of the bilge-type oil-in-water content monitors. Informal discussions were held between the USN and USCG in March 1976, with consideration being given to monitor accuracy, response to various interferences, and cost and maintainability, in both the breadboard and prototype stages. Overall analysis failed to indicate a substantially superior monitor. However, based on USN selection criteria, which emphasized response to detergents and particulates, the Baird Atomic breadboard was rated slightly superior to the Enviro Control and General Electric monitors. Concurrently, an interagency agreement was proposed between the USCG and ERDA (Energy Research and Development Administration), which in part allowed for additional technical evaluation of the three breadboards at the USCG Fire and Safety Test Facility in Mobile, Alabama.

Prior to the actual initiation of the technical evaluation at Mobile, the USN supplied funding to support Baird Atomic in the development of a prototype monitor. The USCG re-evaluated the breadboards, and from a strictly technical standpoint, agreed that the USN decision to proceed with the oil fluorescence concept was sound. The decision was made, however, to also proceed with the Mobile technical evaluation.

During the final planning stages of the Mobile evaluation program, the Coast Guard's Office of Research and Development became aware of significant changes in the IMCO monitor specifications, which raised doubts as to the feasibility of continuing the bilge monitor development program. During the May 1976 IMCO meeting, the monitor specifications were revised to establish two monitoring device categories - wide range oil content monitors (ballast) and 15 ppm oil content alarms (bilge), in lieu of one general category, as in the previous specifications. The ballast monitor was required to successfully complete the original 13 performance tests established in the earlier specifications, while the bilge monitor was required to complete only 5 tests. Among those tests eliminated for the bilge monitor were particulate matter and entrained air tests. Consequently, less sophisticated, state-of-the-art monitoring

devices were now considered capable of satisfying the IMCO requirements, which to date, were thought unobtainable. In light of these revisions, the continuation of a bilge monitor development program was no longer considered feasible, and the Mobile program was cancelled.

Since the completion of Phase II, additional research has been conducted on these breadboard devices. The Baird Atomic, Inc. monitor has undergone laboratory tests at the D. W. Taylor Naval Ship Research and Development Center, Annapolis, Maryland, and the General Electric, Co. and Enviro Control, Inc. monitors have been shipped to the Naval Coastal Systems Laboratory, Panama City, Florida for observation on the effluent side of a General Electric, Co. OPC-3000 gpm deballasting oil-water separator.

Additionally, monitor research continued toward the development of a prototype monitor capable of operation in both bilge and ballast applications. This program, a joint effort funded by the USN and administered using USCG contracting services, was based on the Baird Atomic, Inc. breadboard monitor developed under the previous USCG contract. The envisioned monitor was to have refined the oil fluorescence concept, concentrating on increased monitor response expected to result from emulsifier optimization, optical mask improvements, incorporation of total luminescence holographic polychromators, transmission/scatter channel improvements and flow cell modifications, however this effort has since been terminated.

5.0 REFERENCES

1. Shipboard Oil-In-Water Content Monitor Based on Light Scattering at Ninety Degrees; Enviro Control, USCG Report CG-D-49-75, NOV 1974. (NTIS AD 003 854)
2. Shipboard Oil-In-Water Content Monitor Based on Small Angle Forward Light Scattering; General Electric, USCG Report, CG-D-32-75, AUG 1974. (NTIS AD 003 863)
3. Shipboard Oil-In-Water Content Monitor Based on Oil Fluorescence, Baird Atomic, USCG Report CG-D-87-75, FEB 1975. (NTIS AD 010 475)
4. Shipboard Oil-In-Water Content Monitor Based on Small Angle Forward Light Scattering; General Electric, USCG Report CG-D-35-76, DEC 1975. (NTIS ADA 022 895)
5. Shipboard Oil-In-Water Content Monitor Based on Light Scattering at 45°, 90°, and 135° and Turbidity at 0°; Enviro Control USCG Report CG-D-25-76, JAN 1976. (NTIS ADA 023 839)
6. Shipboard Oil-In-Water Content Monitor Based on Oil Fluorescence, Baird Atomic, USCG Report CG-D-54-76, FEB 1976. (NTIS ADA 027 262)
7. Oil-In-Water Content Monitor Developmental Program Summary (INTERIM REPORT), R. W. Montfort, U. S. Coast Guard (G-DET-1), USCG Report CG-D-188-75, DEC 1975. (NTIS ADA 022 960)