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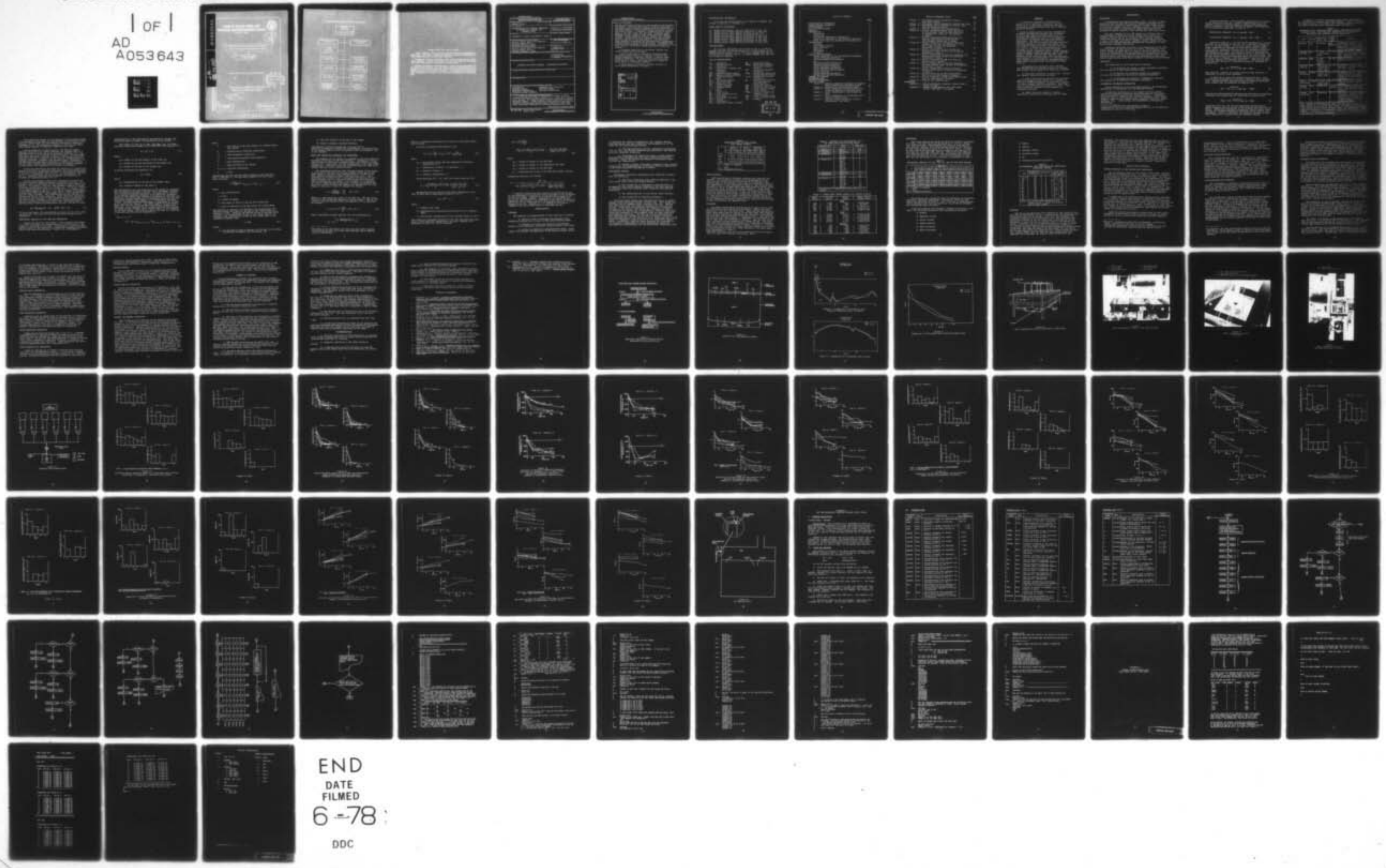

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BIODEGRADATION OF SHIPBOARD WASTEWATER IN COLLECTION, HOLDING, AND TRANSFER TANKS

by

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Alexander E./Lard[illegible]
Andrew T./[illegible]

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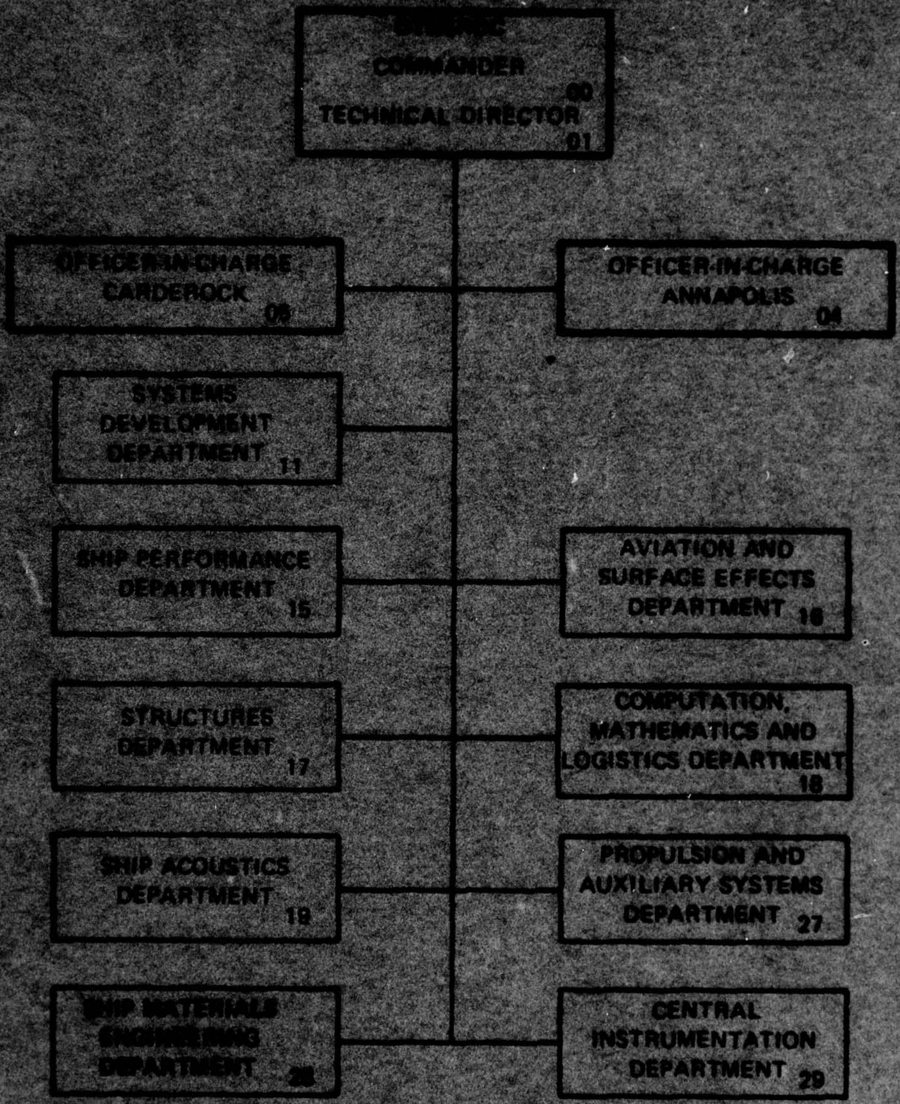

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A study was conducted to determine the extent to which anaerobic biological activity occurs in U. S. Navy ship collection, holding, and transfer system holding tanks and to identify potential hazards. Eight different waste mixtures representing shipboard holding-tank contents were incubated in test tanks under controlled conditions to determine gas-generation rates

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and the quantitative effects of varying specific environmental parameters. Indicators of biological activity monitored in the waste mixtures included oxidation/reduction potential, pH, dissolved oxygen, and the concentrations of sulfate, nitrate, and volatile acids. In addition, concentrations of various gases in the tank ullage were monitored, including oxygen, hydrogen sulfide, carbon dioxide, ethyl mercaptan, methyl mercaptan, carbon monoxide, methane, ammonia, and hydrogen cyanide. Gas-generation rate constants and other relevant data were applied to the development of a gas-generation model capable of predicting the concentrations of potentially hazardous gases in shipboard holding tanks. Recommendations concerning tank cleaning, tank gas-freeing, and general collection, holding, and transfer system operational safety are offered:

- Anaerobic conditions in collection, holding, and transfer tanks should be avoided.

- Tank ullage must be analyzed for hazardous gases and oxygen content before it is opened; it must be considered dangerous to personnel entering it without proper breathing apparatus. The tanks must be ventilated positively prior to entry. Tank vents should be located to avoid exposure of shipboard personnel.

- Tanks should be cleaned at regular intervals to avoid high concentrations of sludge.

ADMINISTRATIVE INFORMATION

This task was accomplished at the request of NAVSEC (SEC 6159B), references (a) through (h).

ADMINISTRATIVE REFERENCES

(a) NAVSEC Work Request N65197-75-WR-50776 of Jan 1976
(b) NAVSEC Project Order N65197-75-PO-50176 of May 1975
(c) NAVSEC Project Order N65197-75-55794 of May 1975
(d) NAVSEC Work Request N65197-75-WR-55564 of May 1975
(e) NAVSEC Project Order N65197-76-PO-60020 of Aug 1975
(f) NAVSEC Project Order N65197-76-PO-60020 of Nov 1975
(g) NAVSEC Project Order N65197-76-PO-60020 of Jan 1976
(h) NAVSEC Project Order N65197-76-PO-60371 of July 1976

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LIST OF ABBREVIATIONS

atm - atmosphere
° C - degrees Celsius
cc - centimeter
CHT - collection, holding, and transfer
cm - centimeter
COD - chemical oxygen demand
DCA - damage control assistant
DO - dissolved oxygen
g - gram
GC - gas chromatograph
g/hr - grams per hour
g/L - grams per liter
ID - inside diameter
° K - degrees Kelvin
L - liter
m - meter
m^3 - cubic meter
MEF - mass emission factor
mg - milligram
mg/L - milligrams per liter
min - minute
mm - millimeter
mole - molecular weight in grams
MW - *molecular weight*
NEPSS - Naval Environmental Protection Support Service
ORP - oxidation/reduction potential
OSHA - Occupation Safety and Health Administration
P-.90 - probability at 90th percentile
pH - negative logarithm of the hydrogen ion concentration
ppm - parts per million
TLV - threshold limit value
TOC - total organic carbon
TS - total solids
TSTEL - tentative short-term exposure limit
TVA - total volatile acids
TVS - total volatile solids
vol - volume

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ABSTRACT

A study was conducted to determine the extent to which anaerobic biological activity occurs in U. S. Navy ship collection, holding, and transfer system holding tanks and to identify potential hazards.

Eight different waste mixtures representing shipboard holding-tank contents were incubated in test tanks under controlled conditions to determine gas-generation rates and the quantitative effects of varying specific environmental parameters. Indicators of biological activity monitored in the waste mixtures included oxidation/reduction potential, pH, dissolved oxygen, and the concentrations of sulfate, nitrate, and volatile acids. In addition, concentrations of various gases in the tank ullage were monitored, including oxygen, hydrogen sulfide, carbon dioxide, ethyl mercaptan, methyl mercaptan, carbon monoxide, methane, ammonia, and hydrogen cyanide. Gas-generation rate constants and other relevant data were applied to the development of a gas-generation model capable of predicting the concentrations of potentially hazardous gases in shipboard holding tanks.

Recommendations concerning tank cleaning, tank gas-freeing, and general collection, holding, and transfer system operational safety are offered:

- Anaerobic conditions in collection, holding, and transfer tanks should be avoided.
- Tank ullage must be analyzed for hazardous gases and oxygen content before it is opened; it must be considered dangerous to personnel entering it without proper breathing apparatus. The tanks must be ventilated positively prior to entry. Tank vents should be located to avoid exposure of shipboard personnel.
- Tanks should be cleaned at regular intervals to avoid high concentrations of sludge.

INTRODUCTION

BACKGROUND

In compliance with Executive Order 11507, the Chief of Naval Operations has directed that nonoily wastewater systems aboard existing naval vessels be back-fitted with a CHT* system as part of the Navy's general pollution abatement program. This system provides one method of disposing of sewage and other nonoily wastewaters ashore instead of into harbors and restricted waters.

The main component of the CHT system is a holding tank (or tanks) designed to hold black water (sewage from urinals and commodes) for periods up to 12 hours, while the ship transits restricted waters of the United States or of foreign countries. In port, black and gray waters (laundry, shower, galley, etc) are collected in holding tanks and subsequently transferred to shore-based sewage treatment facilities.

Biological processes occurring in the wastewater within shipboard holding[1] and CHT tanks are of concern. The absence of dissolved oxygen in sewage due to a lack of efficient aeration will result in anaerobiosis. The end products of the metabolism of many anaerobic and facultative anaerobic bacteria include toxic and/or explosive gases. The existence of those substances in Navy shipboard sewage holding tanks would represent a potential health hazard.

OBJECTIVES

The objectives of this study were as follows:

- To determine the extent to which anaerobic biological activity occurs in CHT system holding tanks.
- To analyze the potential hazards the anaerobic activity will present to the ship and shipboard personnel.
- To determine the effects of temperature, salinity and seeding on the anaerobic biological processes.

BIOCHEMICAL WASTEWATER DEGRADATION

Before discussion of the laboratory studies, the biochemical degradation of wastewaters will be examined briefly.

Biochemical degradation is the process by which complex organic and inorganic substances are broken down by autotrophic and heterotrophic organisms into simpler products. Autotrophic types use CO_2 as a carbon source for cell synthesis, while heterotrophic types utilize organic carbon compounds (proteins, carbohydrates, etc). Heterotrophs are predominant in decomposing wastewaters.

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*A list of abbreviations used appears on page i.

[1] Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

Aerobic digestion is the biological decomposition of wastes in the presence of free O_2. Aerobic organisms use O_2 as the hydrogen acceptor following metabolic energy transformations. Common biochemical reactions mediated by aerobic microorganisms are illustrated in equations (1) and (2).[2,3]

$$\text{Carbonaceous Compound} + O_2 \longrightarrow CO_2 + H_2O, \qquad (1)$$

$$\text{Nitrogenous Compound} + O_2 \longrightarrow CO_2 + H_2O + NH_3 \quad . \qquad (2)$$

Anaerobic digestion is the biological decomposition of waste material in the absence of free O_2. It is generally thought to occur in two main stages. In the first stage, complex organic carbon compounds are degraded to short-chain volatile organic acids (acetic, propionic, butyric, etc) by saprophytic bacteria.[4] Consequently, this stage is referred to as the acid-forming or acid-fermentation stage. The volatile acids are converted into CH_4 and CO_2 by methane-forming bacteria in the second stage. The methane formers are strict anaerobes which grow very slowly, and are sensitive to changes in the environment. They are the rate-limiting organisms in anaerobic digestion.[4] These methane bacteria may also use CO_2 as a hydrogen acceptor as indicated in equation (3).

$$CO_2 + 8H \xrightarrow{\text{Bacteria}} CH_4 + 2H_2O \ . \qquad (3)$$

CO_2 reduction, however, is a minor route for CH_4 formation in comparison to acetic acid breakdown.[5]

In addition to acid- and methane-forming bacteria, other heterotrophic anaerobes are involved in anaerobic waste degradation. Sulfate-reducing bacteria mediate biochemical reactions which produce H_2S, as indicated in equation (4).

$$SO_4 + 10H \xrightarrow{\text{Bacteria}} H_2S + 4H_2O \ . \qquad (4)$$

Facultative nitrate-reducing bacteria are involved in biochemical reactions which produce N_2, as illustrated in equation (5).

$$2NO_3 + 12H \xrightarrow{\text{Bacteria}} N_2 + 6H_2O \quad . \qquad (5)$$

(Equations (3), (4), and (5) are simplified representations. Energy transfers and the states of the reacting particles are not shown.) Additional by-products produced during the second stage include the extremely malodorous compounds indole, skatol, and mercaptans. Figure 1 summarizes the metabolic pathways of anaerobic digestion of organic wastes by microbial action.

