CHEMICAL TANK TESTING OF MODIFIED COMMERCIAL DIVING HELMETS AND DRESS

by

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources; to preserve and treat public drinking water supplies; and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communiations link between the research and the user community.

Under normal Agency surveillance and analysis activities, the acquisition of bottom samples and biota in polluted waterways for research purpose, Section 311 of the Clean Water Act and now under the Comprehensive Environmental Response Compensation and Liability Act (Superfund), governmental personnel from the USEAP, Coast Guard Strike Teams, National Oceanic & Atmospheric Administration (NOAA) and the Navy are required to perform work functions in hazardously contaminated underwater environments. This report presents the results of controlled field evaluation of modified commercial diving dress and helmets at the EPA-Oil & Hazardous Material Spill Environmental Test Tank (OHMSETT). The recommendations of this report will assist operational diving personnel assess the capabilities of modified commercial gear for hazardous underwater environments.

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The assistance, advice and comments of the EPA Project Officer, Richard P. Traver of the Oil & Hazardous Materials Spills Branch, Edison, New Jersey have been of great value in coordinating the field evaluation program and the preparation of this report. Dr. J. Morgan Wells, Jr., Director of the National Oceanic & Atmospheric Administration Diving Office was instrumental in the preparation of the various modified diving dresses and helmets.

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SECTION 1

INTRODUCTION

Between the years of 1977-1981, 64,609 spills of petroleum products, hazardous materials and other miscellaneous substances were reported to the U.S. Coast Guard Office of Marine Environment and Systems (see reference 1). This represents a total of 75.6 x 10^6 gallons of material releases into navigable waterways alone. From 1974 to 1981, 454 spill or release incidents were reported involving 20.9 x 10^6 pounds of dry hazardous and other substances.

The Environmental Protection Agency (EPA), National Oceanic and Atmospheric Administration (NOAA), Navy and U.S. Coast Guard engage in activities which require personnel to perform work tasks of hazardously contaminated underwater environments. Because of inadequate protection and understanding in hazard assessment, many diving personnel have suffered acute injuries (see reference 2).

NOAA has extensive involvement and expertise in underwater diving. NOAA's activities include production of the NOAA Diving Manual, the development of certification standards, and the operation of a diver certification training program for civilian government divers. NOAA divers have participated in numerous research programs that involved diving in waters infested with pathogenic microorganisms. To protect its divers against these microorganisms, procedures and equipment were modified or developed, and then tested. NOAA's experience in the development of

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No degree of static laboratory test will be adequate to determine the effectiveness of suit and helmet modifications. Actual diver operations are necessary to test equipment changes. This is due to the various complexities of body movements and "in-water" positions during underwater work tasks. Seals and position straps can easily become weakened through strenuous diving operations, thereby allowing contaminated leakage.

Many diving tanks exist in the various governmental agencies which serve as training sites for new divers. However, none of these installations are capable of receiving either a representative pollutant or surrogate contaminate to allow for realistic, controlled testing and evaluation of newly modified diving gear. The existing EPA Oil & Hazardous Materials Simulation Environmental Test Tank (OHMSETT) is capable of simulating open water diving conditions while providing suitable high-efficiency water treatment operations.

Initial evaluations of the modified commercial diving dresses and helmet assemblies were completed during March 7-12, 1983 at OHMSETT in Leonardo, New Jersey. This operation utilized a 18.9 m^3 (5,000 gal) tank containing ammonia and fluorescing dye tracers in which the suits were safely evaluated.

The helmets which were successfully evaluated for chemical exclusion were the Draeger Helmet System, the Desco "Pot" Diving Hat, Diving Systems International Superlite-17B Helmet, Morse Engineering MK-12 Navy Deep Water Helmet System, and Safety Sea Systems Helmax Helmet. Five different suit configurations were evaluated with the above helmets. One diving dress was from Draeger with the remaining four supplied by Viking Technical Rubber.

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

1. The five suit/helmet combinations that were tested in this program were effective in protecting the divers from leaks of contaminated water.

2. Ammonia vapor was detected in the breathing space on three of the five helmet/suit combinations. No concentrations were over the Threshold Limit Value (TLV).

3. The suspected "weakest link" of each of the systems - the gloves/wrist connection - did not show any detectable leaks.

4. Although the Superlite 17/Viking had air escaping from the helmet to suit sealing ring and the Helmax/Viking had air escaping from the umbilical joint at the helmet, no fluids entered the suit.

5. The tests reported here are suitable to determine differences in helmet/suit combinations as far as leaking of a hazardous material (vapor of liquid) while being worn by a diver and without subjecting the diver to undue physical discomfort or danger.

RECOMMENDATIONS

1. In these tests, 1 ppm dye was used as a pollutant tracer. A higher concentration of dye should be used if further tests are to be run.

2. These tests were run at between 300-500 ppm NH_3. A higher concentration of ammonia might be desirable if testing at similar temperatures 5°C (41°F) is to be conducted in the future. Warmer temperatures 15-20° (60-68°F) would preclude the need to do this.

3. Suitable filter pads made of cotton should be made to fit over but not restrict the exhaust valve. A double layer of filter pads is recommended to determine if the ammonia source is the exhaust valve or some other location "up-stream" in the air flow. By analzying each of the pair of pads and determining which has the greater concentration of NH_3 it will be possible to determine the "direction" of the source of NH_3, either the valve or inside the suit.

4. Helmets should be delivered to OHMSETT one week before start of testing to be fitted with detection filters.

5. Personal monitoring sampling pumps, originally intended for use in this testing, were not used because of logistics problems in fitting them into the suits. Modifications to the helmets such as air or exhaust interlocks should be made in order to employ conventional industrial hygiene "work place" exposure level investigations.

6. Since there were no leaks of hazardous fluid into any of the diving suits evaluated in this study it is difficult to evaluate the utility of wearing body stockings for subsequent analysis. It is felt they could still be used in the next test series. Use of these body stockings as a standard piece of equipment is not intended. Before a garment were to be used in real spills, the fabric's ability to absorb various classes of chemicals must be further researched.