A number of the gases generated during waste decomposition are considered to represent potential hazards. Table 1 summarizes the characteristics, TLV, TSTEL, and hazardous properties of various gases associated with anaerobic waste degradation.

TABLE 1
CHARACTERISTICS, THRESHOLD LIMIT VALUES, TENTATIVE SHORT-TERM EXPOSURE LIMIT, AND HAZARDOUS PROPERTIES OF VARIOUS GASES ASSOCIATED WITH ANAEROBIC WASTE DEGRADATION[illegible]

Gas	Formula	Threshold Odor, ppm	TLV* (TSTEL) ppm	Remarks
Methane	CH_4	Odorless	None adopted	Flammable; explosive in air; lower limit - 5.3%; upper limit - 14%; human toxicity: asphyxiant, narcotic, 9% causes nausea
Hydrogen sulfide	H_2S	0.0011, rotton-egg odor	10 (15)	Explosive in air; lower limit - 4.3%; upper limit - 46%; human toxicity: [illegible] for 2 minutes
Ammonia	NH_3	0.037, sharp pungent odor	25 (35)	Explosive in air at [illegible]; human toxicity: [illegible]
Hydrogen cyanide	HCN	Not known, characteristic pungent odor	10 (15)	Flammable in air; human toxicity: 150 ppm - dangerous; 300 ppm - death
Methyl mercaptan	CH_3SH	0.001, decayed cabbage odor	0.5 (0.5)	Flammable in air; lethal concentration for rats: [illegible] human toxicity: nausea, narcotic in high concentrations
Ethyl mercaptan	C_2H_5SH	0.0002, decayed cabbage odor	0.5 (0.5)	May be narcotic in high concentrations; causes nausea
Carbon dioxide	CO_2	Odorless	5,000 (15,000)	Nonflammable; human toxicity: high concentration may cause death by suffocation
Carbon monoxide	CO	Odorless	50 (400)	Explosive in high concentrations; human toxicity: absorbed into body via respiratory system; prolonged exposure causes coma and death

*TLV - refers to time-weighted concentrations for an 8-hour workday and 40-hour work week, and represents conditions under which it is believed that nearly all workers may be repeatedly exposed daily without adverse effect (as established by the American Conference of Governmental Industrial Hygienists, [illegible]). (TSTEL) is considered an absolute ceiling not to be exceeded any time during a 15-minute excursion.

The biochemical status of the substrate on which waste degradation proceeds is important not only because of the bacterial population's sensitivity, but also because the products formed are dependent on it. The presence or absence of free O_2 will determine whether aerobic or anaerobic digestion will occur.

During oxidation of organic matter, the bacteria remove hydrogen atoms from the organic molecule and transfer them to a hydrogen acceptor which may be an inorganic substance (i.e., O_2, NO_3^-, $SO_4^=$, CO_2, etc) or another organic molecule. The microorganisms gain the energy required to sustain life during these biochemical reactions. A measure of the relative concentrations of hydrogen acceptors (oxidants) and hydrogen doners (reductants) is the ORP which is expressed as positive or negative (millivolts). A positive ORP indicates high concentrations of oxidants compared to reductants, and consequently, an aerobic environment.

Biological degradation processes are sensitive to temperature. Bacterial activity is generally classified into three groups based on the temperature ranges they can grow in: psychrophilic bacteria (0 to 30° C), mesophilic (25° to 40° C), and thermophilic (40° to 60° C). Anaerobic digestion and consequent gas generation is retarded at temperatures above 60° C.[9]

Another environmental factor that influences the growth of bacteria and hence gaseous by-product formation is the pH. The pH has an effect on both NH_3 and CO_2 generation under aerobic conditions. For example, urea is a very unstable molecule in wastewater and rapidly breaks down to the NH_4^+ ion. If the pH is below 9, it remains mainly in this form; if the pH is 9 or above, most of the NH_4^+ changes to NH_3 gas. CO_2 that is formed in wastewater combines with the water to form H_2CO_3, which in turn dissociates into H^+, HCO_3^-, and $CO_3^=$. The concentration of each species is a function of the pH of the substrate. Under anaerobic conditions the pH will have an effect on CH_4 formation and on the amounts of H_2S that will be liberated. The growth of methane-forming bacteria is inhibited at pH values lower than 4 and higher than 10. H_2S dissolves in water and dissociates into HS^-, $S^=$, and H^+ ions:

$$H_2S \rightleftarrows HS^- + H^+ \rightleftharpoons 2H^+ + S^= . \qquad (6)$$

If the pH decreases, this equilibrium is driven to the left, forming more H_2S. This gas will then be partially released to the atmosphere.

THEORETICAL ANALYSIS OF CHT TANK GAS GENERATION

During the course of this study, it was considered desirable to be able to predict the concentration of a specific gas in the ullage of a CHT tank at any time. Accordingly, a predictive mathematical model of gas generation by unaerated shipboard wastewaters held in CHT tanks was developed. Figure 2 is a diagrammatic representation of the hypothetical gas-generation scheme upon which this model is based. The derivation is as follows.

The amount of a gas (e.g., H_2S, CO_2, NH_3, etc) in a tank partially filled with sewage can be calculated from equation (7).

$$y_t = y_s + y_f \,, \tag{7}$$

where:

y_t = weight of the gas present in the tank, mg.

y_s = weight of the gas dissolved in the sewage, mg.

y_f = weight of the gas in the ullage, mg.

y_s can be evaluated with equation (8),

$$y_s = C_s V_s \,, \tag{8}$$

where:

C_s = concentration of the gas in the sewage, mg/L.

V_s = volume of sewage in the tank, L.

The concentration of a gas dissolved in the sewage is computable when the partial pressure of the gas above the sewage is known and if diffusion equilibrium exists. As indicated in figure 2, if the gaseous anaerobic metabolic end products are generated mostly by the sludge layer formed on the bottom of the tank, the gases must migrate through the two wastewater zones and the gas/wastewater boundary layer before it is liberated to the tank ullage. The gas/liquid boundary layer is considered to be made up of two distinct regions. Proceeding upward from the liquid phase they are the liquid and gas film regions, respectively.[10] Therefore, a gas liberated by the sludge zone must pass through two zones and two boundary layer regions before it is liberated to the tank ullage. The flux of a gas in any zone as a function of position and time can be expressed as:

$$F_{(x,\,y,\,z,\,t)} = -(D + \varepsilon_d)\,\nabla C_{(x,\,y,\,z,\,t)} + V_{(x,\,y,\,z,\,t)}\,C_{(x,\,y,\,z,\,t)}\,, \tag{9}$$

where:

F = the flux of a gas with respect to a fixed coordinate system

D = diffusivity or diffusion coefficient

ϵ_d = eddy dispersion coefficient

∇C = concentration gradient (Del operator)

C = gas concentration

V = mass velocity of the system

x, y, z = position coordinates

t = time.

Considering only the vertical flow of gases in the tank (^{+}Z = zone 1 $\longrightarrow$ zone 4), the continuity equation for any volume takes the form:

$$V \frac{dC_{(z,\ t)}}{dt} = F_{(z,\ t)} + Vr_{(z,\ t)}\ , \qquad (10)$$

where:

C = gas concentration

t = time

V = volume of sewage

F = the input of flux of a gas in the Z direction

r = rate of reaction of the gas within the liquid phase.

The solution of equation (10) describes the concentration distribution along the Z-axis of the gas in the liquid phase as a function of time. Assuming equilibrium exists at the gas/liquid interface, the concentration of gas in the ullage (zone 4) is related to the concentration of gas at the liquid side of the interface by Henry's Law:

$$P = HX, \qquad (11)$$

where:

P = the equilibrium partial pressure of the gas in the ullage of the tank in contact with the sewage, atm

X = the mole fraction of the gas in the sewage

H = Henry's constant, atm/mole fraction.

Simultaneous solution of equations (10) and (11) is required to compute accurately the concentration of dissolved gas in the sewage; however, with the present state of knowledge, this is not feasible.

MODEL FOR PREDICTING HAZARDOUS CHT CONDITIONS

The purpose of this model is to provide a tool for predicting hazardous situations in CHT tank operation. Assumptions, which must be made to construct a workable model, will result in establishment of a "worst-case" for gas accumulation in the tank ullage. Consequently, predicted ullage gas concentrations will tend to be greater than the actual expected value.

The assumptions made are that the liquid phase of the system is well mixed, and that the partial pressure of the gas in the vapor phase is related to the concentration of the gas in the bulk solution directly by Henry's Law (equation (11). (The applicability of Henry's Law to wastewater mixtures is not precisely defined, but it is believed that errors resulting from this discrepancy are not large.) The variable, X, in equation (12) can be computed by converting C_s to moles of dissolved gas per liter, and by dividing the number thus obtained by the total number of moles in 1 liter of solution* as follows:

$$X = \frac{C_s/\omega_m}{1000/18} = \frac{C_s}{\omega_m} \cdot 18 \times 10^{-3}, \tag{12}$$

where ω_m = gram molecular weight of the gas, mg. The gas concentration in the ullage was measured in ppm by volume. PPM is converted to partial pressure (atm) and equation (12) is rewritten as follows:

$$P = C_f \times 10^{-6} = \frac{C_s H}{\omega_m} \cdot 18 \times 10^{-3}, \tag{13}$$

which, rearranged, yields equation (14) for calculating Y_s.

$$Y_s = V_s \left(C_f \frac{(55.6 \times 10^{-6})}{H} \omega_m \right), \tag{14}$$

---

*The moles of gas and wastes per liter are very small compared to the moles of water in a liter and therefore can be omitted from the denominator.

where C_f = measured concentration of the gas in the tank ullage, ppm by volume.

Y_f can be calculated from equation (15).

$$Y_f = V_f \times \frac{C_f}{10^6} \times \rho_{T_r} \times 1000 \times \frac{T_r}{273 + T_c} \quad , \tag{15}$$

where:

ρ_{T_r} = the density of the gas when measured at reference temperature, g/L

T_c = temperature at which ρ is measured, ° C

V_f = volume of ullage, L

T_r = reference temperature, K.

Using equations (8), (14), and (15) yields equation (16).

$$Y_t = V_s\left(\frac{C_f(55.6 \times 10^{-6})\ \omega_m}{H}\right) + \frac{V_f\ (C_f)\ \rho_{T_r}\ (T_r)}{(273 + T_c)\ 10^3} \quad . \tag{16}$$

Gas-generation rates during early waste degradation (less than 12 days) may be expressed by equation (17).[11]

$$Y_t = e^{Kt} + C \quad , \tag{17}$$

where:

t = elapsed time, days

K = experimentally determined gas-generation rate constant, days^{-1}

C = the initial concentration of gas (assumed equal to zero).

This study will determine values of K for each CHT tank waste mixture at each condition (temperature, salinity, seeding, etc). Equations (16) and (17) can be combined:

$$Y_t = e^{Kt}\left(\frac{V_{s_1}}{V_{s_2}}\right)$$

$$= \frac{(V_{s_1})\ P_1\ (55.6 \times 10^{-6})\ (\omega_m)}{H} + \frac{V_{f_1}\ (P_1)\ \rho_{T_r}\ (T_r)}{(273 + T)\ 10^3}, \qquad (18)$$

where:

V_{s_1} = volume of sewage in the CHT tank

V_{s_2} = volume of sewage in the laboratory test tank

V_{f_1} = volume of ullage in the CHT tank

P_1 = concentration of gas in the CHT tank ullage, vol/vol.

Transposing equation (18) yields:

$$P_1 = \frac{e^{Kt}\ V_{s_1}}{(V_{s_2})\left[\dfrac{(V_{s_1})\ 55.6 \times 10^{-6}\ (\omega_m)}{H} + \dfrac{(V_{f_1})\ \rho_{T_r}\ (T_r)}{(273 + T_c)\ 10^3}\right]}. \qquad (19)$$

A computer program has been written to facilitate the use of the gas-generation prediction model developed in the foregoing for Navy CHT tanks. Appendix A is a manual which explains the use of the "GASGEN" program. Knowledge of an applicable gas-generation rate constant, as developed in this study, permits the prediction of the concentration of a hazardous gas after a given incubation period. Appendix B is an example of the use of "GASGEN" with results applicable to USS DIXON (AS 37).

INVESTIGATION

APPROACH

The approach to accomplishment of this task was as follows:

- Develop a plan to evaluate the anaerobic waste degradation process as it occurs in CHT system holding tanks.

- Implement the plan with results of preliminary studies in the laboratory and aboard selected ships of the Fleet.

- During the laboratory experimentation phase, investigate the anaerobic decomposition of CHT system influent wastes to determine the effect of temperature, pH, loading, seeding, flushing medium, and other factors on the decomposition of the waste and the associated gas buildup.

- From the laboratory results, extrapolate representative 12-, 24-, and 48-hour hazardous gas generation, and identify potential hazardous situations.

- Investigate the nature and types of odors stemming from anaerobic decomposition that may be sensed by shipboard personnel. Obtain and analyze gas samples to determine concentrations and compositions.

- Prepare a report containing a summary of test results, conclusions, and recommendations concerning potential hazards due to CHT system anaerobic degradation of waste.

PRELIMINARY STUDIES

Preliminary laboratory experiments were conducted to determine the following:

- The daily variability that could be expected in the waste stock (head, food, and laundry wastes).

- The variability in degradation characteristics to be expected from similar wastes collected at the same time and at different times and incubated under identical environmental conditions.

- The reproducibility of the various waste mixtures.

- The reliability of sampling procedures.

Food and laundry wastes were obtained from the U. S. Naval Academy dining halls and laundry, respectively. Head wastes were obtained from the DTNSRDC sewage treatment test site. Samples were taken from stock solutions and analyzed for COD, TOC, TS, and TVS. These data were analyzed statistically to determine variance in the stocks. The results are indicated in table 2. To determine the variability in degradation, identical waste mixtures were incubated in test chambers under the same controlled environmental conditions. The ORP, pH, and DO concentrations were monitored and recorded as plotted in figures 3 through 5. The reproducibility of the results gives an indication that a high degree of confidence could be placed on the large-scale experiments. In addition, identical waste mixtures were incubated at two different temperatures to assess degradation trends and instrumentation requirements for the large-scale laboratory tests.

TABLE 2
CHARACTERISTICS OF STOCK WASTES
(ALL VALUES IN MG/L)

	Head (n = 15)		Food (n = 13)		Laundry (n = 13)	
	$\overline{x}$	SD	$\overline{x}$	SD	$\overline{x}$	SD
COD	3,700	210	19,000	1,100	1,500	140
TOC	890	50	2,100	110	490	40
TS	16,000	1,100	24,000	1,200	2,900	240
TVS	9,800	1,000	21,000	1,300	2,000	190

n = number of samples
$\overline{x}$ = mean
SD = standard deviation

WASTE MIXTURES

Eight significantly different mixtures were selected for testing. The selection was based on an investigation of the waste mixtures predicted to be received by 28 different CHT holding tanks on 13 different ship types as indicated in table 3. The composition is also indicated in table 3. The mixtures were targeted to the P-.90 NEPSS data base mass-emission factor values for in-port, head, galley, and laundry wastes.* These waste sources constitute at least 95% of the total waste load in any given CHT system holding tank. A range of values for the waste stock was selected from the MEF values and is presented in table 4. The selection of the waste concentration values for use in the experiments (target values) is based on the 90th percentile of the concentration values, measured, and corrected for the type of data distribution and sampling error.