SECTION 3

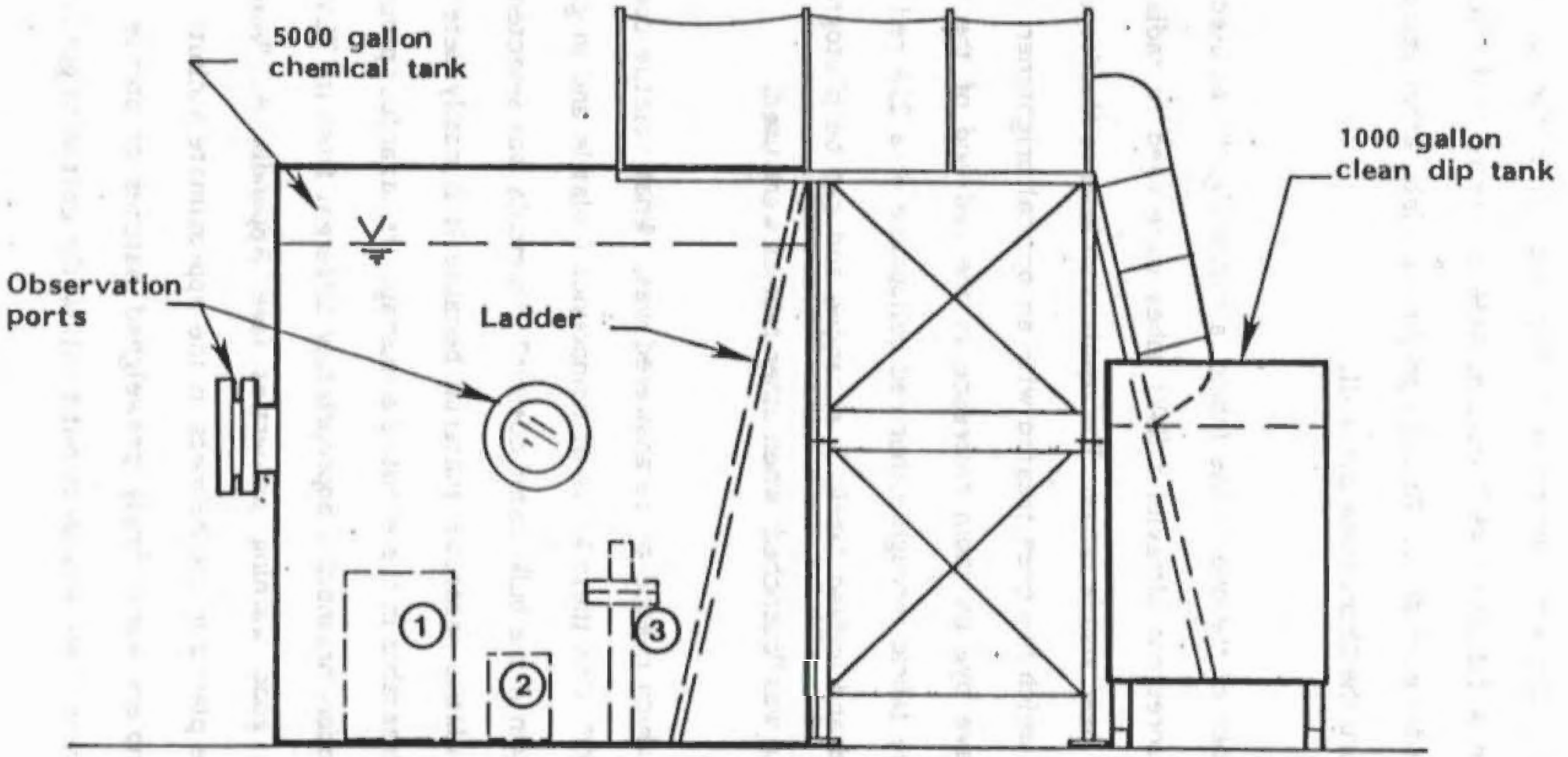
TEST EQUIPMENT AND PROCEDURES

TANK SETUP

The main chemical dive tank was 3 m (10 ft) high and 3 m (10 ft) in diameter, 18.9 m^3 (5,000 gal) capacity. A preliminary 1.8 m (6 ft) high x 1.2 m (4 ft) diameter 3.8 m^3 (1,000 gal) dip tank was incorporated in the equipment setup. In order to allow observations of the diving dress, helemt assembly and diver activity, two 305 mm (12 inch) view ports were welded into the tank walls. In addition, a 254 mm (10 inch) diameter pipe stub and flange was welded to the interior bottom of the tank for assembly/disassembly as one of the two diver activities. The second diver activity involved the use of a 114 liter (30 gal) tight-head metal drum which was submerged along with a 208 liter (55 gal) open-head drum, lid and closure ring. This task was to overpack the 114 liter (30 gal) drum into the 208 liter (55 gal) drum thus simulating a standard drum recovery procedure prior to slinging for removal from underwater. Figure 1 shows the test tank layout.

EVALUATION SETUP

The process to establish the sampling and analytical techniques is covered in Appendix A. The resulting technique presented here was used because of its simplicity. It is not a universal technique, but quite specific to the hazardous materials (ammonia and dye) used in this testing.



1 55 gallon drum

2 30 gallon drum

3 10-inch pipe and flange.

Station 1 is one of four station. The other three are shown in Figure 2.

Figure 1. Tank and platform test set-up for Diver Protection Program.

In order to evaluate the diving dresses for gross leaks, there had to be a way of determining the origin of the water. "Is it a leak?" or, "Is it condensation/ perspiration?" A fluorescing dye was selected as a visual indictor in the tank water. Body stockings made from a fabric of 46% cotton, 46% polyester and 8% Lycra spandex were custom made for each diver. Through preliminary laboratory testing this material was shown to adsorb the fluorescent dye well.

To detect the presence of the dye on the fabric, a "black light" was used. Two 4-foot 40 watt filtered fluorescent ultraviolet (UV) tubes were used to radiate the fabric with UV light in the near visible range. The result is an intense fluorescence of blue light from the fabric which has been treated with an optical brightener. Those portions of fabric that have dye on them fluoresce in the red end of the visible spectrum. By observing the fabric through either red cellophane or a 25A red filter, the contrast between dyed and undyed fabric is enhanced and can be photographed. The fluorescence of this dye was "quenched" when other fabrics were used.

A second question which needed to be answered was, "What volatile contaminants should be considered?" Can these kinds of compounds (volatile and in gaseous state) get in the helmet even if the bulk water doesn't? Ammonia was selected to be added with the dye as a volatile hazardous material because it is easily detectable, disposable, and medically treatable in the event of a mishap. Its hazardous property is that of an irritant and its odor threshold is appropriately different from its TLV to be considered a vapor with good warning properties (see Appendix A, "Ammonia Sampling"). Samplers were placed in the helmets in the approximate vicinity of the exhaust valves. The samplers were simply preweighed patches of sterile cotton purchased at a local pharmacy. Care was taken not to allow the cotton to get into the exhaust valve.

It was found during the preliminary laboratory evaluation that the cotton was a good sampler for $NH_3 \cdot (H_2O)_n$ (hydrated ammonia). This test program found that the cotton acted as an excellent sampler for anhydrous ammonia also. After a dive was over, the diver and suit were decontaminated. The diver's helmet was then removed by tenders in a clean area, the cotton sampler was taken from the helmet, and placed in a clean glass vial. Once in the lab, the cotton was extracted with 50 ml of distilled water; the water was then analyzed for ammonia using a colorimetric procedure and a Hach visible spectrophotometer (see Appendix A).

TEST PROCEDURES

The sequence of events for each of the five tests was to be identical except for minor variations as noted. In order of occurrence:

1. If required, additional anhydrous ammonia was bubbled into the previously dyed and "ammoniated" tank water. The desired quantity was 500 ppm.

2. Water samples were checked for pH using an Orion model 701A/ Ionanalyzer and common pH electrodes. By using Figure A-4, Appendix A, the concentration as NH_3* could be determined.

3. If the NH_3 concentration was suitable (300-600 ppm) the diver would start to suit-up.

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* Ammonia (NH_3) when in water exists in ionized NH_4^+ and hydrated $NH_3 \cdot (H_2O)_n$ form. Reporting concentration as NH_3 is a convenience.

Each helmet/suit combination required its own donning procedure, as well as thermal protection between the suit and the diver. Some divers were "blacklighted" prior to getting into the diving dress. Each diver wore the body stocking over the thermal underwear so that the body stocking would be in contact with the diving suit.

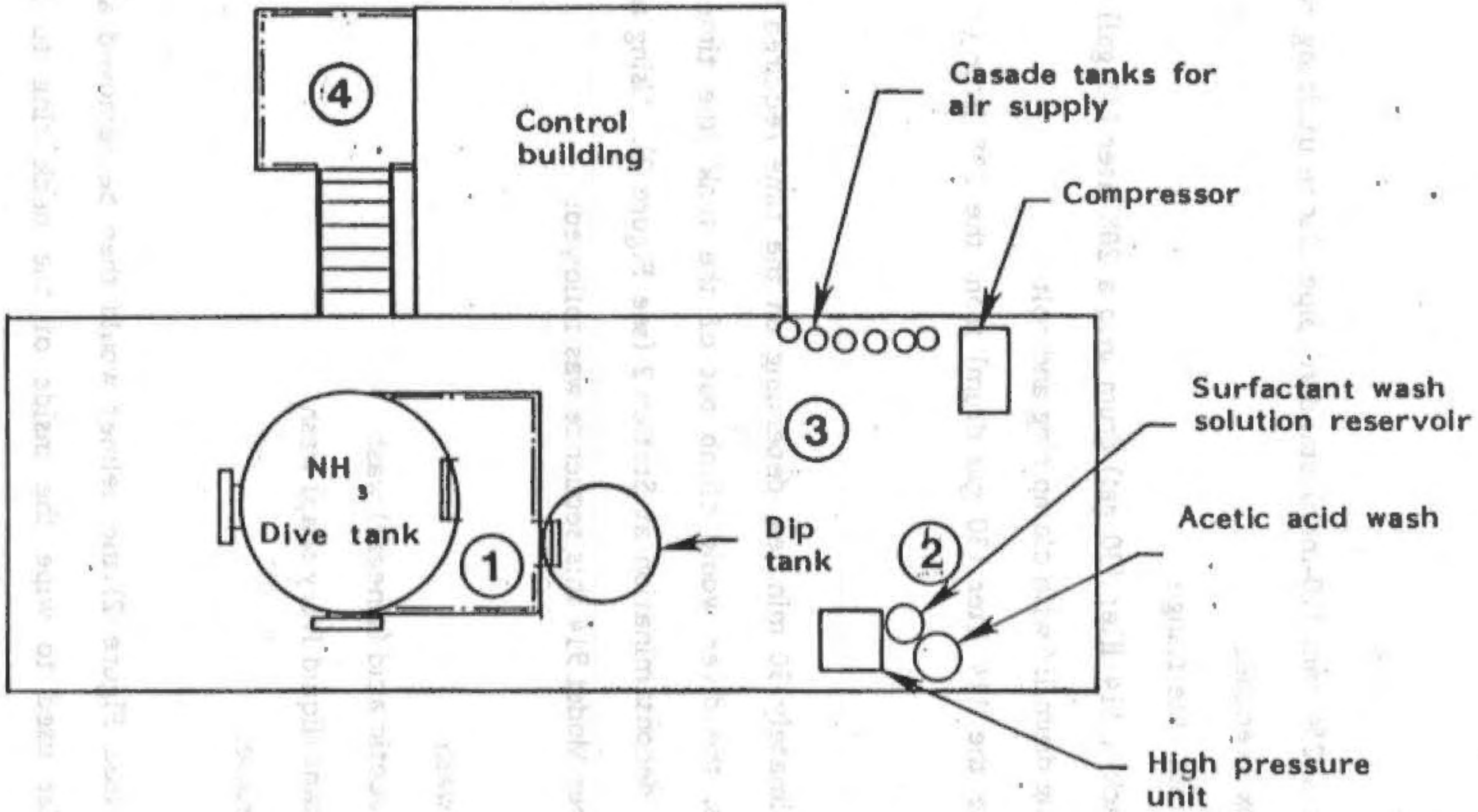
4. A cotton sampler (approximately 0.3 grams) was placed in the helmet. The helmet was then placed on a chair on the tank platform.

5. With the full suit on (less the helmet) the diver was then brought to the tank platform, Station 1 on Figure 2, where last minute checks were made and the helmet donned.

6. The diver was connected through a hard-wire communications box which was monitored by a three-man tender team. Test (or dive) start time and pressure reading on air bottles were recorded.

7. The first "check-out" dive was in the 3.8 m^3 (1,000 gal) fresh water dip tank. Observing the diver through a sight window running from the top to the bottom of the tank allowed support personnel to see if there were any visible air leaks emanating from the suit before the diver would be placed into the hazardous ammonia tank.

8. If no obvious leaks were observed, the diver climbed out of the dip tank and entered the 18.9 m^3 (5,000 gal) ammonia tank. Start time in the 18.9 m^3 (5,000 gal) tank was recorded.



Numbers designated the stations referred to in the text under "Test Program"

1 helmet is put on

2 decontamination

3 helmet removal and sampler removal

4 suit removal (before study of unitard under ultraviolet light)

Figure 2. Plan view of test layout.

9. While in the 18.9 m^3 (5,000 gal) tank the diver carried out four operations:

   a. unbolt a 254 mm (10-inch) standard pipe flange utilizing rachet and box wrenches
   b. reassemble the flange
   c. overpack a 114 liter (30 gal) drum into a 208 liter (55 gal) drum securing drum lid with clamp ring and bolt
   d. remove the 114 liter (30 gal drum) from the 208 liter (55 gal) drum.

10. After approximately 30 minutes, depending on the time required to do the exercises, the diver would climb out of the tank (the time was recorded) for decontamination at Station 2 (see Figure 2). Using an LA pressure washer Model 914 this sequence was followed:

    a. water wash
    b. dilute acetic acid (vinegar) wash
    c. surfactant (liquid Ivory soap) wash
    d. water rinse.

11. At Station 3 (see Figure 2) the helmet would then be removed and a cotton sampler used to wipe the inside of the neck ring to later determine the presence of ammonia, or for the immediate determination of the presence of dye. The cotton sampler from inside the helmet was removed at this time and sealed in their own 40-ml, teflon-capped, glass vials.

12. The diver then went to Station 4 (see Figure 2) where the the diving suit, including gloves, was carefully removed by the tenders. This ultimately exposed the body stocking.

13. The diver then stood under ultraviolet light while the body stocking was examined for the presence of dye. Photographs of the examination were taken using a 25A red filter.

14. The body stocking was then removed and kept for any future laboratory analysis or reference.

Figures 3 through 13 show photo highlights of the step-by-step procedure.

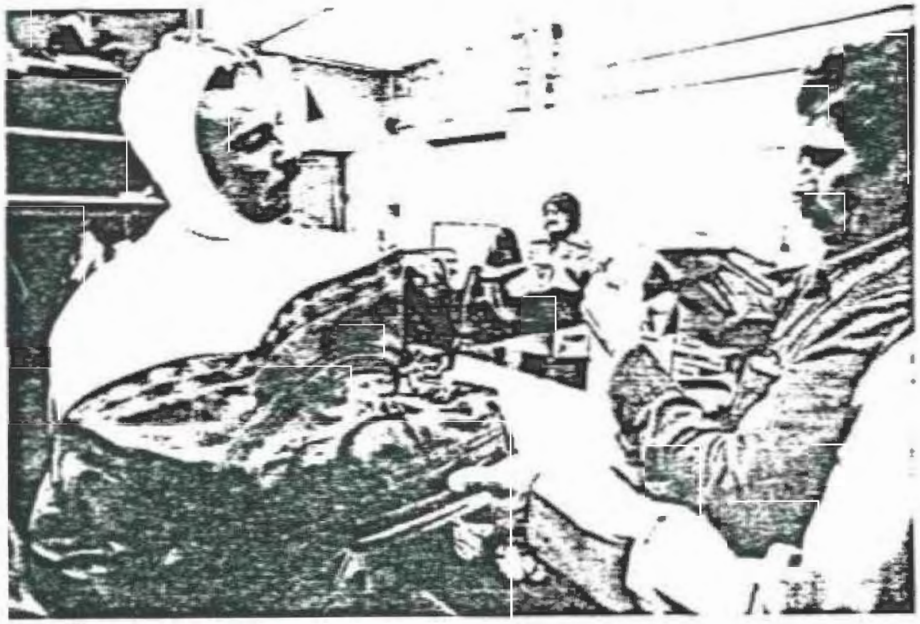


Figure 3. The diver is being assisted putting on a dry suit. The cuffs of each of the suits were given special attention. Here the first of four pair of gloves are being fitted. This glove will be fastened over a rigid ring. The head and shoulder portion of the body stocking is also shown here. (Test #5, Helmax/Viking, Photo Video File #2659)

Figure 4. The Helmax helmet is positioned against the mounting flange, creating an airtight fit. Note the white cotton glove. Two rubber gloves and two cotton gloves were used; the inner cotton glove was intended to adsorb any dyed ammonia in the event of a leak. (Test #8 Helmax/Viking PVF 2659)

Figure 5. The diver shown here is wearing a chafing coverall over his dry suit to prevent abrasion to the suit. The tenders are adjusting 5# ankle weights to help prevent the diver from losing control if he becomes inverted while under water. This diver is not wearing an outer cotton glove. (Test #1 Desco/Viking PVF 2656)

Figure 6. With full gear, and connected to an umbilical, the diver tests the integrity of his suit for leaks in the 3.8 m^3 (1,000) gal fresh water tank before entering the ammonia hazardous tank. Note the cuff area. Both rubber gloves can be seen on the right hand of the diver along with an outer cotton chafing glove to help prevent abrasion of the primary rubber glove. (Test #8 Helmax/Viking PVF 2657)

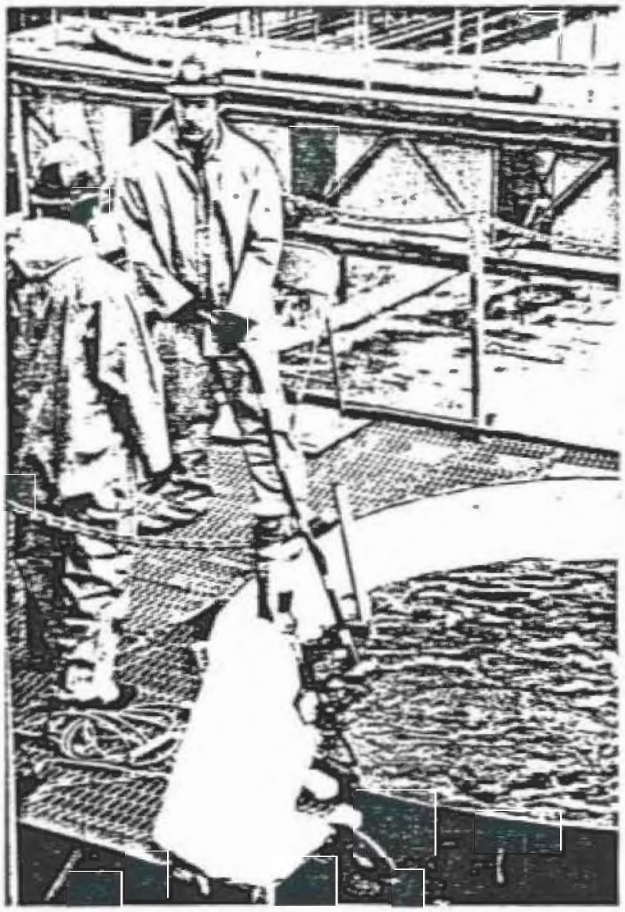
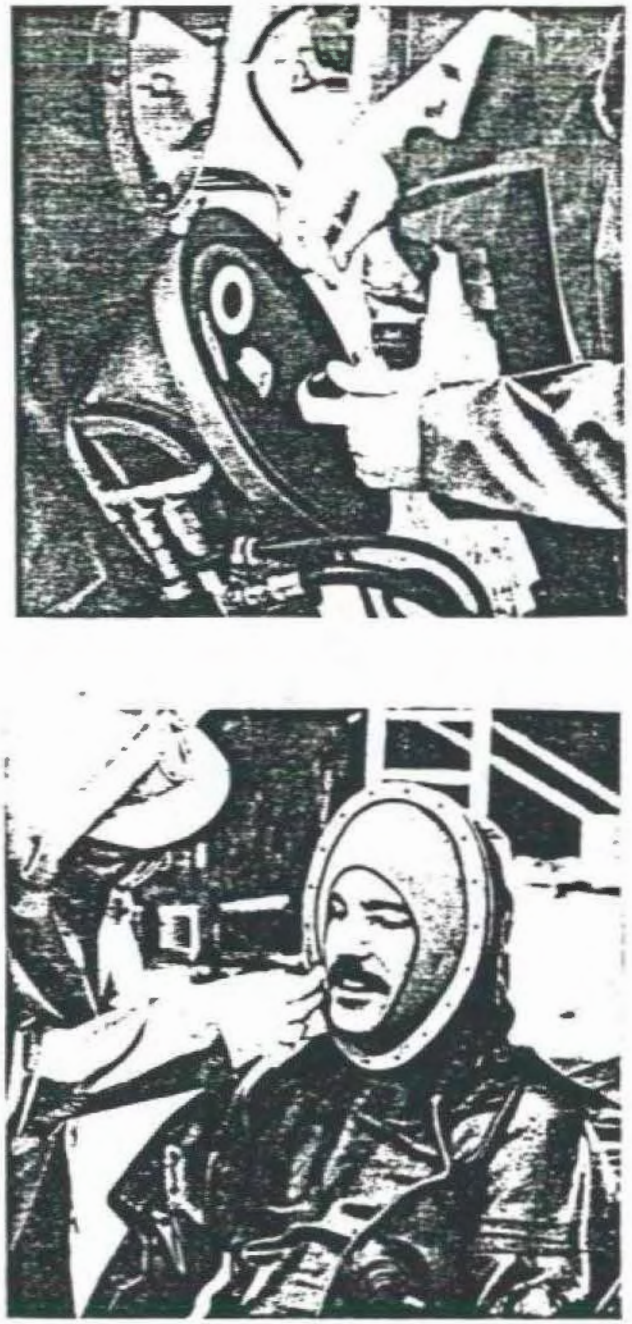