APPARATUS

Six tanks, measuring 61 cm wide by 61 cm long by 76 cm high were constructed with 13-mm-thick Plexiglas. These tanks were placed in a 1.5- by 3.5-m water bath. Each tank was secured by a drain which penetrated the bottom of the bath tank. Four sampling ports, spaced vertically, penetrated the side walls of the water bath and each tank as depicted in figures 6 and 7. Each port was sealed with soft rubber septum. A removable lid was bolted to the top of each tank, as indicated in figure 8. Each lid was fitted with a bulkhead fitting connected to a 38-mm ID pipe. The water bath tank was insulated and provided with a pump for circulating water to a heating/cooling device as shown in figure 9. A 3.8-m^3 plastic mix tank, fitted with drain line and stirrer, was elevated on scaffolding and placed on a stand adjacent to the water bath, also illustrated in figure 9.

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*This data available from Naval Environmental Protection Support Service, NCBC, Port Hueneme, California 93403.

TABLE 3 - MIXTURES AND CORRESPONDING SHIP CHT TANKS WHICH RECEIVE THAT WASTE

Mixture No.	Ship	Tank No.
1 (30/70/-)*	CVA 67	4-6
2 (59/41/-)	LPD 4	2-3
3 (-/54/46)	LST 1179	2
4 (34/37/29)	AD 14	2
	AS 11	2
	DLG 26	1
5 (45/31/24)	AE 26	1
	AFS 6	1
	ARS 6	1
	AOG 50	2
	ASR 7	1
	ATF 76	1
	LKA 112	1
	AS 37	1
6 (65/19/16)	LST 1179	1
7 (29/20/51)	LPD 4	1
	CVA 67	7-8
8 (100/-/-)	AD 14	1
	AOG 50	1
	AS 11	1
	DLG 26	2
	CVA 67	1-3
	AS 37	2

*Proportion of head/food/laundry waste in % ratio.

TABLE 4 - WASTE STOCK TARGET RANGES (ALL VALUES IN MG/L)

Waste Stock	P-.90 MEF Value	Target Value	Range ±10% of Target Value
		Head	
COD	3,080	3,710	3,339-4,081
TOC	678	880	800-960
TS	13,400	16,100	14,490-17,710
TSS	3,180	4,010	3,509-4,411
TVS	6,968	9,982	8,984-10,980
		Food	
COD	15,500	19,300	17,370-21,230
TOC	1,680	2,120	1,908-2,332
TS	18,000	23,900	21,510-26,290
TSS	6,420	7,970	7,173-8,767
TVS	15,930	21,510	19,359-23,661
		Laundry	
COD	998	1,550	1,395-1,705
TOC	290	531	478-584
TS	1,680	2,970	2,673-3,267
TSS	359	568	511-625
TVS	801	1,925	1,732-2,117

PROCEDURES

Each waste mixture was mixed in 189-liter aliquots and placed in a tank. The food waste was ground prior to use in a commercial garbage pulper. Approximately 38 liters of seed material were used for "seeded" runs (waste sludge added to the mixtures) so that they contained a total of 227 liters of waste. A sample of each mixture was obtained before incubation and analyzed for COD, TOC, TS, TVS, NO_3^-, $SO_4^=$, and TVA. These data were compared to successive mixtures to ensure that the compositions deviated less than 10% from run to run. A statistical analysis of COD, TOC, TS, and TVS values for the mixtures is presented in table 5.

TABLE 5
STATISTICAL ANALYSIS OF COD, TOC, TS, AND TVS FOR EACH MIXTURE

		Mixture							
		1	2	3	4	5	6	7	8
		n = 13	n = 13	n = 13	n = 7	n = 12	n = 8	n = 6	n = 2
COD mg/L	$\overline{x}$	14,000	9,900	11,000	7,300	7,800	6,100	5,300	3,800
	SD	1,100	550	630	260	300	170	300	350
TOC mg/L	$\overline{x}$	1,600	1,400	1,400	1,200	1,100	1,100	650	910
	SD	140	120	110	41	92	78	390	57
TS mg/L	$\overline{x}$	20,000	22,000	1,300	13,000	15,000	16,000	11,000	16,000
	SD	1,700	780	1,300	1,300	570	390	400	1,600
TVS mg/L	$\overline{x}$	17,000	15,000	12,000	11,000	11,000	12,000	8,700	11,000
	SD	1,700	1,600	1,200	780	1,000	1,200	390	2,400

n = number of samples
$\overline{x}$ = mean
SD = standard deviation

The mixtures were incubated under six different environmental conditions involving temperature, comminution, salinity, and seeding as indicated in table 6. Run 1 was done in quadruplicate; runs 2 through 6 were done in duplicate; run 1E was an extended run lasting 359 hours (15 days).

After the mixtures were prepared, sampled, and placed in the tanks, the following parameters were periodically measured:

- Methane
- Hydrogen sulfide
- Carbon dioxide
- Carbon monoxide
- Ethyl mercaptan
- Methyl mercaptan

- Oxygen
- Ammonia
- Hydrogen cyanide
- Dissolved oxygen
- pH
- Oxidation/reduction potential.

TABLE 6
ENVIRONMENTAL TEST CONDITIONS FOR LARGE-SCALE LABORATORY STUDIES

Run	Incubation Temperature ° C	Salinity %	Total Time	
			Days	Hours
1A-1C	45	1	3.8	91
1D	45	1	4.9	117
1E	45	3	15	359
2	45	3	4	95
2A	45	3	3.8	91
3	35	3	4	97
3A	35	3	5.9	142
4	25	3	3.9	94
4A	25	3	3.8	90
5	15	3	4	95
5A	15	3	3.8	92
6	25	3	8	193
6A	25	3	5.9	143

Note: All fluids were comminuted and seeded except in cases 1A-1E which had not been seeded.

ANALYSES

CH_4 and O_2 concentrations were measured in the ullage of each tank with an Antek model 500 GC. An Antek model 650 programmer was incorporated into the GC system to allow for the automatic and sequential sampling of each tank every hour. The programmer also controlled a series of six air pumps that circulated the ullage atmosphere of each tank for 10 minutes prior to the drawing of a sample. A schematic of the automated GC system is shown in figure 10. CH_4 and O_2 concentrations were automatically recorded on a strip-chart recorder. The pH and ORP were monitored by probes placed within each test tank and read on an Orion model 701 ion meter. The DO and temperature were measured with a Yellow Spring DO meter. H_2S, C_2H_5SH, CH_3SH, NH_3, CO, HCN, and CO_2 concentrations were measured with a Matheson Gas Products model 8014K toxic gas detector. CO_2 concentration was also measured with a Firerite™ CO_2 detector. COD, TOC, TS, TVS, NO_3^-, $SO_4^=$, and TVA analyses were performed in accordance with "Standard Methods."[12] Liquid samples from inside each test tank were drawn periodically during each run for the determination of NO_3^-, $SO_4^=$, and TVA. A 50-cc syringe with a 12-inch needle was inserted in one of the sampling ports on the side of each tank and a sample extracted. During runs 1A through 1C, a sample was extracted, in the manner mentioned above, from different depth levels in each tank. The pH and ORP were measured to determine whether there was any appreciable difference from top to bottom. There was none found. Samples for TVS analysis were obtained from the seed material left in each tank by means of a length of Tygon™ tubing and a hand-held vacuum pump.

RESULTS AND DISCUSSION

OXYGEN DEPLETION IN THE HOLDING-TANK ATMOSPHERE

The O_2 depletion rates in the ullage of the tanks, expressed as grams of O_2 removed per hour, are shown in items (a) through (h) of figure 11 for each mixture, during each run.* The rate of O_2 depletion was found to be related to the temperature of incubation and whether or not the mixture was provided with seed material. There was no significant difference in rates between 1% and 3% salinity of the flushing water. The effect of temperature is indicated by the declining O_2 depletion rates during runs 2 (45° C), 3 (35° C), 4 (25° C), and 5 (15° C), respectively. This concurs with a study on the influence of temperature on anaerobic biological digestion; it was found that increased temperatures (up to an optimum) induce increased rates of bacteriological decomposition of organic matter.[13]

A comparison of O_2 depletion rates during runs 1E (unseeded) and 2 (seeded) suggests the influence of seeding. Results of runs 1 (1% salinity) and 1E (3% salinity) indicate that this salinity difference produced no significant effect. Analysis of data acquired during runs 1E (unseeded, 45° C) and 3 (seeded, 35° C) signifies the seeding is a more important factor in O_2 depletion than temperature, since faster rates were generally found during run 3 even though the temperature was lower.

Oxygen depletion has practical significance in that health standards, as prescribed by OSHA, call for a minimum O_2 concentration of 19.5% in spaces where personnel may work without a

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™Firerite - Registered trade name of Bacharach, Incorporated.
Tygon - Registered trade name of Norton Company.

*Information concerning mixtures and test conditions for each run can be obtained by cross-referencing tables 3 and 6.

respiratory device.[14] The O_2 concentration in the tank atmospheres dropped below 19.5% in a majority of cases within 18 hours, and in all cases within 24 hours.* Therefore, the absence of O_2 in a CHT tank, as well as the presence of toxic and/or explosive gases, must be considered a potential hazard to personnel entering the tank.

DISSOLVED OXYGEN DEPLETION

The DO depletion for each set of conditions is indicated in items (a) through (h) of figure 12. The depletion rates were found to increase in the following order: run 5 (15° C, seeded), run 4 (25° C, seeded), run 3 (35° C, seeded), run 1 (45° C, unseeded), run 2 (45° C, seeded). The effects of seeding and temperature during these runs are evident. The lower temperature during run 5 substantially hindered microbial activity as evidenced by the O_2 utilization. DO concentrations were below 1 mg/L within 24 hours during a majority of the runs. Small concentrations of DO detected during runs 1 through 4 were measured 10 cm below the liquid surface and were derived from the tank atmosphere via simple diffusion.

OXIDATION/REDUCTION POTENTIAL

The development of anaerobic conditions within 24 hours is further illustrated by ORP data acquired during various runs. Items (a) through (d) of figure 13 show representative cases. As indicated, the substrates were well within the negative millivolt range within 24 hours.

pH

The variations of pH as a function of time for each mixture, during each run, are illustrated in items (a) through (h) of figure 14. In most cases, the pH decreased continuously for approximately 48 hours, at which time it leveled off at values between 2 and 4. During the extended runs (1E and 3), the pH did not rise above a value of 4 following the initial decline. The two exceptions were: mixture 7 during run 3 (item (g) of figure 14) and mixture 8 during run 6 (item (h)). In the former instance, it is suspected that the laundry waste stock used had an unusually high alkalinity which helped to buffer this particular batch during the incubation period. In the latter case, the slight variation of pH agrees well with observations made aboard USS SURIBACHI (AD 21) during shipboard monitoring of black water in CHT tanks.[15]

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*O_2 depletion, DO, ORP, and pH data should be used on a qualitative basis. While general trends in tank data should be analagous to that of the CHT tank, extrapolation is not sufficiently reliable.

The initial decrease in pH is believed to have been produced by an increase in the concentration of dissolved CO_2 resulting from aerobic metabolism. Upon depletion of the substrate DO, anaerobic conditions develop, and consequently, the production of volatile organic acids continues the pH depression. The production of organic acids continues until the pH inhibits further microbial growth, at which point the system stabilizes. This marks the beginning of development (growth) of methane-producing bacteria.[3]

HYDROGEN SULFIDE GENERATION

H_2S generation rate constants for each mixture, during each run, are given in items (a) through (h) of figure 15. Seeding, temperature, relative concentration of $SO_4^=$ and pH were the most important factors influencing the rate of H_2S generation. The effect of seeding is indicated in figure 15, items (a) through (e). All mixtures exhibited faster rates during run 2 (45° C, seeded) than run 1E (45° C, unseeded). As indicated, the unseeded runs exhibited the longest initial lag period for all mixtures. The initial lag in gas generation is brought about by the absence of sulfate-reducing organisms. During the seeded runs, however, a population was already established, and consequently, H_2S generation began in a relatively shorter period of time.

Rate constants were proportional generally to the incubation temperature. The difference between rates at 35° C (run 3) and those incubated at 25° C (run 4) were moderate. A similar observation was made by Baumgartner[16] who, in his studies of the effect of temperature and seeding on H_2S formation in sewage, noted that samples incubated at 37.5° C did not demonstrate a great rate increase over those incubated at 30° C. During experiments at the Center (run 5, 15° C), low temperatures suppressed H_2S generation in all mixtures as expected.

The generation of H_2S is markedly affected by the pH. The pH of the substrate decreased with time (figure 14, items (a) through (g), resulting in a shift of equation (6) to the left (figure 2) and the liberation of additional H_2S to the tank atmosphere. The pH of run 6 (25° C, head waste, seeded) remained fairly constant in the neutral range (item (h) of figure 14). Consequently, the H_2S generation rate is substantially lower (see figure 15, item (h)) than would be expected from the effects of temperature and seeding alone.

The effect of salinity on H_2S generation is indicated by data from runs 1 (1% salinity) and 1E (3% salinity). The increased rate of H_2S generation during run 1E could be due to the higher initial $SO_4^=$ concentrations which accompany higher salinity.

H_2S was detected in all mixtures during runs 1, 1E, 2, and 6 within 24 hours. H_2S was detected in all mixtures during runs 3 and 4 within 92 hours, and only once after 92 hours during run 5, and only in mixture 1. During run 2 (45° C, 3% salinity, seeded all mixtures generated H_2S in excess of the detector's upper limit (1700 ppm). Therefore, it is evident that all the mixtures have the potential for generating large amounts of H_2S under the proper environmental conditions. The amount of H_2S produced was proportional to the amount of head waste incorporated in the mixture (see table 3).

Items (a) through (h) of figure 16 indicate the variation of $SO_4^=$ concentrations for each mixture with time. The mean concentration of $SO_4^=$ in the mixtures at the beginning of each run was approximately 500 mg/L. As expected, a close correlation between H_2S generation and $SO_4^=$ reduction was exhibited. Furthermore, the rate of $SO_4^=$ reduction was enhanced by increased incubation temperatures and seeding.

CARBON DIOXIDE GENERATION

CO_2 was generated in copious amounts in all mixtures during all runs. It is apparent that the upper stratum of the tank contents underwent aerobic degradation (utilizing O_2 diffused from the tank ullage), while the lower stratum underwent anaerobic degradation. Thus, a stratified system was maintained in the tanks. Items (a) through (g) of figure 17 indicate CO_2 generation rate constants for the various waste mixtures. With the exception of mixtures 3 and 6, increased incubation temperatures resulted in increased CO_2 generation rates. The effect of seeding was inconclusive.

ETHYL MERCAPTAN GENERATION

Concentrations of C_2H_5SH after 92 and 142 hours of incubation are shown for each mixture in items (a) through (h) of figure 18. The effects of temperature and seeding were not readily apparent. There appeared to be an inhibition of C_2H_5SH in runs 2 (45° C, 3% salinity, seeded) and 5 (15° C, 3% salinity, seeded). The highest concentration (100 ppm) of C_2H_5SH was encountered in mixture 5 during run 3 following 142 hours of incubation.

METHYL MERCAPTAN GENERATION

CH_3SH was not detected during runs 1, 1E, or 2. A maximum concentration of 70 ppm was measured in mixture 5 during run 3 after 142 hours of incubation. CH_3SH was also detected during runs 4 and 6. The gas was liberally generated in mixture 8 during run 6, with a minimum of 2 ppm after 24 hours of incubation to a maximum of 45 ppm after 143 hours. CH_3SH generation was inhibited at temperatures above 35° C and below 25° C.

TOTAL VOLATILE ACID PRODUCTION

Items (a) through (h) of figure 19 indicate TVA variation with time for each wastewater mixture. In all cases, a gradual increase in TVA concentration continued throughout the incubation period. Increased temperature and the presence of seed material resulted in greater production of TVA. Increase in TVA concentration was instrumental in depressing pH and indicative of the aforementioned *acid-forming* phase of anaerobic decomposition.

DENITRIFICATION

Initial NO_3^- concentrations in the mixtures were generally between 4 and 7 mg/L. In all cases, a gradual decrease in NO_3^- continued throughout the incubation period. Increased incubation temperatures, as well as the presence of seed material, resulted in a larger decrease in NO_3^- concentration. NO_3^- concentration versus time plots for all runs are given in items (a) through (h) of figure 20.

CARBON MONOXIDE GENERATION

CO was detected only during run 1E in mixtures 1, 2, 4, and 5. Run 1E was an extended run (359 hours), and CO was found only after 120 hours of incubation. Following 191 hours of incubation, the CO concentration reached a maximum of 70 ppm with no additional increase. It was never detected in mixture 3. CO is generated primarily as an oxidation product from petrochemical and industrial wastes and is not usually found in domestic sewage. Its presence during these runs was unusual because industrial wastes were excluded from the mixtures. However, past experience at the Center indicates that petroleum products can occasionally be encountered in the black water distribution system, although its occurrence is rare. It is possible, therefore, that an oil may have been discharged into the system from a toilet facility. Inference of this possibility may be found in the fact that the mixture which contained no head waste (from distribution system) did not produce CO under otherwise similar conditions.

METHANE AND AMMONIA GENERATION

CH_4 and NH_3 were not detected in any mixture during any of the runs. It is believed that CH_4 was not detected primarily because of the low pH of the mixtures and the extended incubation period required for establishment of a stable methane-forming bacteria population. Methane-forming bacteria can survive within a pH range of 5-9.[5] The pH dropped below 5 in all the mixtures during all runs except mixture 7 in run 3 and mixture 8 in run 6. However, these bacteria are also sensitive to concentrations of volatile acids greater than 2000 mg/L.[4] Figure 19, items (g) and (h), indicate that the TVA concentrations increased to 3000 mg/L in mixture 7 and 3300 mg/L in mixture 8. This indicates that even though the pH was conducive to CH_4 generation, the process may have been inhibited by the TVA concentrations. Run 1E was extended to 359 hours to ascertain whether the decreasing trend in pH would reverse and thus produce an environment more conducive to CH_4 generation. The pH continued to decrease for 119 hours; then it stabilized between 1.6 and 2.2 fluctuating slightly until the run was terminated. This situation is analagous to "digester souring" in conventional anaerobic wastewater treatment facilities.

The pH is also considered instrumental in its inhibition of NH_3 production. For NH_3 to exist to any degree, the pH must be greater than 9. At no time, during any of the runs, was this value attained. HCN was detected only once during the experiments (in concentrations of less than 1 ppm). This is not considered significant.

SUMMARY OF FINDINGS

A brief background of aerobic and anaerobic waste degradation principles with emphasis on anaerobic processes was presented, followed by a report of the work done. The results and findings can be summarized as follows:

- The rate of O_2 depletion in the tank atmosphere and the DO of the wastes were found to be related to the temperature of incubation and whether or not the mixture was provided with seed material. The faster rates were related to higher temperatures of incubation and the presence of seed material. There was no significant difference in depletion rates between 1% and 3% salinity of the flushing water. The lack of sufficient concentrations of O_2 may present a hazard to personnel entering a CHT tank, even though other hazardous gases are not detected.

- The ORP values decreased from positive to negative potentials in all mixtures during all runs.

- The pH values decreased continuously until approximately 48 hours then level off and fluctuate slightly between 2 and 4.

- The rate of H_2S production was influenced by seeding, temperature, and relative concentration and availability of sulfates. Greater amounts of H_2S were generated and at a faster rate during seeded runs than unseeded runs, and during higher incubation temperatures than lower ones. The TLV (10 ppm) was surpassed whenever H_2S was detected, and concentrations greater than 1700 ppm were often detected. The flushing medium with a salinity of 3% appeared to give faster rates than when 1% was used. This occurred presumably because of the higher concentrations of available $SO_4^=$ in the 3% medium. The effect of low pH values on H_2S generation is discussed. Additionally, H_2S production was related to the amount of head wastes incorporated into each mixture. The mixtures with greater proportions of head waste to other wastes produced greater amounts of H_2S.

- $SO_4^=$ and NO_3^- concentrations decreased with time. A relation between temperature of incubation and presence of seed material was evident in that greater reductions were observed during the seeded and higher temperature runs.

- CO_2 above ambient levels was detected during all runs. The unusually large amounts of CO_2 during anaerobic degradation is indicative of a stratified system wherein the upper levels of the tank contents were undergoing aerobic digestion (utilizing available O_2 from the ullage atmosphere) and the lower strata were undergoing anaerobic digestion. The effect of temperature, salinity, and seeding on CO_2 generation was inconclusive.

- C_2H_5SH was detected in concentrations ranging up to 100 ppm (after 142 hours of incubation). The effect of temperature and seeding was not readily apparent.

- TVA in all the mixtures increased with incubation and was indicative of acid-forming microbial activity. Increased temperatures and the presence of seed was related to faster production rates of volatile acids. The increased TVA concentration was instrumental in depressing the pH.

- CO was detected only during run 1E at a maximum concentration of 70 ppm (TLV = 50 ppm) and only after 120 hours of incubation. The potential threat from CO to personnel is considered insignificant.

- CH_3SH was not detected during runs incubated at 45° and 15° C. It was detected only once in runs incubated at 35° C and only after 142 hours. The maximum concentration at that time was 70 ppm. CH_3SH was generated during runs incubated at 25° C (runs 4 and 6) with a minimum concentration of 2 ppm after 24 hours and a maximum of 45 ppm after 143 hours. Temperatures greater than 35° C and lower than 25° C appeared to inhibit CH_3SH formation.

- CH_4 and NH_3 were not detected in any of the mixtures during any of the runs. This was attributed to the low pH of the waste mixtures.

- HCN was detected once in concentrations less than 1 ppm.

- A predictive mathematical model of gas generation by unaerated shipboard wastewaters has been developed and programmed. Data from the real-time studies can be used with this model to identify potentially hazardous conditions in CHT tanks.

RECOMMENDATIONS

- Positive ventilation of CHT tanks prior to personnel entry should be emphasized, and all current safety practices as concerns CHT tanks must be followed.

- Anaerobic conditions in CHT tanks should be avoided.

- A sampling port should be installed in each CHT holding tank in the ullage above the high level mark (see figure 21).

- Each shipboard DCA/gas free engineer should be provided with a detector for H_2S and mercaptans.

- Gas analysis for hazardous gases and oxygen content should always be conducted prior to opening CHT tanks. CHT tanks should always be considered dangerous to personnel entering them without proper breathing apparatus because of the possible presence of toxic gases.

- CHT tanks should be relocated when necessary to avoid exposure of shipboard personnel to potentially dangerous concentrations of hazardous gases.

- CHT tanks should be cleaned at regular intervals utilizing an effective tank cleaning system to avoid seeded conditions.

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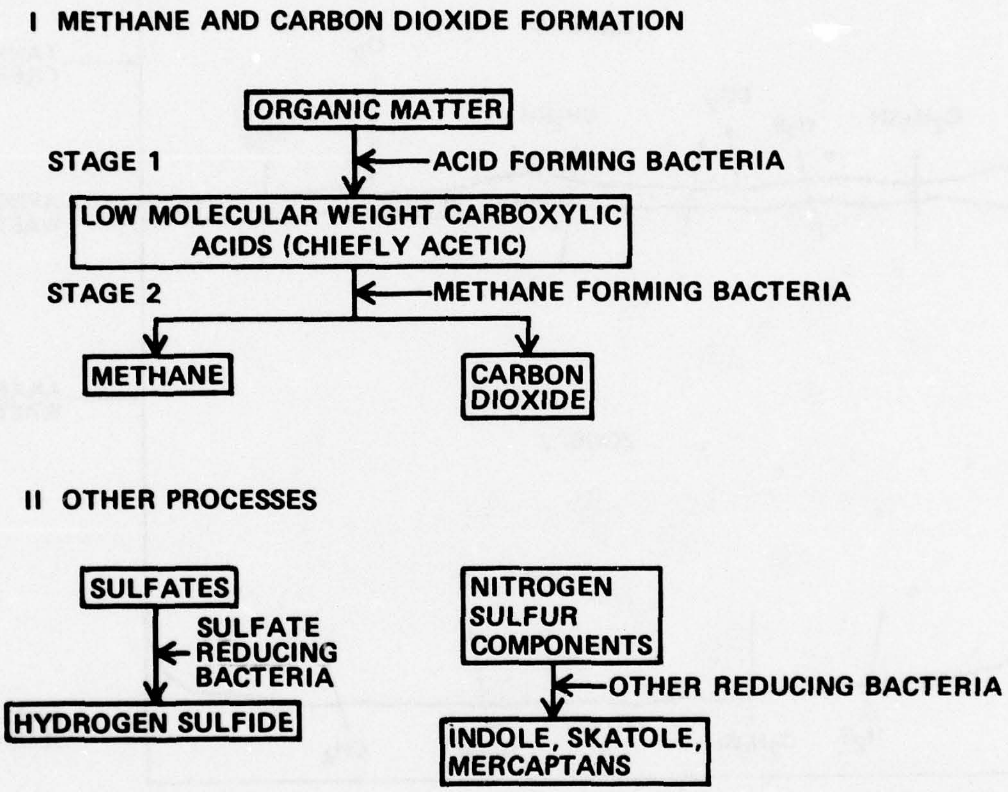