Figure 7. While in the hazardous ammonia tank, a three-man surface support team is responsible for the diver's well being. Shown here are two tenders, one holding the umbilical air and communication line. A third man (not shown) maintains voice communication and advises the diver. Note that all tenders are wearing full splash gear to prevent ammonia contamination. Ambient air sampling using an MSA detector tube system indicated there was no need for respiratory protection for tenders. (Test #8 Helmax/Viking PVF 2657)

Figure 8. Following the completion of the dive, the suit is thoroughly decontaminated. During this time the diver breathes through the umbilical. The suit will not be opened until decontamination procedures are completed. (Test #8 Helmax/Viking PVF 2657)



Figures 9 & 10. The cotton sampler is taken from the helmet. A second cotton swab is used to wipe the ring where the helmet joins the suit. This cotton is later analyzed for ammonia or inspected for red dye. (Test #8 Helmax/Viking PVF 2657)

Figures 11 & 12. The diving dress is removed to allow inspection of the body stocking under ultraviolet light. No dye was detected on any of the suits. All body stockings have been retained for reference. (Tests #1 and #8 Desco/Viking and Helmax/Viking (PVF 2656, 2659)

Figure 13. The interior of the helmet, especially in and around the exhaust valve, was checked under the ultraviolet light for any traces of dye. (PVF 2656)

SECTION 4

TEST RESULTS

TEST OBSERVATIONS

Table 1 on the following page summarizes observations made just prior to, during, and just after each diver was in the tank. These notes and records cover the time from the fresh water dip tank through observation under the ultraviolet light and include: the PH measurement which was immediately translated to concentration of NH^3 by use of Figure A4. Also included is air tank pressure to give an idea of the amount of air used between donning the helmet and exiting the hazardous tank. "Air time" is the hour and minute the diver went on air from the cylinders. "In time" is the hour and minute the diver submerged in the hazardous tank and "out time" is hour and minute the diver exited the hazardous tank. The water temperature of the tank water is also recorded. The only recorded data on fluorescence appears in "Notes for Table 1."

LABORATORY AMMONIA ANALYSIS

An estimation of the ammonia concentration in the divers air space could not be made for this evaluation. The cotton samplers were positioned as close to the exhaust valves as possible, but in none of the tests could it be assumed that all the air passed through the cotton, nor that a specific percentage of air contacted the sampler due to the different positioning of the cotton in the various helmets.

TABLE I. PRE-TEST AND POST-TEST OBSERVATION SUMMARY

Test No. Helmet/Suit Diver's Name	PRETEST						POST-TEST				
	pH	NH_3 ppm	Tanks Pres.	°C	Air Time	In Time	pH	NH_3 ppm	Tanks Pres.	°C	Out Time
#1 Desco/Viking Morgan Wells	10.53	320	2500	5.5	10:51	11:00	10.53	320	1485	5.5	11:35
#2 SUS/Draeger Steve Urich	10.83	450	2450	5.5	14:51	15:04	10.34	240	2300	5.5	15:26
#3 Superlite 17/Viking Art Francis	10.85	450	2150	5.6	10:35	11:09	10.62	360	1700	5.6	11:45
#4 Mark 12/Viking Paul Pegnato	10.90	480	-	6.1	14:14	14:39	10.28	210	-	6.1	15:10
#5 Helmax/Viking Ric Traver	Cancelled										
#6 Mark 12/Viking Paul Pegnato	Cancelled										
#7	Cancelled										
#8 Helmax/Viking Ric Traver	10.96	500	2380	5.5	14:04	14:10	10.97	500	1950	5.5	14:36

NOTES FOR TABLE I. PRE-TEST AND POST-TEST OBSERVATION SUMMARY

TEST #1	No dye on body stocking. Some question of "burning on right hand." Right cotton glove to be analyzed for NH_3. No dye inside helmet, no dye inside exhaust valve or sealing surface.
TEST #2	Dye smudge on right wrist right on wrist crease. One speck of dye inside the first series exhaust vent, no dye on cotton suit, feet wet. There is a chance smudge was from his being tender in previous dive.
TEST #3	Diver was removed from tank after 5 min due to a helmet leak. Corrected. Test proceeded.
TEST #4	Some dye on neck ring of suit taken with cotton and on helmet ring. Viking suit has smooth skin with Navy chafing coveralls.
TEST #5	Cancelled. Leak around helmet gasket in dip tank (see test 8).
TEST #6	Loose fit helmet to neck ring. Lower breach ring would not match to helmet due to manufacturing defect. MK12 Viking suit has built-in weight pockets.
TEST #7	Cancelled. Because of leaks.
TEST #8	Started out with small leak in umbilical joint. Cascade regulator started freezing. Fluorescence in mask. Some questions to origin.

The micro-grams (µg) of ammonia picked up on the cotton only serves as an indicator of the amount of ammonia in the breathing space. The divers' olfactory observations (none of them detected an ammonia odor during their dives) would have indicated that any concentrations of ammonia in the suit were below 25 ppm and perhaps below 5 ppm. (See Appendix A, "Ammonia Sampling.")

Each µg of ammonia represents a volume of 0.0013 ml at standard temperature (20°C) and pressure (760 mm Hg). Table 2 lists four samples that are significantly above blanks for milligrams of NH_3-N. The values in Table 2 were calculated from quanities in Table 3 using the equation:

$$\mu g\ NH_3 = mg(NH_3\text{-}N) \times 1000 \times 1.22$$

where 1000 is the conversion of milligrams to micrograms

and 1.22 is the ratio of $\frac{NH_3 \text{ molecular weight}}{N \text{ molecular weight}}$

and $ml NH_3 = 0.0013\ ml/\mu g \times \mu g NH_3$.

TABLE 2. AMMONIA DETECTED DURING THE TEST PROGRAM 35 USING A MODIFIED HACH PROCEDURE

Test No. Helmet Type Suit Type	Sample	Mg NH_3-N	µg NH_3	@ STP ml NH_3
2(Sus/Draeger)	SN3	0.150	183	0.24
2	SN5	0.104	127	0.17
3(Superlite 17/ Viking)	SN6	0.575	701	0.93
4(Mark 12/Viking)	SN8	0.150	183	0.24

DYE DETECTED

There was no dye detected on any of the five body stockings used during the test program. However, with the Mark 12/Viking some dye was found on the neck ring.

Approximately 2 ml of dye was found inside the exhaust vent of the SUS helmet. There was some fluorescence of questionable origin near the nosepiece in the Helmax. The diver that wore the SUS/Draeger had a smudge of dye on his right wrist which appears to have happened when he was a tender in a previous test. There were no leaks in his gloves.

See the following tables for a summary of the test data. Table 3 presents the analytical data that was obtained afterwards by use of the Hach method (p 32, 35) for analyzing for ammonia. Particular attention should be paid to the information depicted in the right hand column of Table 3. The information in this column was used to determine the four tests which showed significant amounts of ammonia. Table 4 is a summary of the weights of the cotton sampler that were used.