Figure 1
Anaerobic Digestion of Organic Wastes
Mediated by Microbial Action

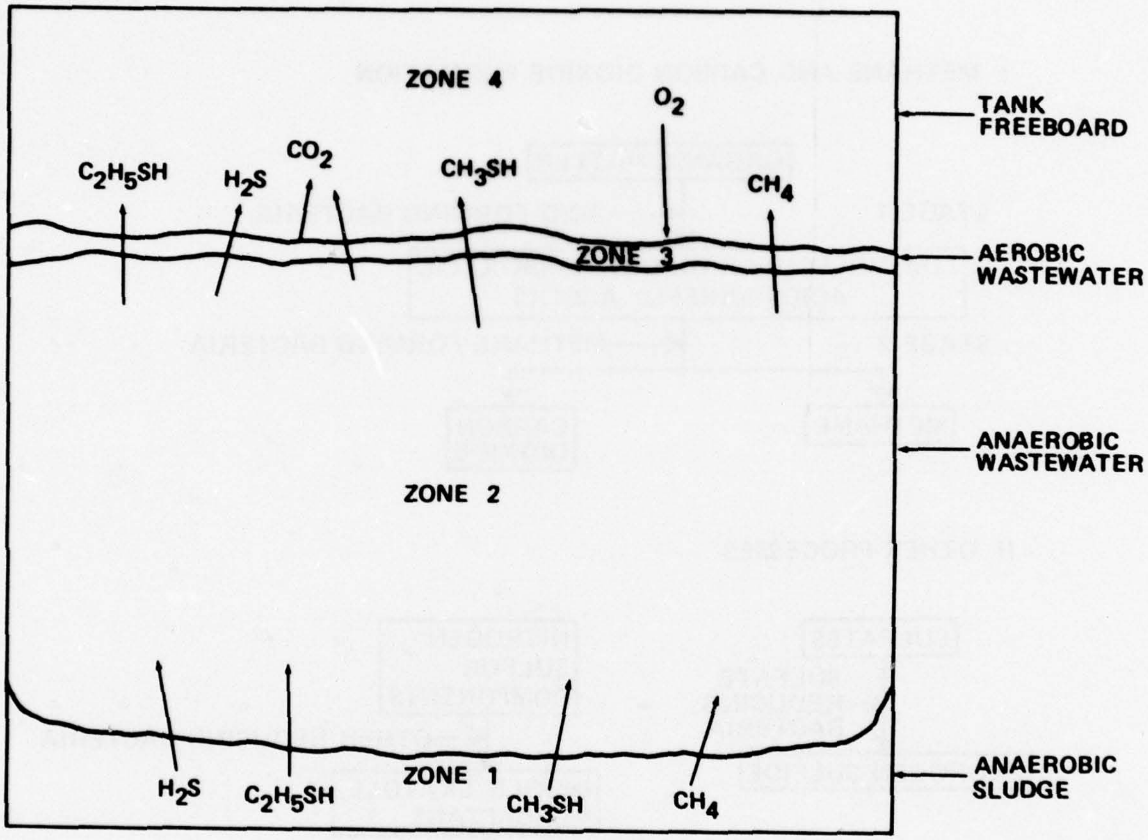


Figure 2
Hypothetical Gas-Generation Model

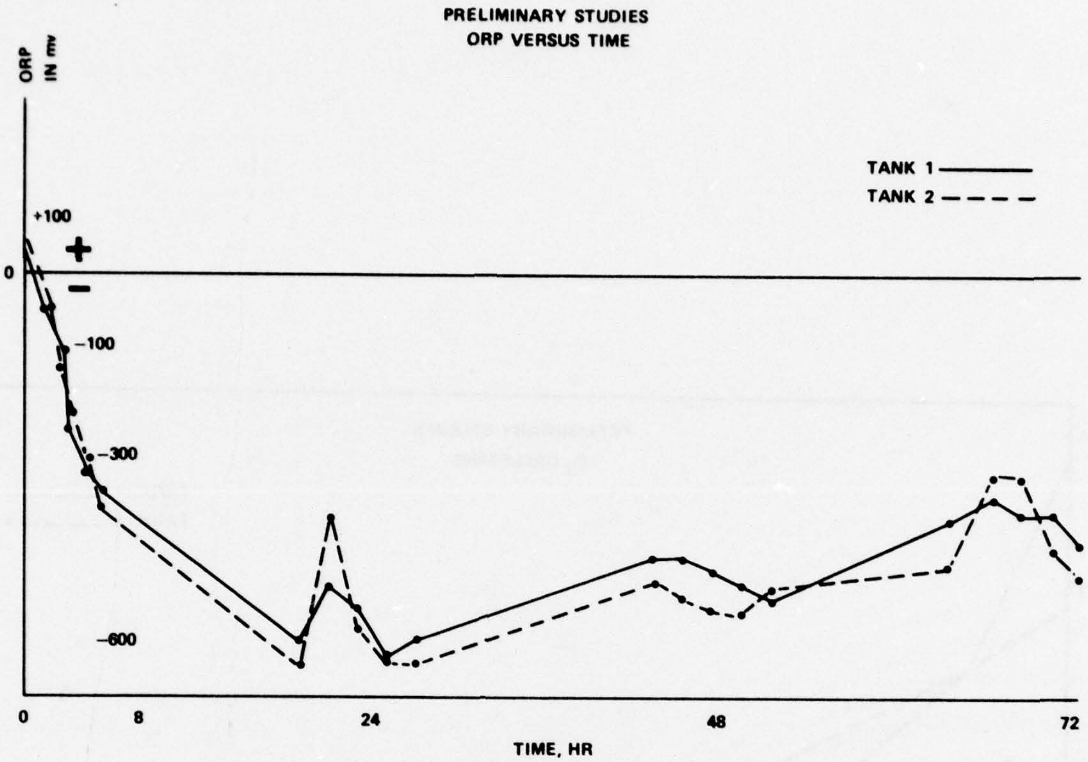


Figure 3 - Comparison of Preliminary Test Oxidation Reduction Potential Data

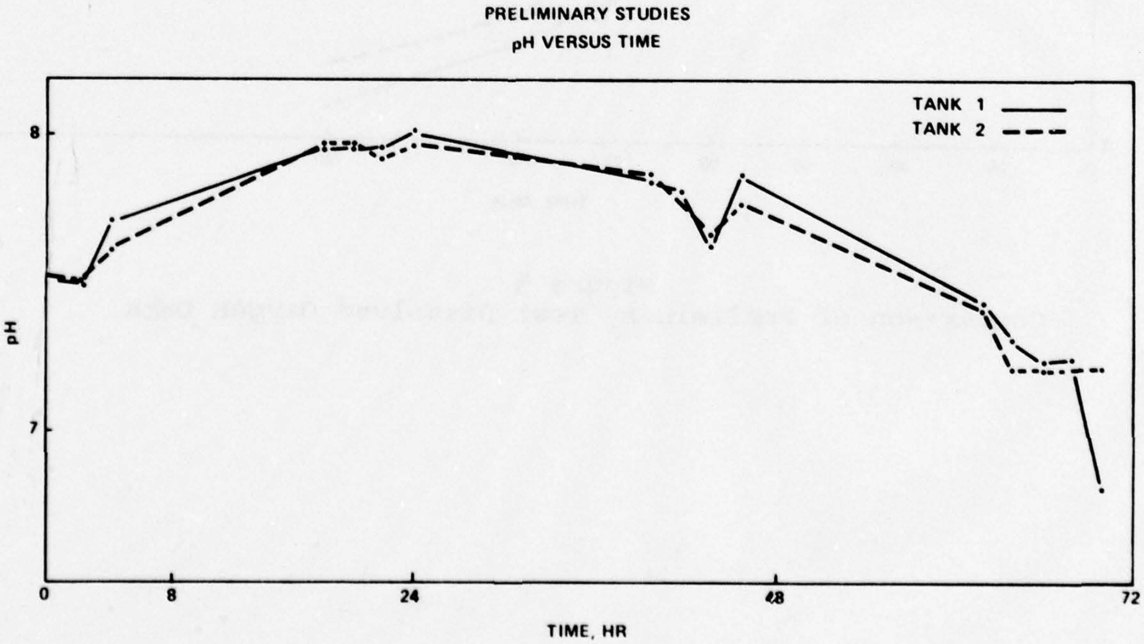


Figure 4 - Comparison of Preliminary Test pH Data

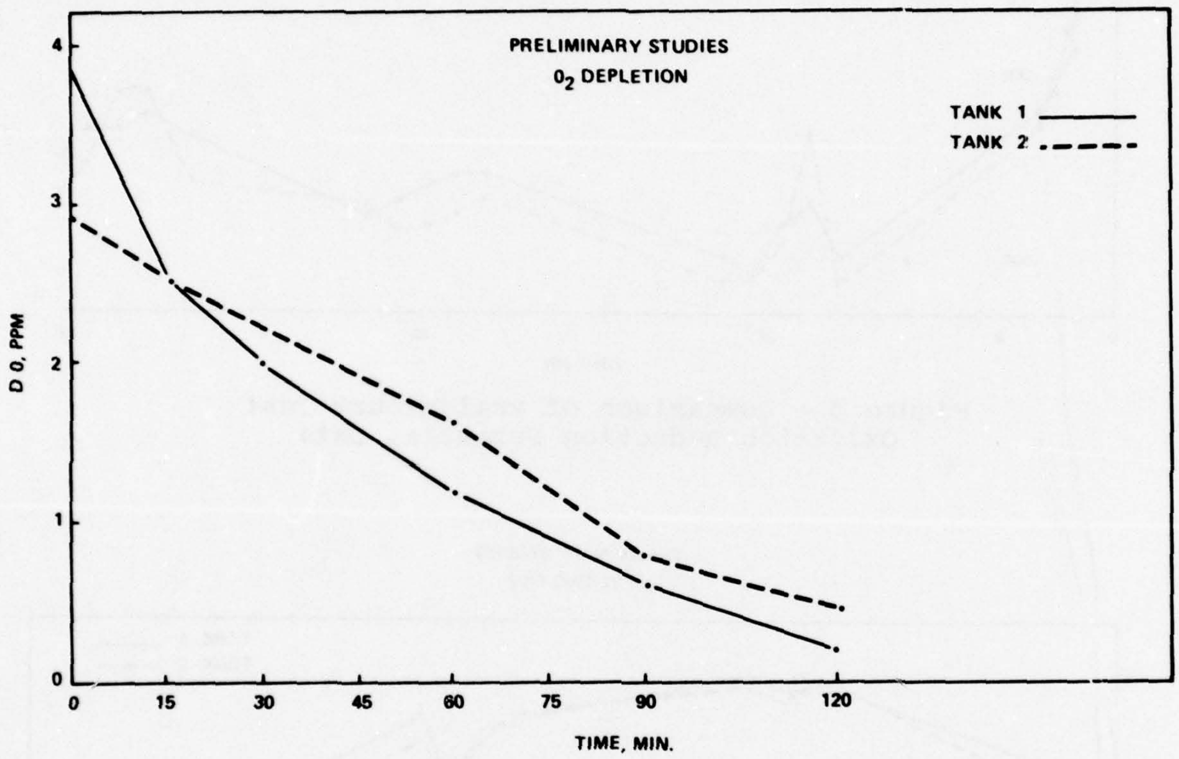


Figure 5
Comparison of Preliminary Test Dissolved Oxygen Data

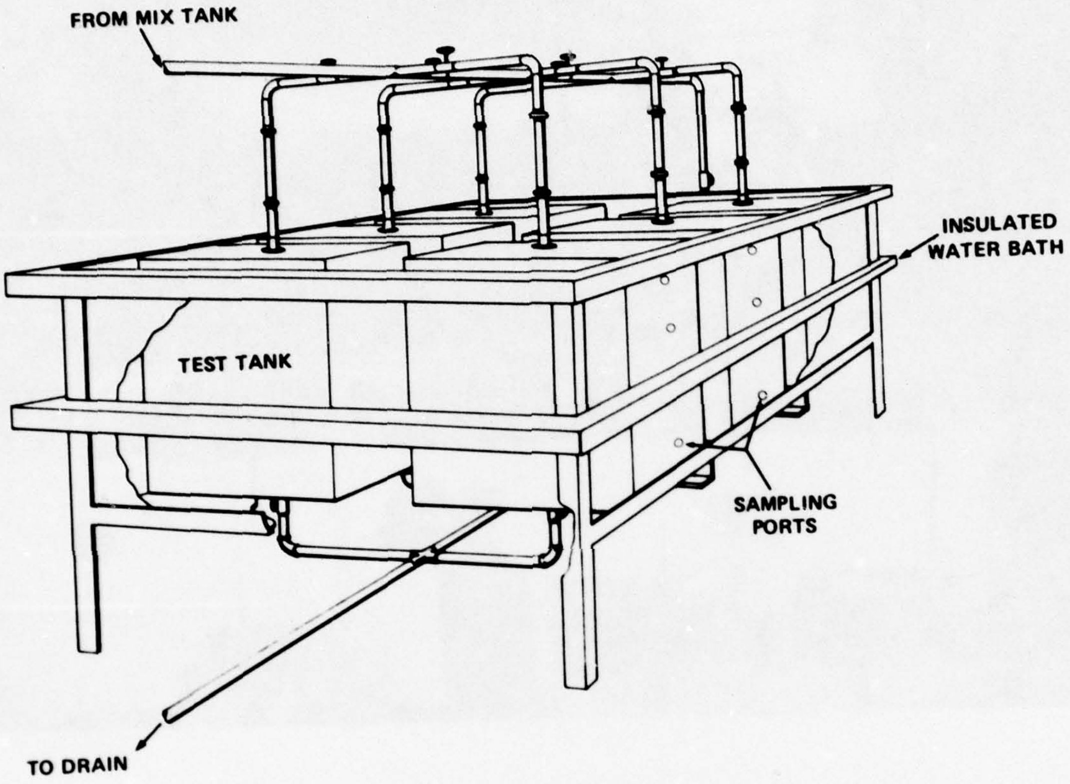


Figure 6
Waste Degradation Studies Experimental Tank Setup

1 - Water Bath
2 - Test Tank
3 - Sampling Ports
4 - Automated Gas Chromatograph
5 - Mix Tank

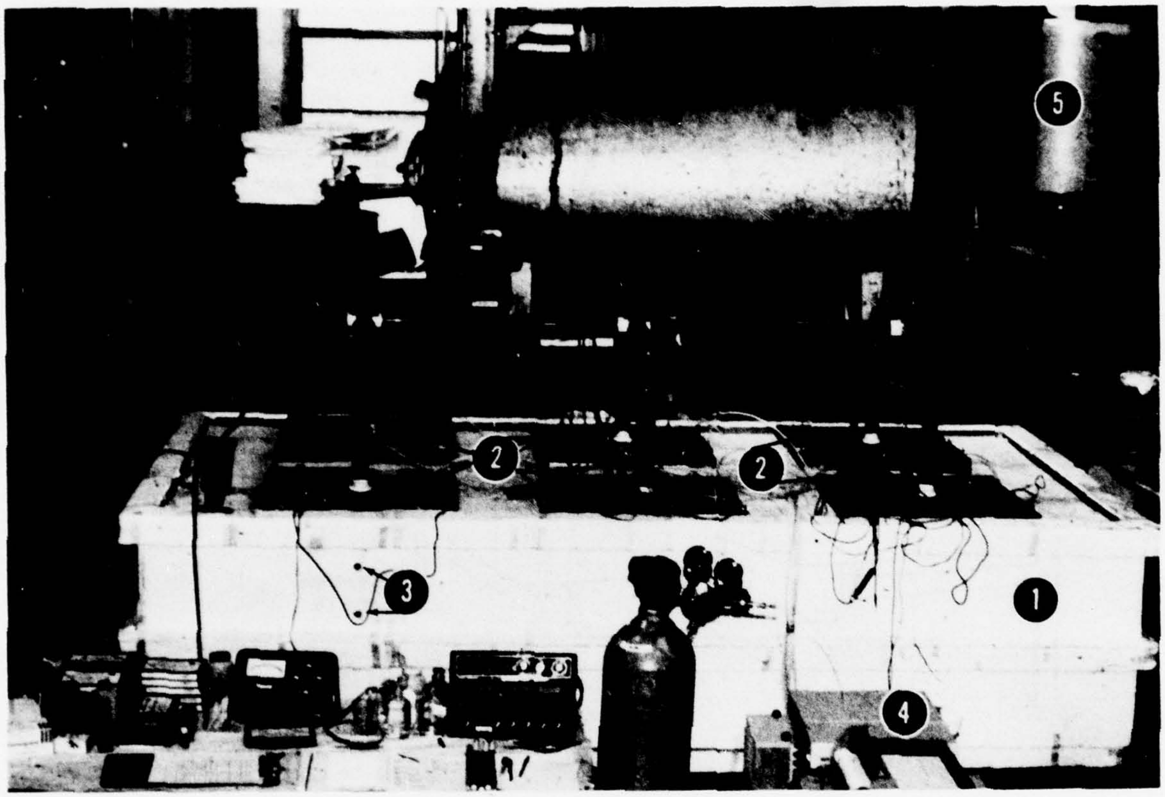


Figure 7
Waste Degradation Studies, Test Tank Assembly

1 - pH, ORP, DO Electrode Leads
2 - Gas Sampling Port
3 - Sampling Lines to Gas Chromatograph

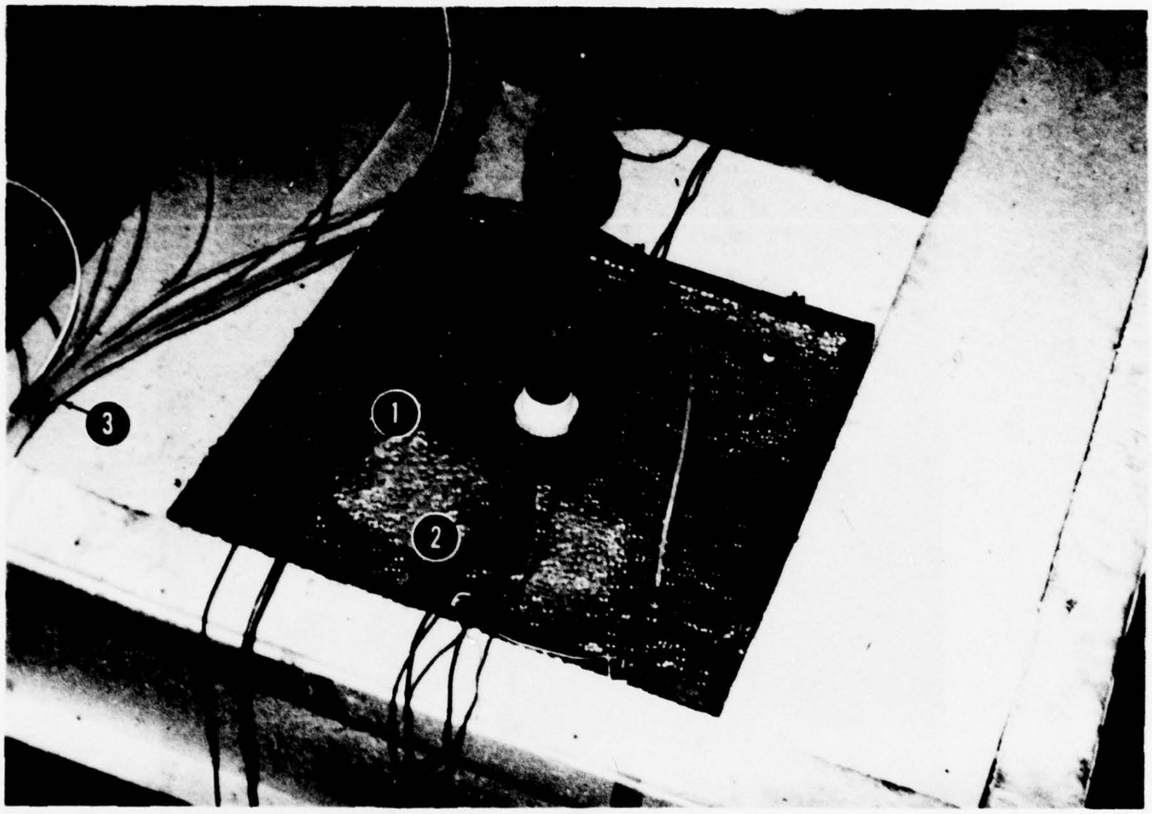


Figure 8
Waste Degradation Studies
Test Tank

1 - Mix Tank
2 - Water Heater/Cooler

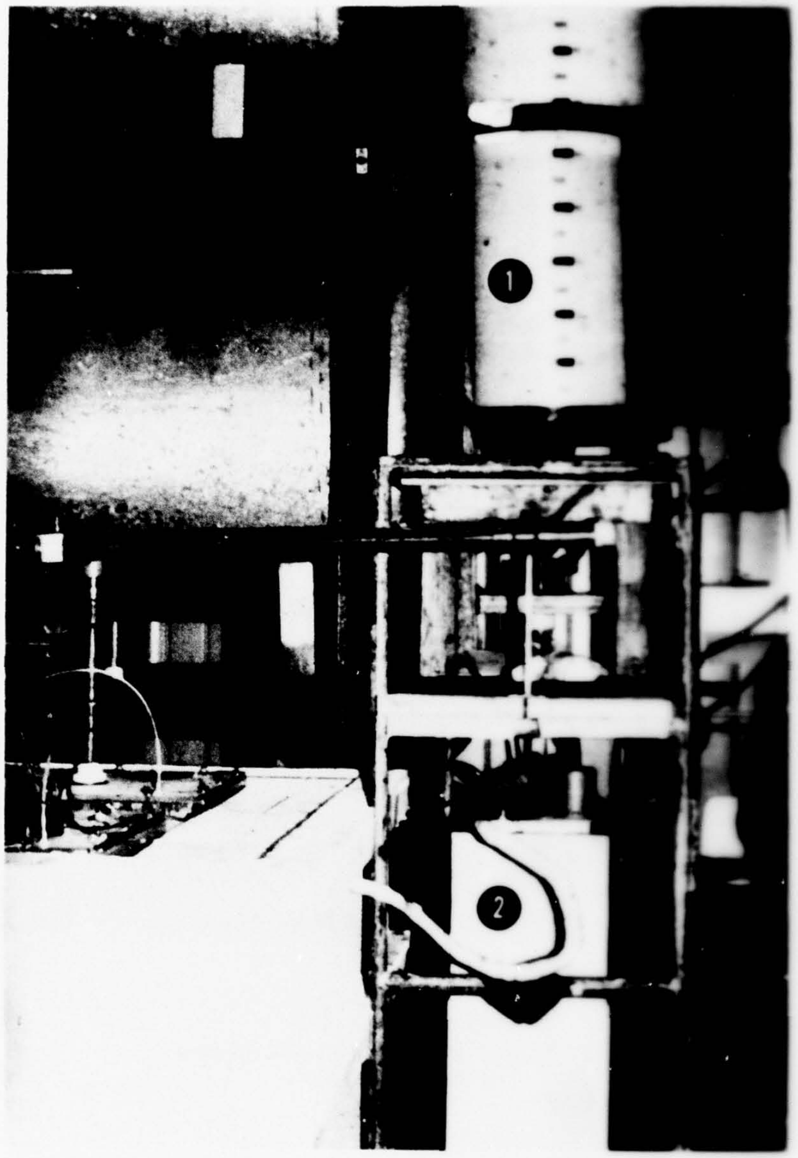


Figure 9
Waste Degradation Studies
Mix Tank and Water Circulator

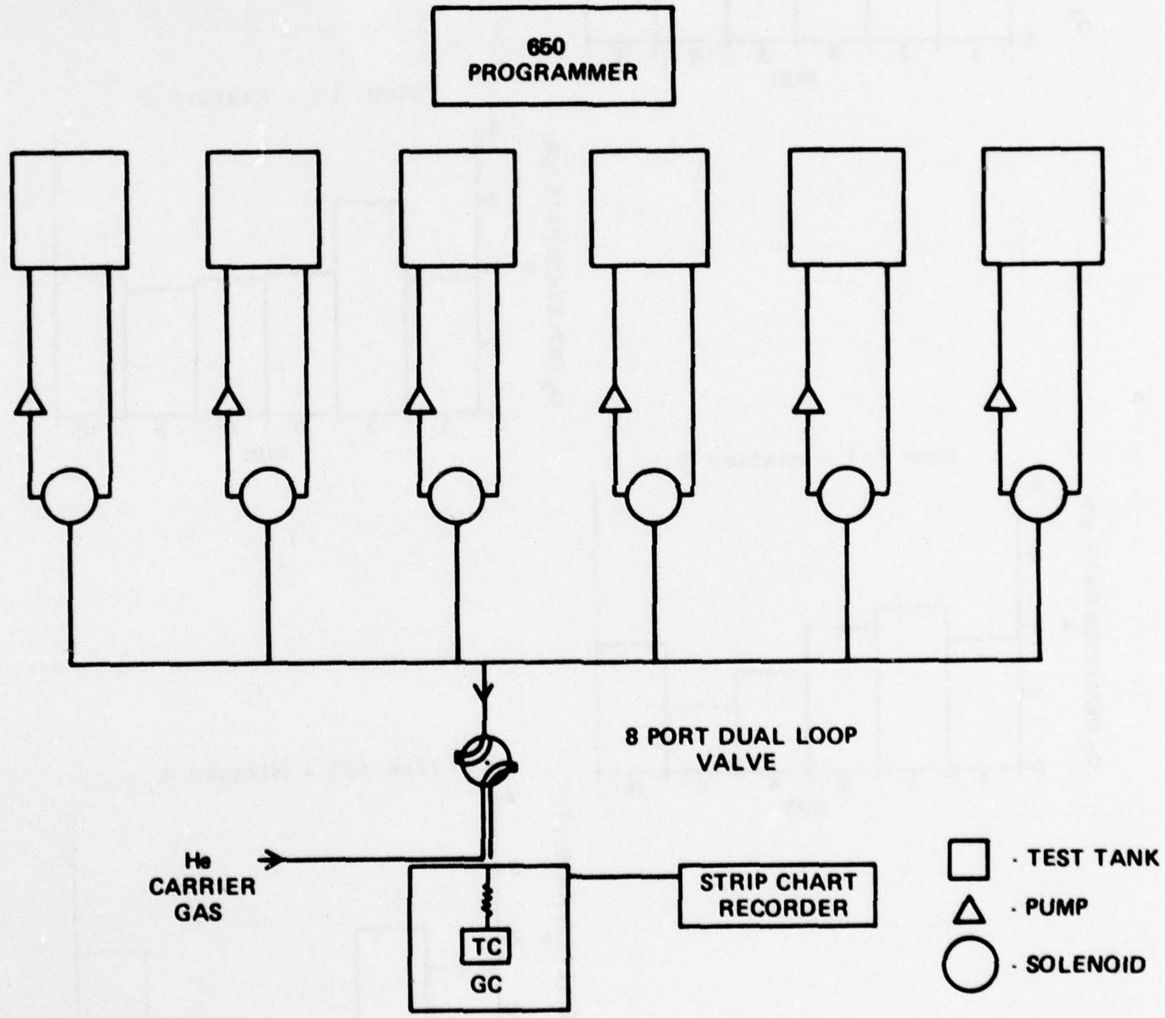
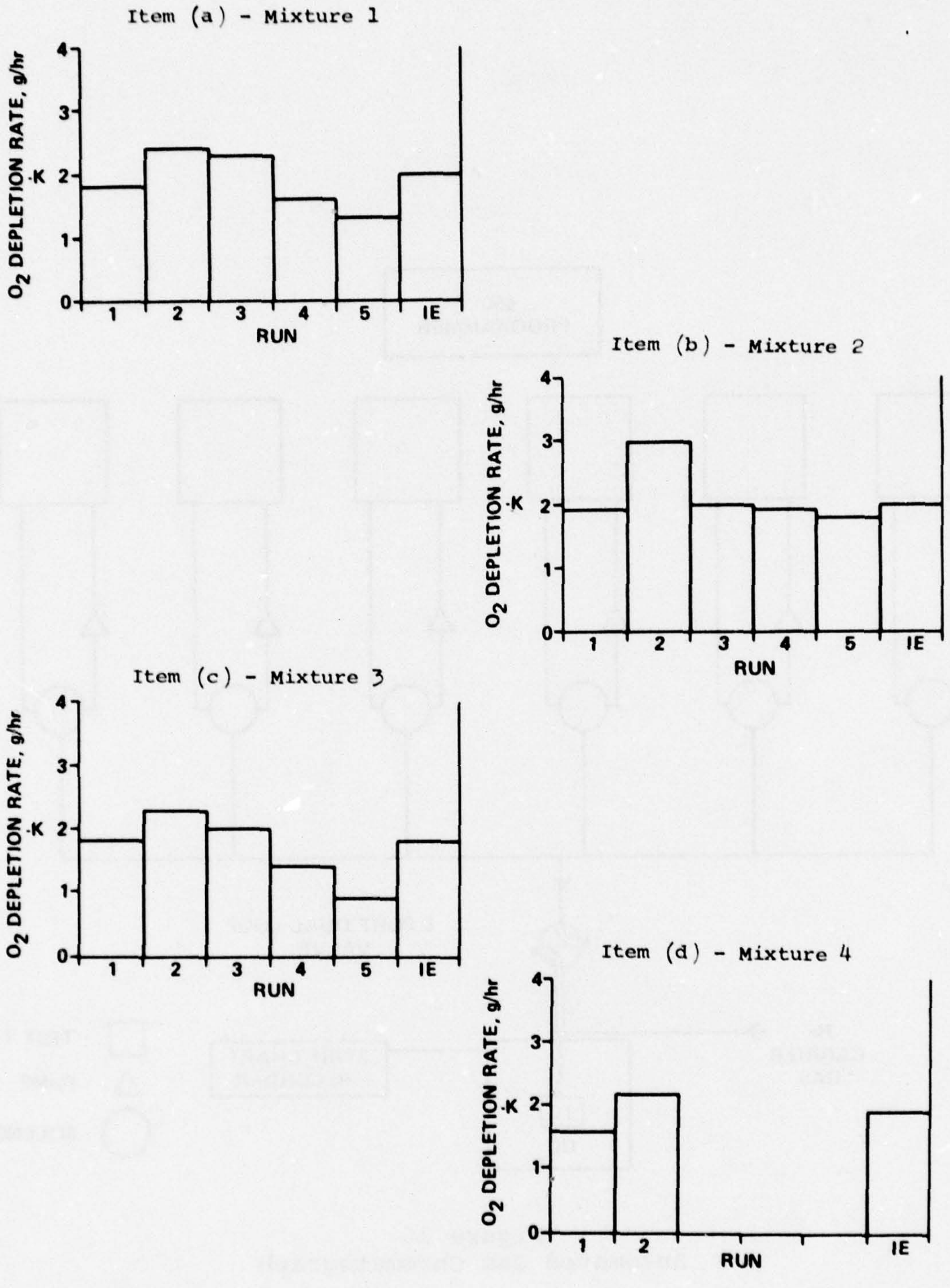


Figure 10
Automated Gas Chromatograph



NOTE: -K = O_2 DEPLETION IN g/hr DERIVED BY LINEAR EXPRESSION y = kx + b.

Figure 11
Freeboard Oxygen Depletion Rates of the Mixtures Under Various Conditions of Temperature, Salinity, and Seeding

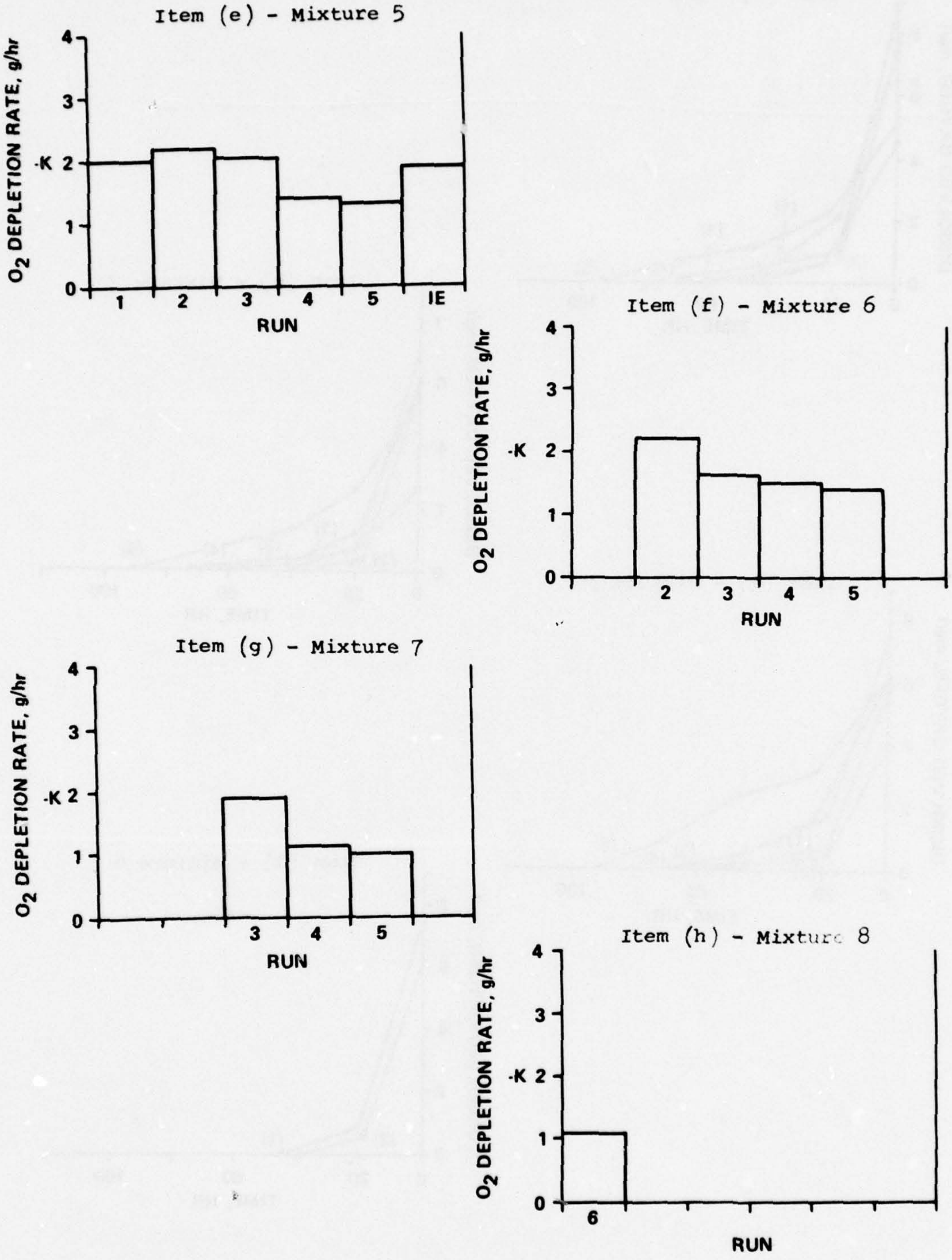


Figure 11 (Cont)