TABLE 3. DIVING SUIT LEAKAGE EVALUATION ABSORPTION COTTON SWAB SAMPLES

Date	Test No.	Sample	Extraction Volume (ml)	Secondary Dilution Factor	NH_3-N Readout (mg/l)	Detected as NH_3-N[1] (mg)
3/8/83	1	[2]SN 1	50	1:1	0.19	0.009
	1	[3]SN 2	50	1:1	0.095	0.005
	2	[2]SN 3	100	1:25	0.06	0.150
	2	SN 4[4]	100	1:1	0.006	0.001
	2	[3]SN 5	50	1:25	0.083	0.104
3/9/83	3	[2]SN 6	50	1:50	0.23	0.575
	3	[3]SN 7	50	1:1	0.08	0.004
	4	[2]SN8	50	1:25	0.12	0.150
	4	[3]SN 9	50	1:1	0.26	0.013
	4	SN10[6]	50	1:1	0.18	0.009
3/10/83	5	3SN 13[5]	50	1:1	0.155	0.008
	5	[2]SN 14	50	1:1	0.15	0.007
	5	SN 15[6]	50	1:1	0.085	0.004
No Exposure		SN 16	50	1:1	0.155	0.008
No Exposure		SN 17	50	1:1	0.10	0.005

[1] Milligrams of NH_3 = Readout (mg/l) x Dilution factor x $\frac{1000\text{ ml}}{\text{Extract Volume}}$

[2] Respiration sample

[3] Inner collar wipe sample

[4] Mask leak wipe

[5] Minor fluorescence selected (May be due to inadequate decontamination/drain into inner collar

[6] Inner helmet-ring wipe

TABLE 4. DIVING SUITS LEAK TEST SAMPLING
Cotton Sampler Evaluations

			Cotton Sampling Specifics				
Date	Suit	SN	Bottle + Cotton (g)	Bottle (g)	Cotton (g)	Cotton + Bottle + Sample (g)	Sample (g)
3/8/83	1	1*	28.7771	28.3993	0.3778	28.8686	0.0915
	1	2**	28.6685	28.2938	0.3748	29.3969	0.7283
	2	3*	28.9682	28.5708	0.3974	32.5024	3.5382
	2	4***	28.9004	28.5039	0.3965	29.6868	0.7864
	2	5**	28.9690	28.5838	0.3852	30.1823	1.2133
	3	6#	28.5868	28.3889	0.1979	29.7054	1.1186
	3	7**	28.8934	28.5309	0.3652	28.9469	0.0535
	4	8*	28.8071	28.4258	0.3813	29.2311	0.4340
	4	9**	28.9389	28.5575	0.3814	29.2874	0.3485
	4	10##	28.8966	28.5167	0.3799	29.0199	0.1233
	5	13**	28.8207	28.4562	0.3645	28.9741	0.1534
	Control	17	28.9155	28.5073	0.4082	28.9155	0
	5	14*	28.9047	28.5503	0.3544	29.1192	0.2145
	Control	16	28.9027	28.4799	0.4228	28.9027	0
	5	15	28.8347	28.4859	0.3488	29.0120	0.1773

*	Helmet by respirator outlet
**	From neck/collar area inner ring wipe
***	Face mask leak
#	Less cotton use
##	Inner helmet-ring wipe

REFERENCES

1. "Polluting Incidents In and Around U.S. Waters," U.S. Coast Guard - COMDTINST M16450.2F.

2. "Evaluation of and Use of Divers and/or Remotely Operated Vehicles in Chemically Contaminated Waters," Steven A. McClellan, R. Frank Busby; Undersea Medical Society Publication CR 60(CW) 2-1-83.

APPENDIX A

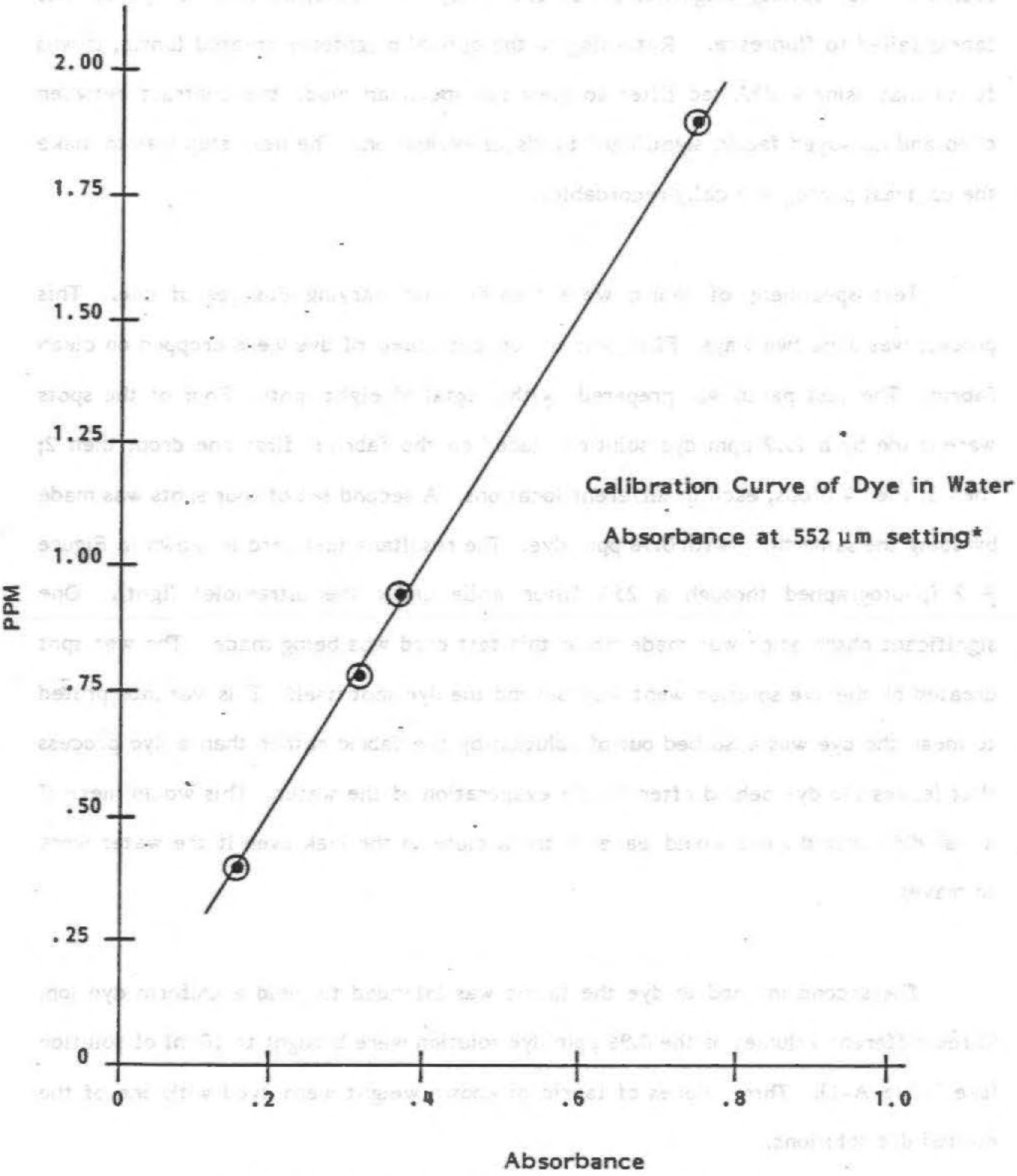
PRELIMINARY LABORATORY STUDIES

Detectability of the fluorescent dye in water solution

The red dye used in the March 7-11, 1983 diver protection study is manufactured by Formulabs of Escondido, California. According to information supplied in their sales literature, the maximum radiation absorbance of the dye is 558 nanometers (nm). The instrument used in this study to measure the absorbance of dye solutions was a Hach spectrophotometer in a DR-EL/4 (serial number 445) field kit. The dial reading on this instrument was 552 nm at maximum absorbance. Four concentrations of dye in the 1.0 ppm range were made up and absorbance measurements were made at the 552 nm setting. The resulting calibration curve of absorbance vs dye concentration in water was then prepared for use in dye concentration control in the tank. (See Figure A-1.)

Detectability of the fluorescent dye on the fabric

The fabric that was finally selected for the body stockings (that were worn by each diver under the suits) was a "white-white" knit blend of of 46% cotton, 46% polyester and 8% Lycra spandex. This same material is commonly used by dance companies in their costuming. At first an optical brightener in the fabric was thought to be an objectionable characteristic. The intense blue fluorescence of the fabric



Calibration Curve of Dye in Water

Absorbance at 552 µm setting*

Figure A-1. Calibration curve of dye in water absorbance at 552 mm setting.

under ultraviolet light masked the red fluorescence for low concentrations of dye. A fabric without optical brighteners was found but low concentrations of dye on this fabric failed to fluoresce. Returning to the optical brightener treated fabric, it was found that using a 25A red filter to view the speciman made the contrast between dyed and non-dyed fabric significant to visual evaluation. The next step was to make the contrast photographically recordable.

Test specimens of fabric were treated with varying dosages of dye. This process was done two ways. First, known concentrations of dye were dropped on clean fabric. The test patch was prepared with a total of eight spots. Four of the spots were made by a 19.2 ppm dye solution placed on the fabric: first one drop; then 2; then 3; then 4 drops, each in different locations. A second set of four spots was made by doing the same thing with 0.96 ppm dye. The resultant test card is shown in Figure A-2 (photographed through a 25A filter while under the ultraviolet light). One significant observation was made while this test card was being made. The wet spot created by the dye solution went well beyond the dye spot itself. This was interpreted to mean the dye was adsorbed out of solution by the fabric rather than a dye process that leaves the dye behind after simple evaporation of the water. This would mean if a leak did occur the dye would leave its track close to the leak even if the water were to travel.

The second method to dye the fabric was intended to yield a uniform dye job. Three different volumes of the 0.96 ppm dye solution were brought to 10 ml of solution (see Table A-1). Three pieces of fabric of known weight were dyed with one of the diluted dye solutions.

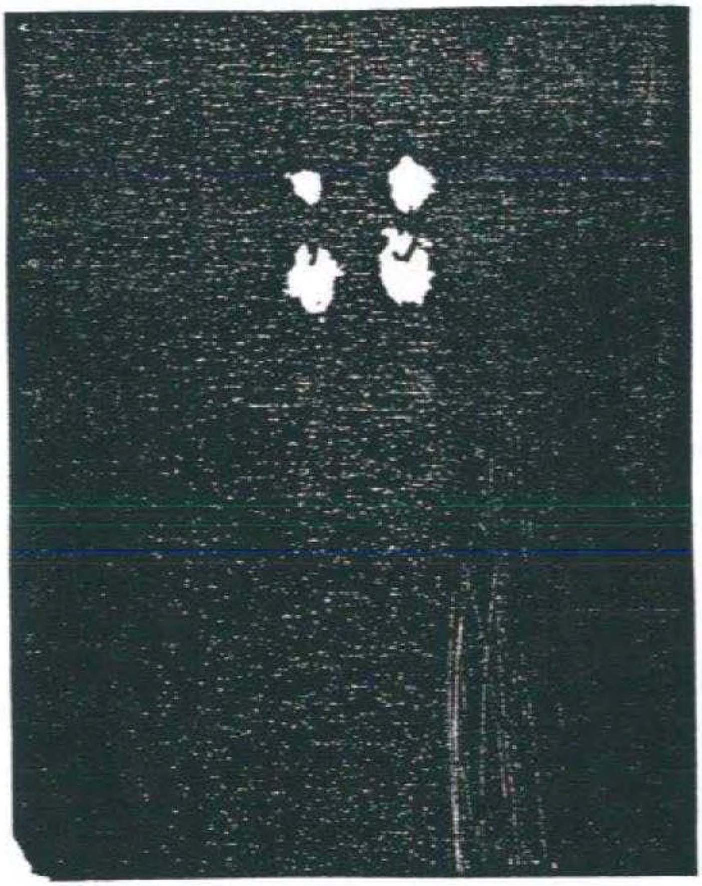


Figure A-2. A photo of several dye test spots made to "calibrate" an observer's eye to quantities of dye on fabric. The intention, to use a comparator method to evaluate fluid leaks into a suit. The photo was taken through a 25A red filter onto Polaroid 55 P/N film while the fabric was under ultraviolet light.

TABLE A-I. "Uniform" Dye Calibration Samples

Vol of 0.96 ppm	Fabric Letter	Weight of Fabric	ppm Dye on Weight of Fabric (OWF)
1.0ml	B	0.7179	1.3
0.1	C	0.4143	0.23
2.0	D	0.4550	4.21

The resulting patches were examined under ultraviolet light using the 25A filter. It was found that the patches had to be placed right next to a non-dyed piece of the same fabric for an observer to determine if there was any fluorescence. The resulting test card is shown in Figure A-3.

Ammonia Sampling

Anhydrous ammonia, NH_3, when added to water becomes:

$$NH_3 + nH_2O \rightleftarrows NH_3 \cdot nH_2O \rightleftarrows NH_4^+ + OH^- + (N-1)H_2O$$

The concentration of ammonia present will determine the rate and direction of these two reactions. For the purpose of using ammonia in the diver protection test program our interest was in the left hand reaction. We wished to make the reaction go sufficiently to the left to make the ammonia detectable but not so much so that the divers are made uncomfortable. According to the report, "Aqueous Ammonia Equilibrium," the percent of un-ionized NH_3 in the temperature and pH range of the 18.9 m^3 (5,000 gal) tank was between 85 and 90%. This information allows us to conclude a significant majority of the ammonia is at least at the middle reaction product. It was determined empirically that a 200 ppm solution of ammonia in tap water was sufficient for some subjects to detect an ammonia smell over a 600 ml

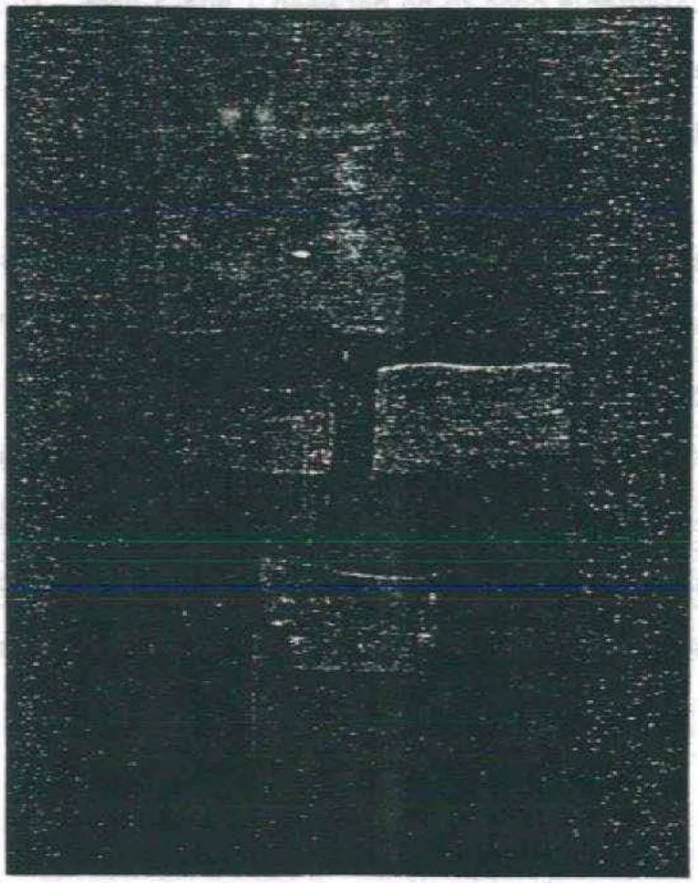


Figure A-3. A photo of more uniformly dyed fabric photographed as in Figure A-2 reveals the necessity of comparison to determine if dye is present. Even with this small spacing it is difficult to determine if fabric B (right) and D (lower) are fluorescing (see Table A-1). The comparison is easy with the spots on the upper fabric.

Griffin beaker. A 500 ppm ammonia solution was sufficient for all subjects to detect the smell. According to reports referenced in the 4th proceedings of "Documentation of the Threshold Limit Values," American Conference of Governmental Industrial Hygienists, the lowest level for detectable odor is between 1 and 5 ppm. The complaint level is reported to be 20-25 ppm. The AIHA Hygienic Guide also reports the lowest level for detectable odor to be between 1 and 5 ppm. The Hygienic Guide reports 55 ppm to be objectionable. The concentration of ammonia in the water was monitored by measuring pH and using the graph in Figure A-4.

The initial work of air sampling was done with Bendix BDX-44 sampling pumps and standard charcoal tubes. Three approaches were taken. The first was to determine the ability of the tubes to collect a known quantity of ammonia. The second phase was to determine the relative amount of ammonia that could be expected to collect on a charcoal tube with known volumes of ammonia solution. The third approach was to determine a maximum quantity the charcoal tube could hold. Ammonia was extracted from the carbon tube by a steam extractor shown in Figure A-5.

Ammonia Analysis

Ammonia analysis was conducted using a Hach method "Nitrogen, Ammonia Salicylate Method for Water, Wastewater and Sea Water" with one addition, the sampler was first extracted with or into 50 ml of distilled water from which a 25 ml aliquot was taken to start the Hach procedure. If the resultant product was off scale a suitable aliquot was taken from the remaining 25 ml extract and diluted to 25 ml to rerun the sample. The method is produced here directly from the Hach procedure.