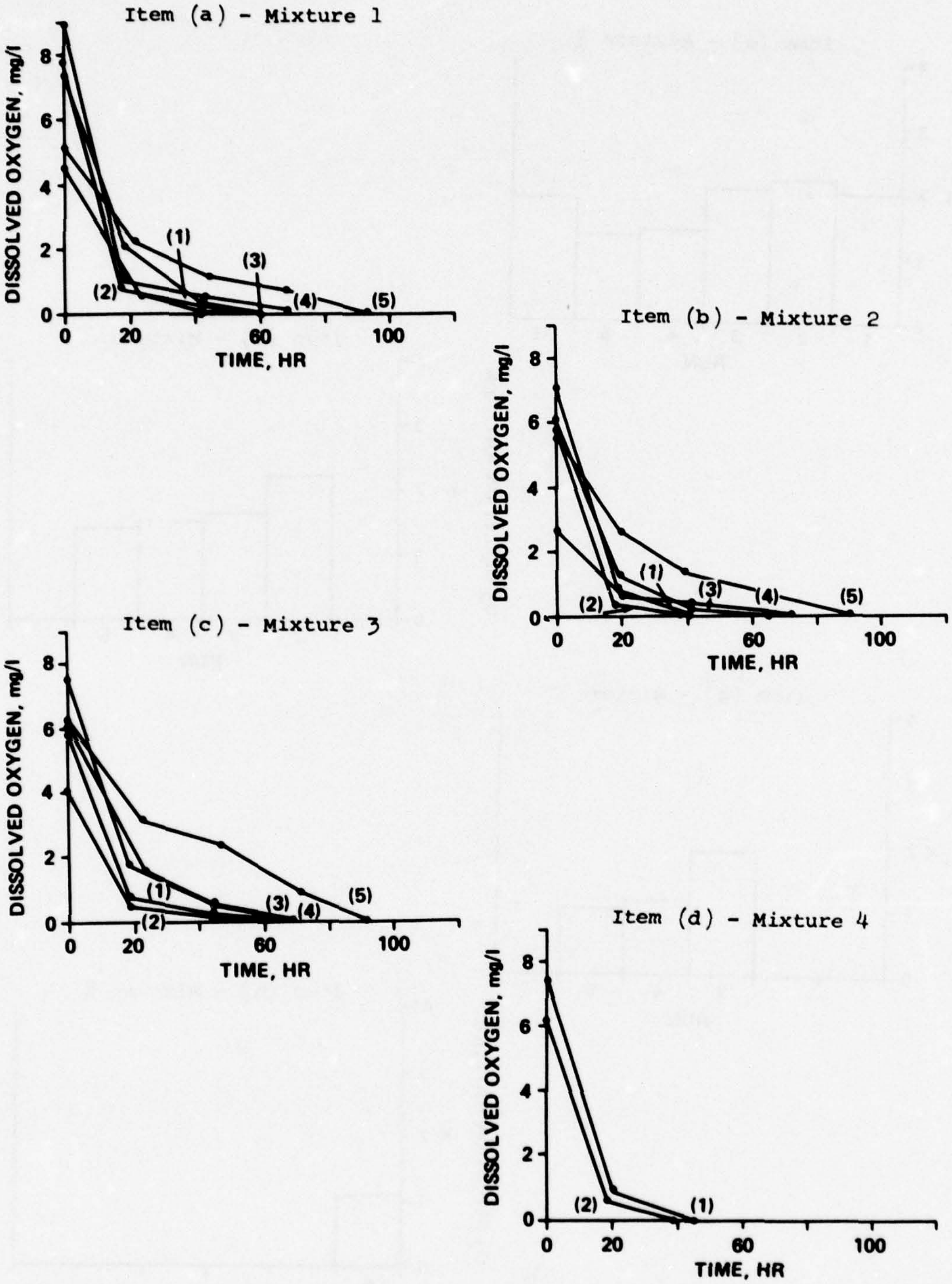
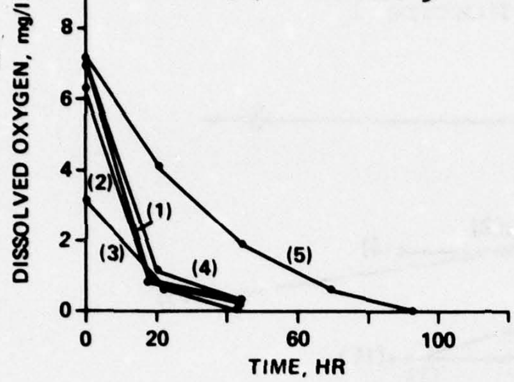
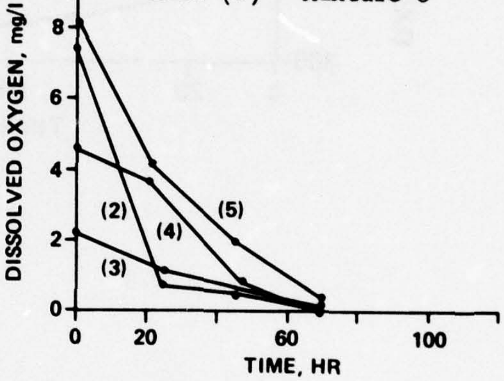


Figure 12
Dissolved Oxygen Depletion with Time for Each Mixture
Under Various Environmental Conditions
(Numbers in Parentheses Indicate Runs)

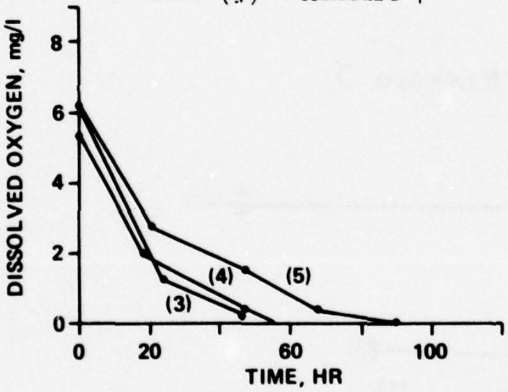
Item (e) - Mixture 5



Item (f) - Mixture 6



Item (g) - Mixture 7



Item (h) - Mixture 8

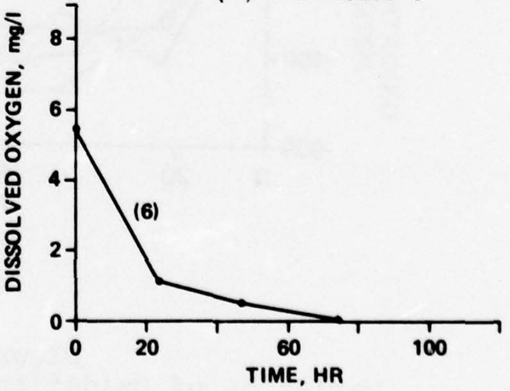
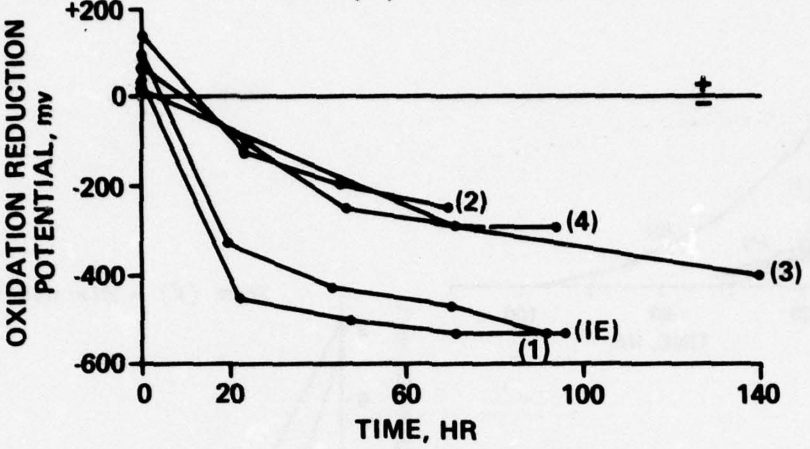


Figure 12 (Cont)

Item (a) - Mixture 1



Item (b) - Mixture 3

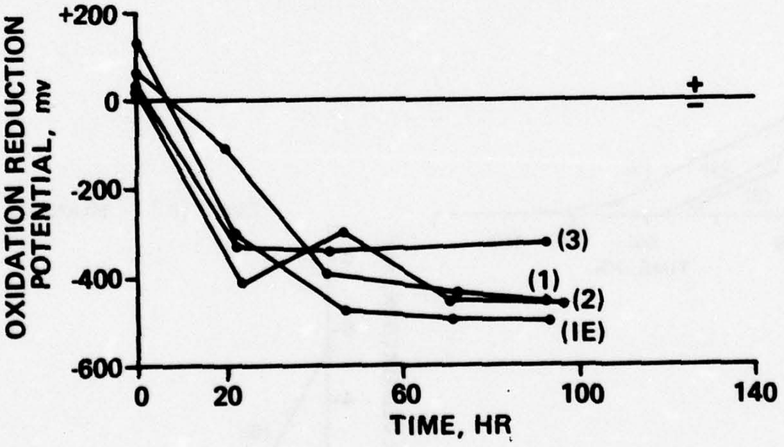
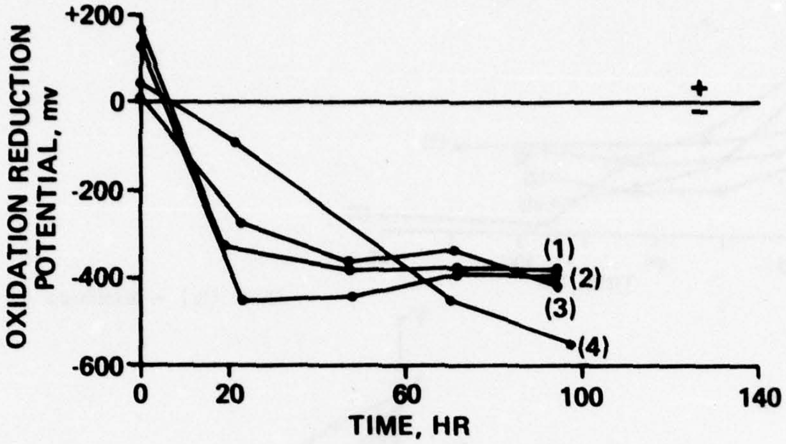


Figure 13
Variation of Oxidation Reduction Potential with Time for Mixtures 1, 3, 5, and 6 Under Various Environmental Conditions
(Numbers in Parentheses Indicate Runs)

Item (c) - Mixture 5



Item (d) - Mixture 6

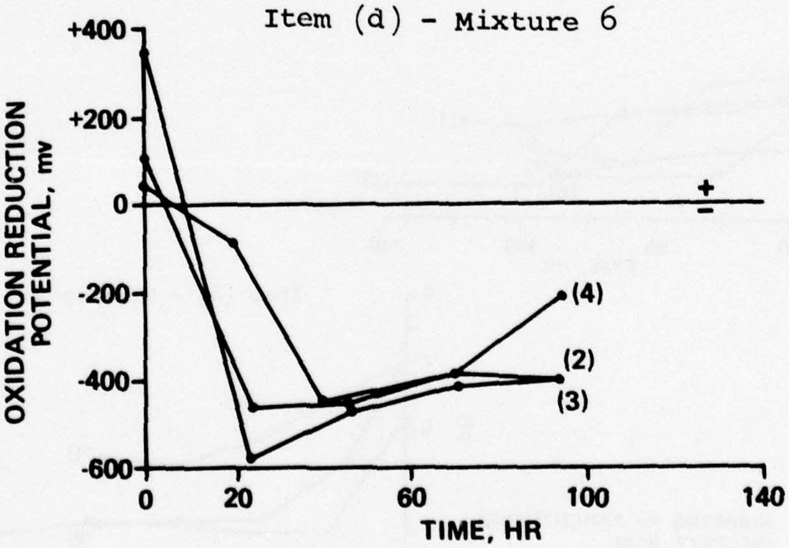
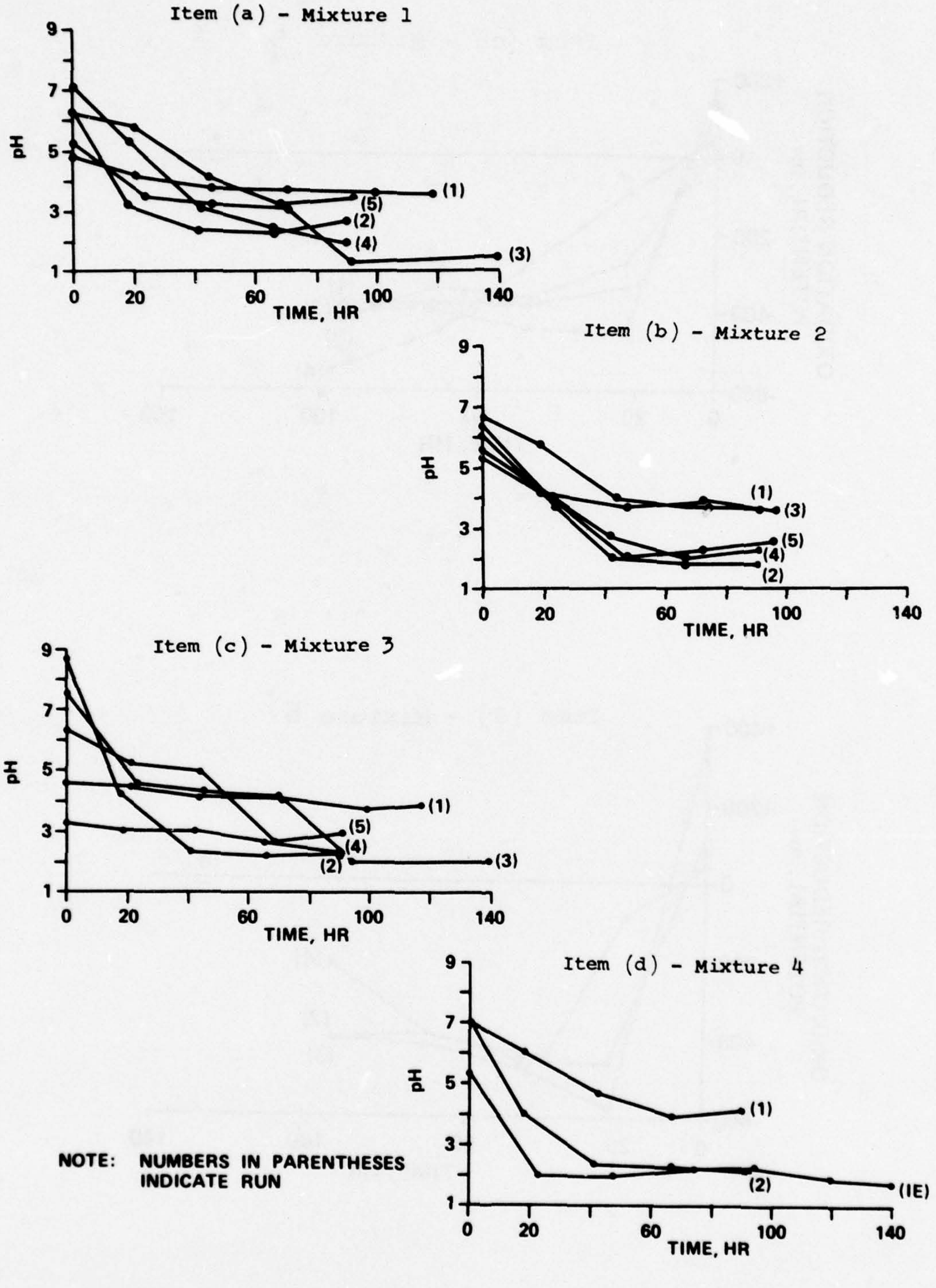


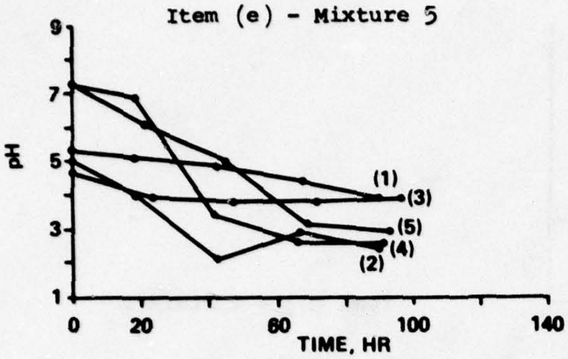
Figure 13 (Cont)



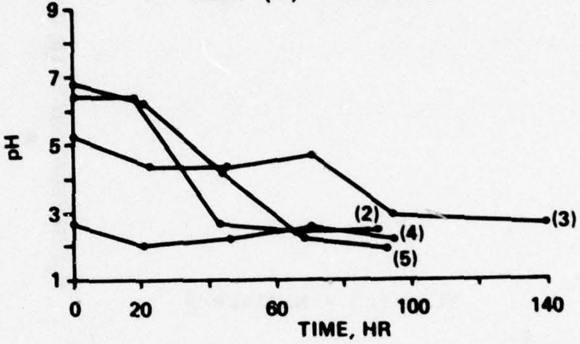
NOTE: NUMBERS IN PARENTHESES INDICATE RUN

Figure 14
Variation of pH with Time for Each Mixture Under Various Environmental Conditions (Numbers in Parentheses Indicate Runs)