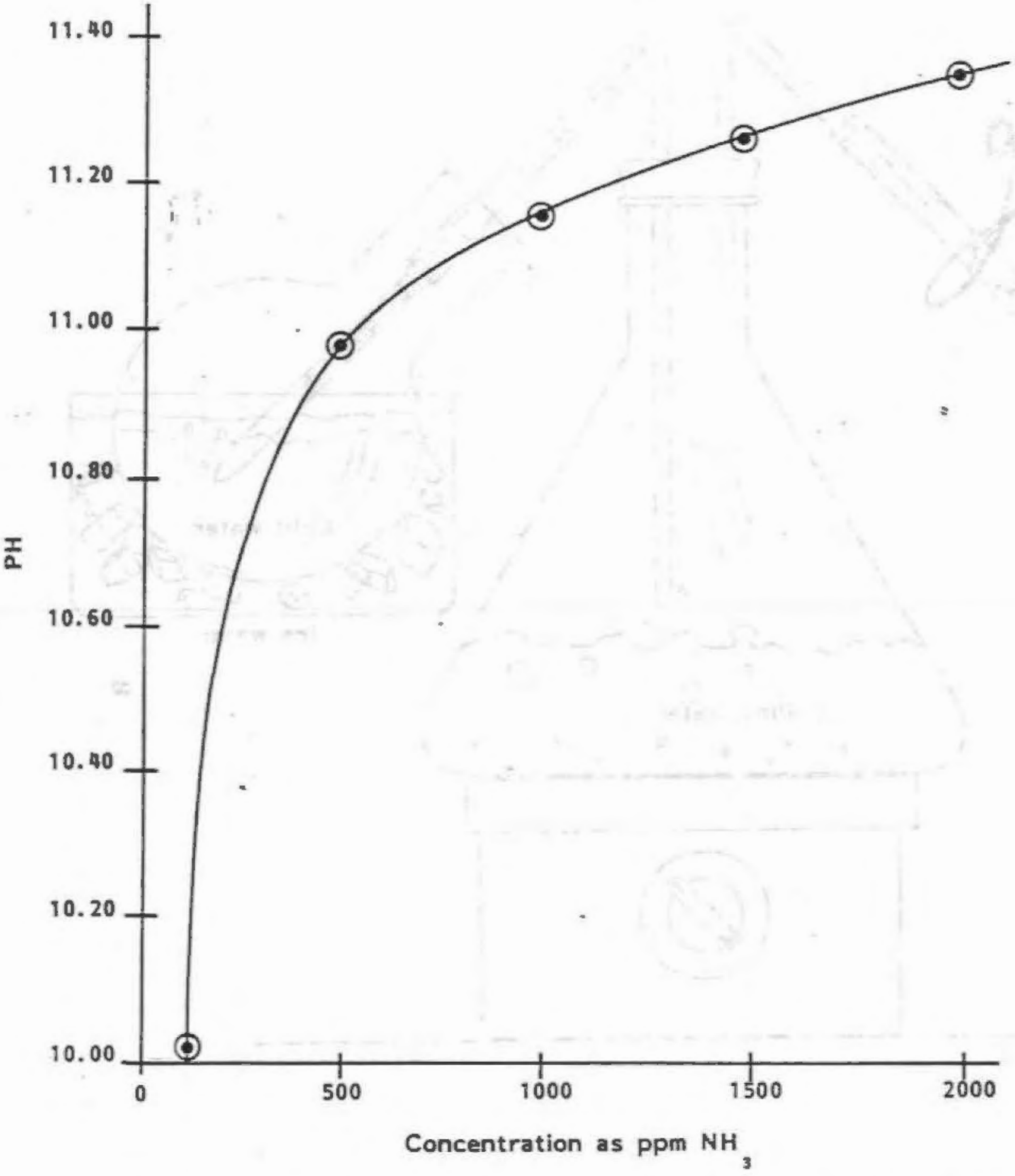


Figure A-4. Calibration curve of ammonia in water produced prior to the start of testing.

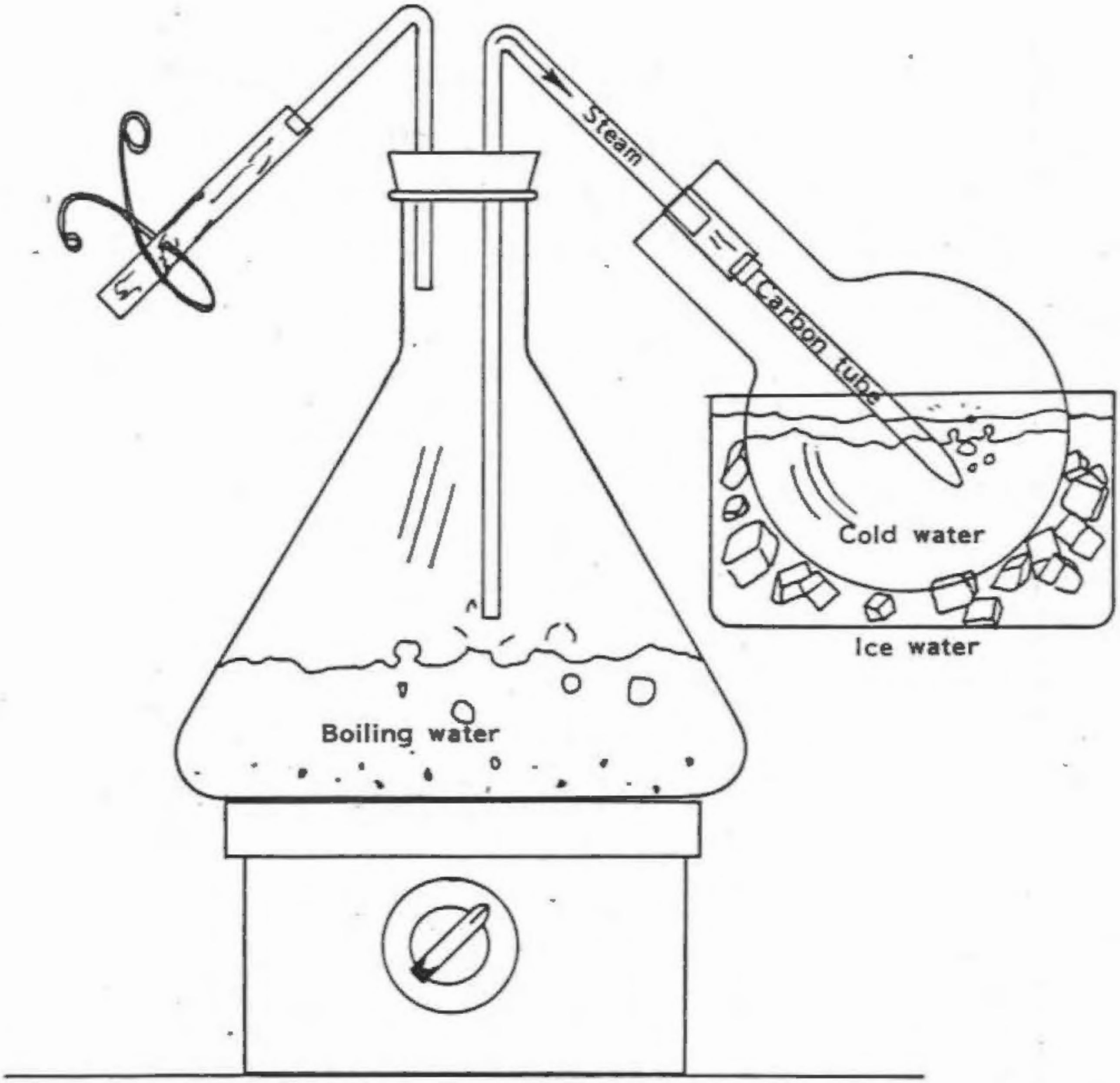


Figure A-5. Steam extractor used to remove ammonia from carbon tubes in preliminary lab work for Diver Protection Project.

NITROGEN, AMMONIA

Range: 0-0.4 mg/l

Salicylate Method

For Water, Wastewater and Sea Water*

Procedure

1. Measure 25 ml demineralized water in a clean 25-ml mixing graduated cylinder.

2. Take a water sample by filling a second clean 25-ml mixing graduated cylinder to the 25-ml mark.

2. Add the contents of one Salicylate Reagent Powder Pillow to each graduate, stopper tightly and mix vigorously. See Note A.

4. After three minutes, add the contents of one Alkaline Cyanurate Powder Pillow to each graduate; mix thoroughly. Allow at least 15 minutes for the color to develop fully. See Note B.

5. Pour the prepared demineralized water and the sample into separate, clean sample cells. Place the sample cell containing the prepared demineralized water solution in the cell holder. Insert the appropriate Nitrogen Ammonia fresh (Salicylate method) Meter Scale into the meter (Use meter scale 41564-00 for fresh water samples and meter scale 41565-00 for sea water samples.)

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* Requires pretreatment.. Refer to Note D in the Nessler Method Ammonia Nitrogen test

Adjust the wavelength Dial to 655 nm. Adjust the Light Control for a meter reading of zero mg/l.

6. Place the prepared sample in the cell holder and read the mg/l Ammonia Nitrogen (N).

NOTES

A. All The Salicylate Reagent Powder must dissolve.

B. The mixing graduates should be kept stoppered to prevent any ammonia fumes from affecting the test.

C. The results may be expressed as mg/l Ammonia (NH_3) or mg/l Ammonium (NH_4^+) by multiplying the mg/l Ammonia Nitrogen (N) by 1.22 or by 1.29, respectively.

D. The following ions interfere at concentrations exceeding those listed below:

Calcium (Ca^{+2})	1000 mg/l as $CaCO_3$
Magnesium (Mg^{+2})	6000 mg/l as $CaCO_3$
Nitrite (NO_2^-)	12 mg/l NO_2^- — N

Sulfate, nitrate and phosphate do not interfere in concentrations normally found in surface water. (At least up to 300 mg/l SO_4^{-2}, 100 mg/l NO_3^- — N, and 100 mg/l PO_4^{-3} — P).

Sulfide will interfere by intensifying the color formed from ammonia and the reagents. Consult the phenols procedure, Note B, for sulfide elimination.

Iron interferes in the test but its effect may be eliminated by first determining the iron content of the sample (see Iron, Total). If the demineralized water sample in Step 1 is made up with the same iron concentration as the sample and taken normally through the test, its use in Step 5 will blank out the effect of iron successfully.

Less common interferences such as hydrazine and glycine will cause intensified colors in the prepared sample. It may be necessary to distill the sample before the test is performed if numerous interferences are present. Using the Hach Universal Still, distill the test sample by following the procedure outlined in Note D of the Nessler Method Nitrogen, Ammonia test.

E. The sample may be adjusted to pH 7 with Sodium Hydroxide Standard Solution, 1N, if the pH is less than 7 or Sulfuric Acid Standard Solution, 1N, if the pH is greater than 7.

F. Residual chlorine must be removed from the sample by the addition of Sodium Arsenite Solution. Use 1 ml of Sodium Arsenite Solution to remove 1 mg/l residual chlorine from a 250-ml sample. More Sodium Arsenite Solution should be used for higher chlorine concentrations.

Using Cotton to Sample Ammonia

In order to be ready to deal with some of the helmet/suit combinations that required an air seal between the suit and the breathing space, an alternate sampling system to the Bendix air pumps was investigated. To use the pumps in this type of situation would have required the pump to be mounted in the helmet which would have been quite impossible.

The first alternate tried was filter paper treated to 1% by weight of the filter paper with boric acid. When placed in the test chamber (see Figure A-6) with 1 ml of proposed test fluid the filter paper/boric acid collected 23 µg of NH_3. Subsequent work identified the mechanics of the "adsorption" to be hydrated ammonia $(NH_3 \cdot N(H_2O))$ absorbing into the fibers of the filter paper. The boric acid was apparently irrelevant.

In order to further develop a sampler that could be adaptable to many situations the idea of water absorption in filter paper was expanded to the absorption in cotton. Sterile cotton was purchased at a local pharmacy and tested in the chamber. Although background readings were significant for the cotton the cotton did demonstrate the ability to absorb the $NH_3 \cdot NH_2O$.

Using a second test set-up, shown in Figure A-7, a moisture absorption mechanism was demonstrated (see Table A-2).

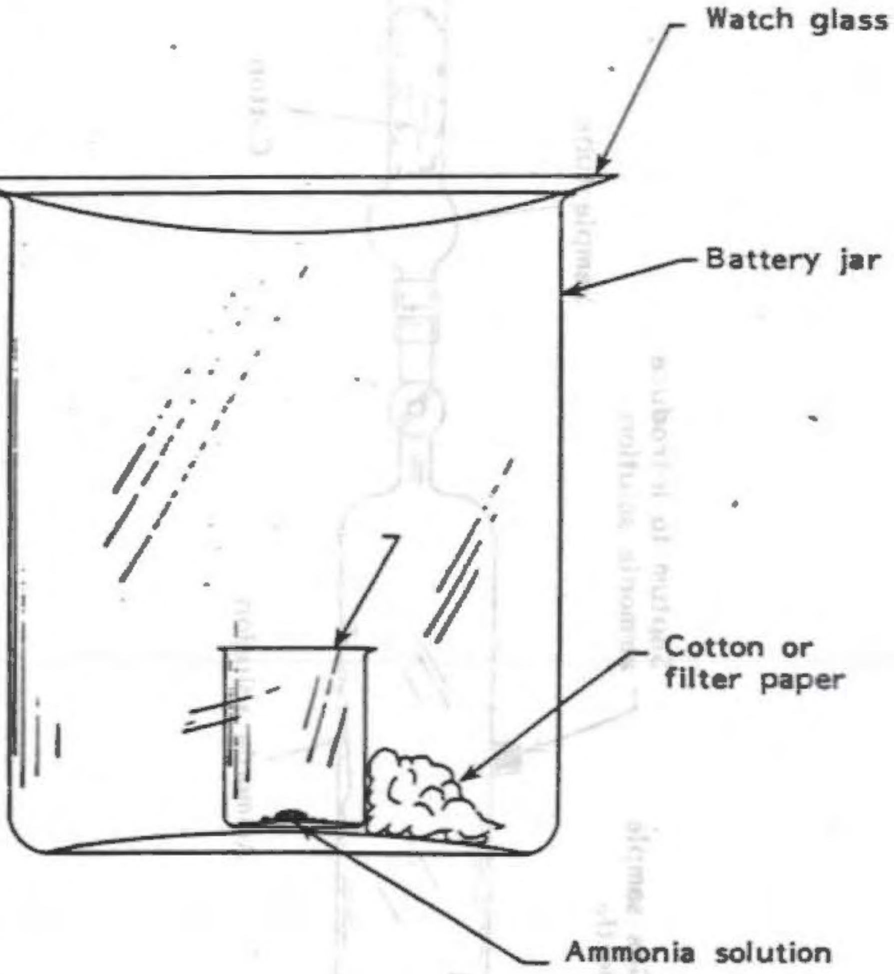

Figure A-6. Ammonia chamber for lab studies of samplers with no air flow.

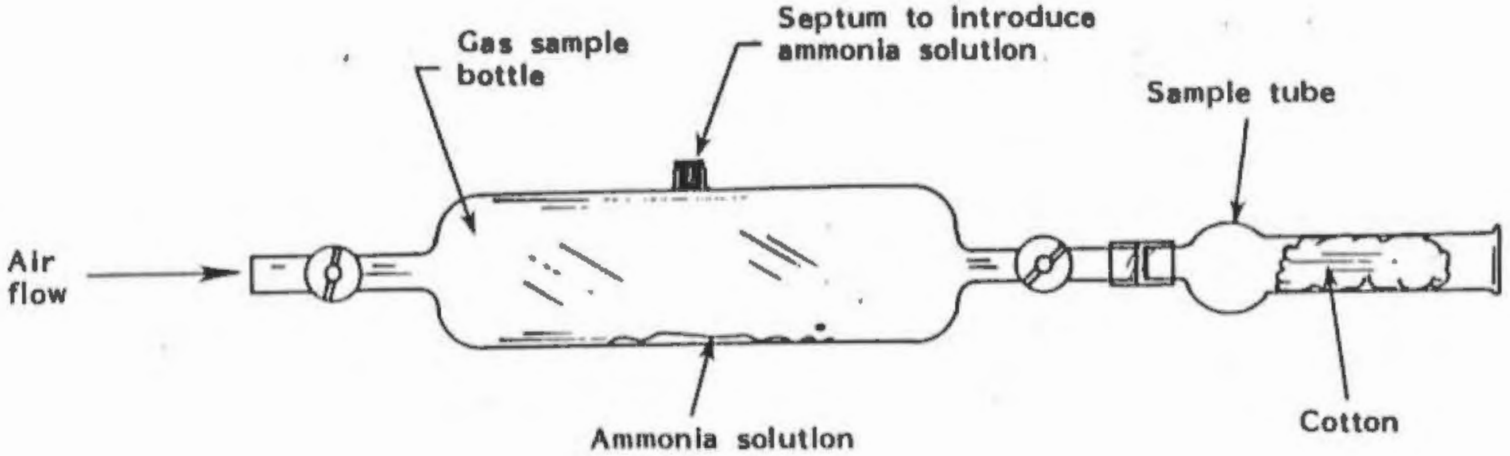

Figure A-7. Lab set-up to study samplers in flowing air. Cotton is being tested in this set-up.

TABLE A-2. HALF-HOUR TESTS OF COTTON AS AN AMMONIA SAMPLER

(See Figure 7)

Cotton % Moisture	NH_3 Source	Air flow Rate L/min	Measured NH_3-N mg/l
0	1 ml of 500 ppm	2 (lab air)	0.145
4	1 ml of 500 ppm	0	0.38
10	1 ml of 500 ppm	2	0.075
4	1 ml of 500 ppm	2	0.035