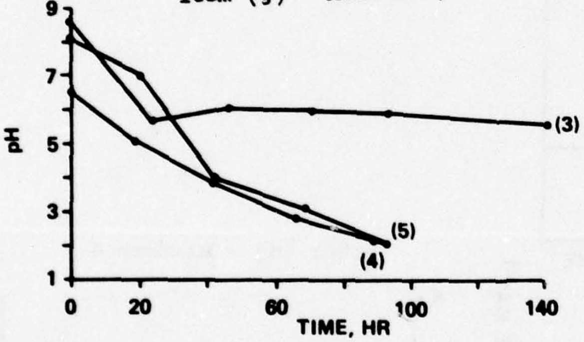
Item (e) - Mixture 5



Item (f) - Mixture 6



Item (g) - Mixture 7



Item (h) - Mixture 8

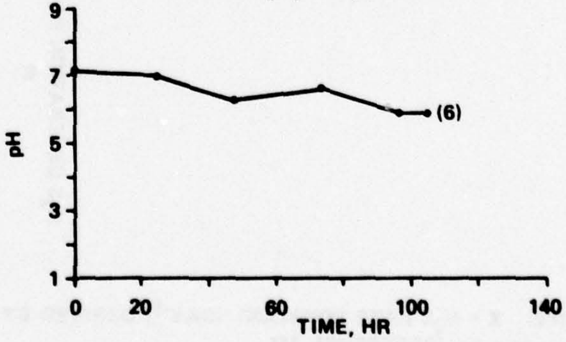
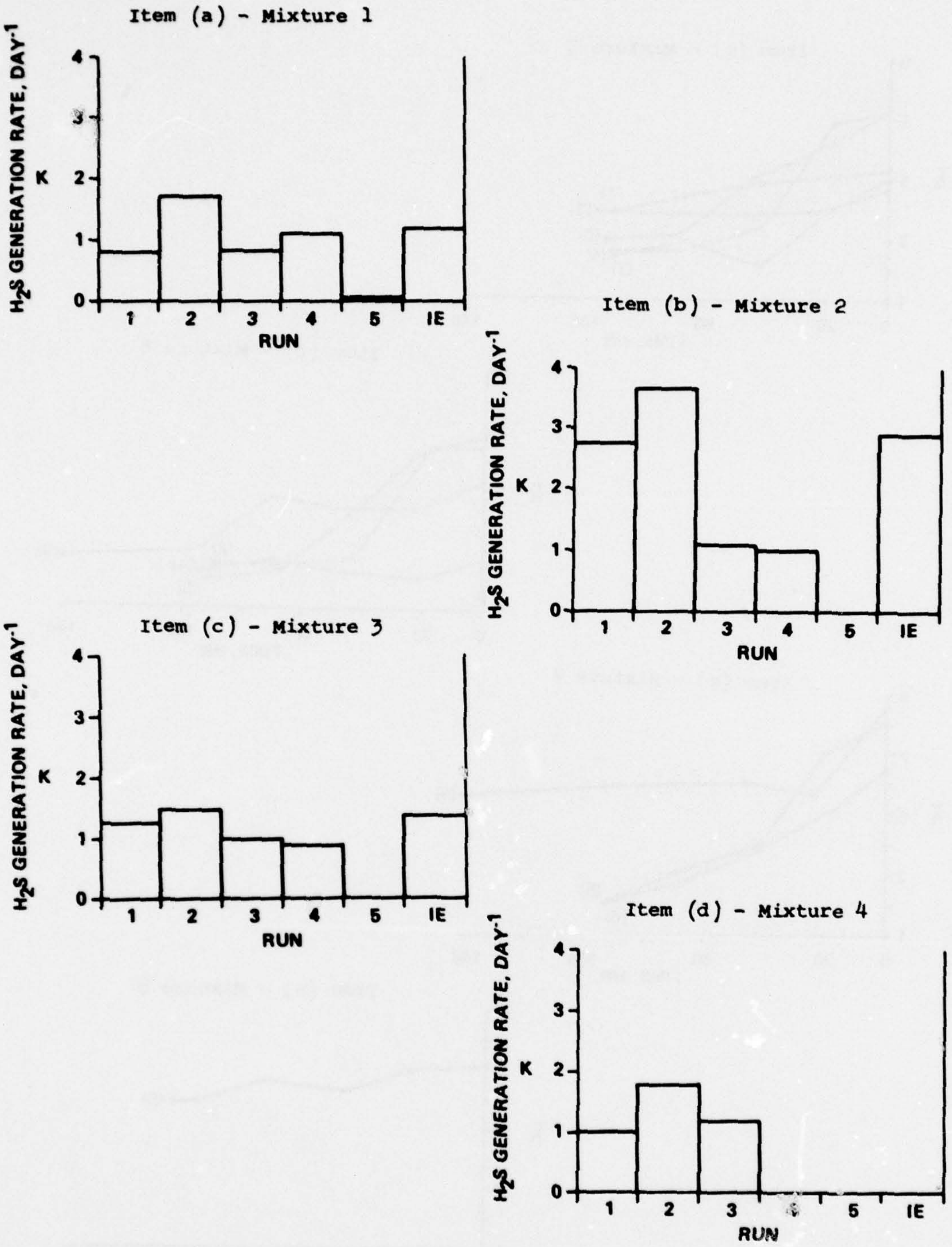


Figure 14 (Cont)



Item (a) - Mixture 1

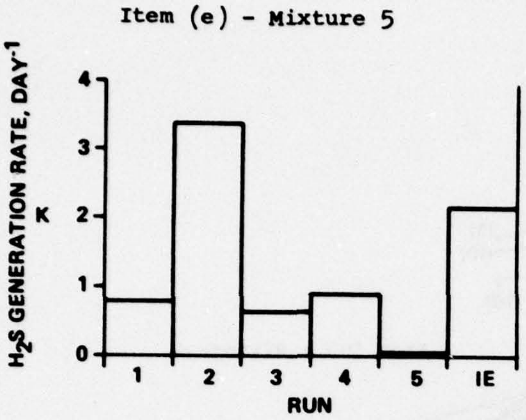
Item (b) - Mixture 2

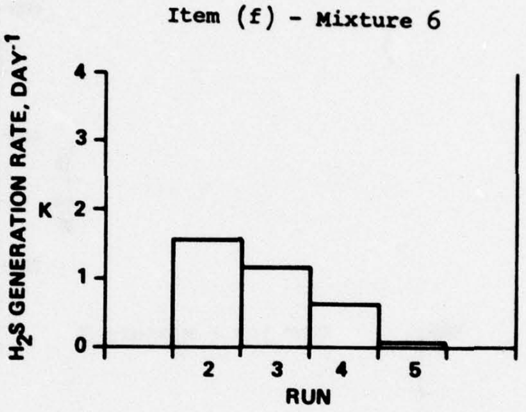
Item (c) - Mixture 3

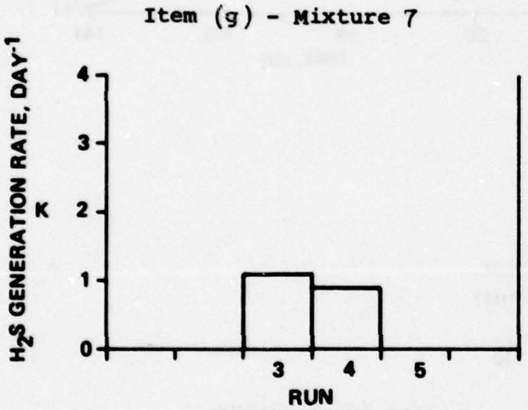
Item (d) - Mixture 4

NOTE: $K = H_2S$ RATE CONSTANT (DAY^{-1}) DERIVED BY LINEAR REGRESSION
$\ln y = kt + \ln c$ (REFERENCE 11)

Figure 15
Comparison of H_2S Rate Constants for Each Mixture
Under Various Environmental Conditions


Item (e) - Mixture 5


Item (f) - Mixture 6


Item (g) - Mixture 7

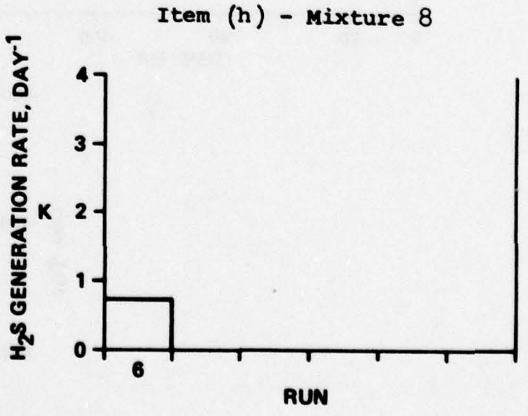

Item (h) - Mixture 8

Figure 15 (Cont)

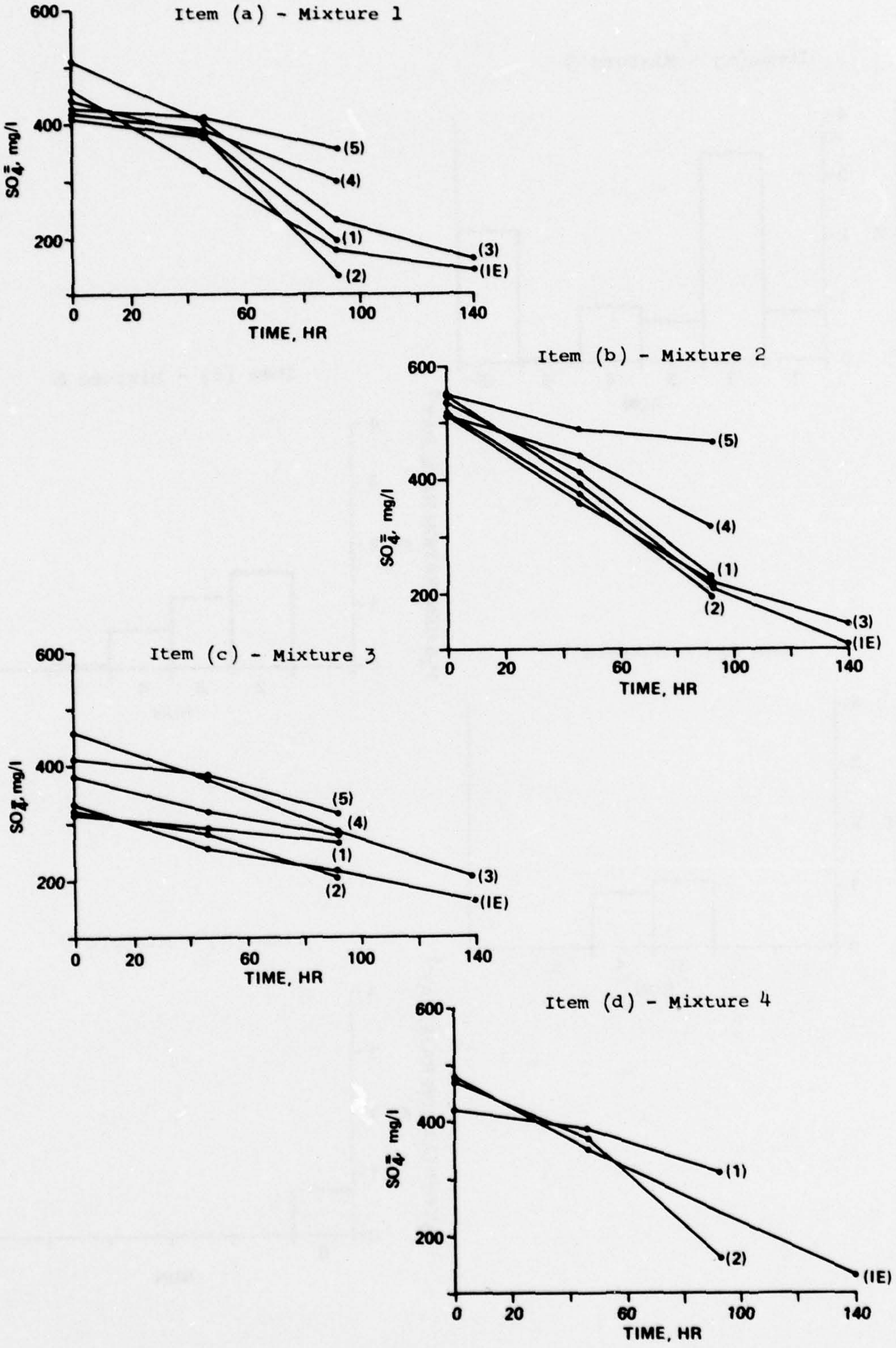


Figure 16
Variation of SO$_4^=$ with Time for Each Mixture
(Numbers in Parentheses Indicate Runs)

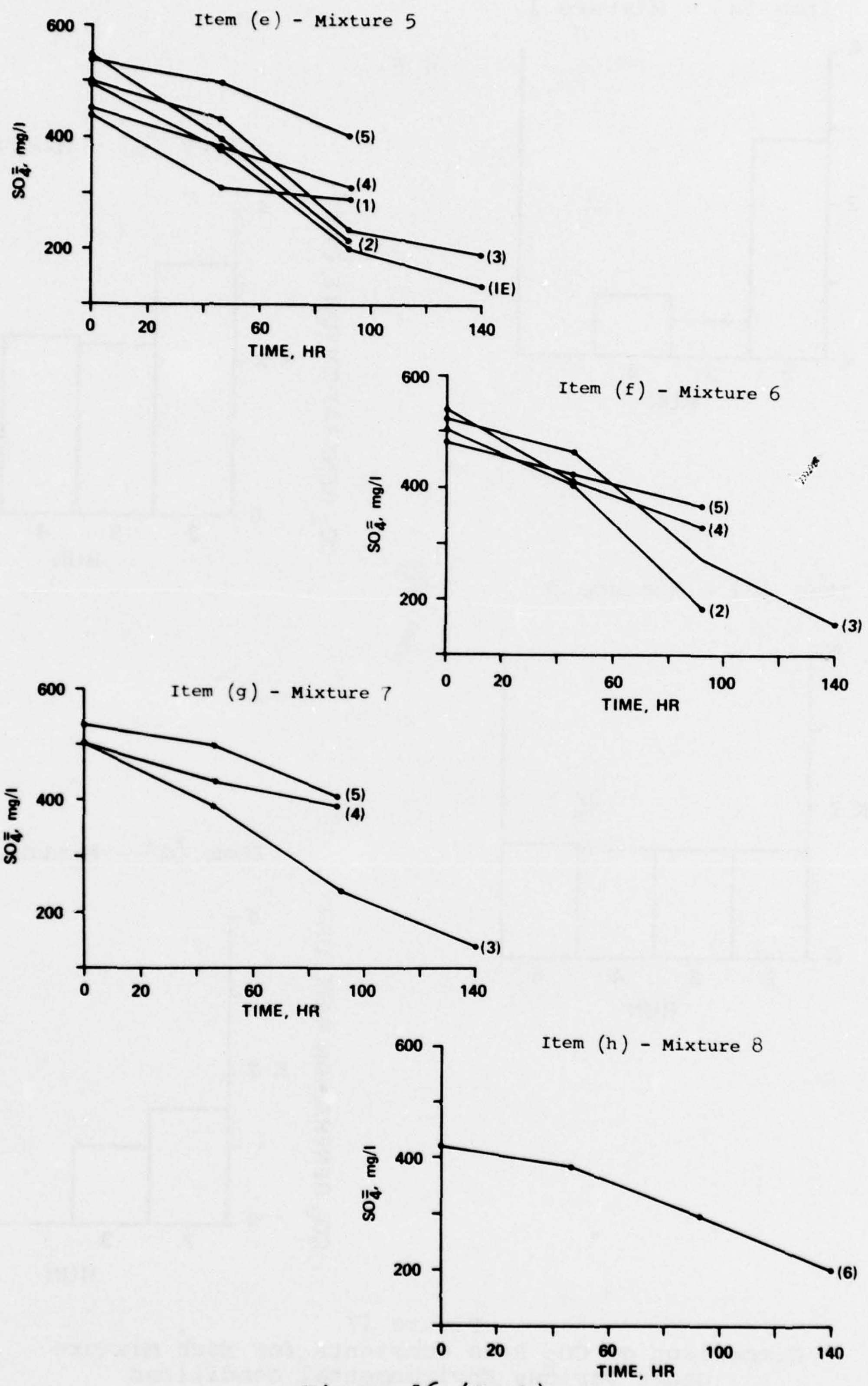


Figure 16 (Cont)

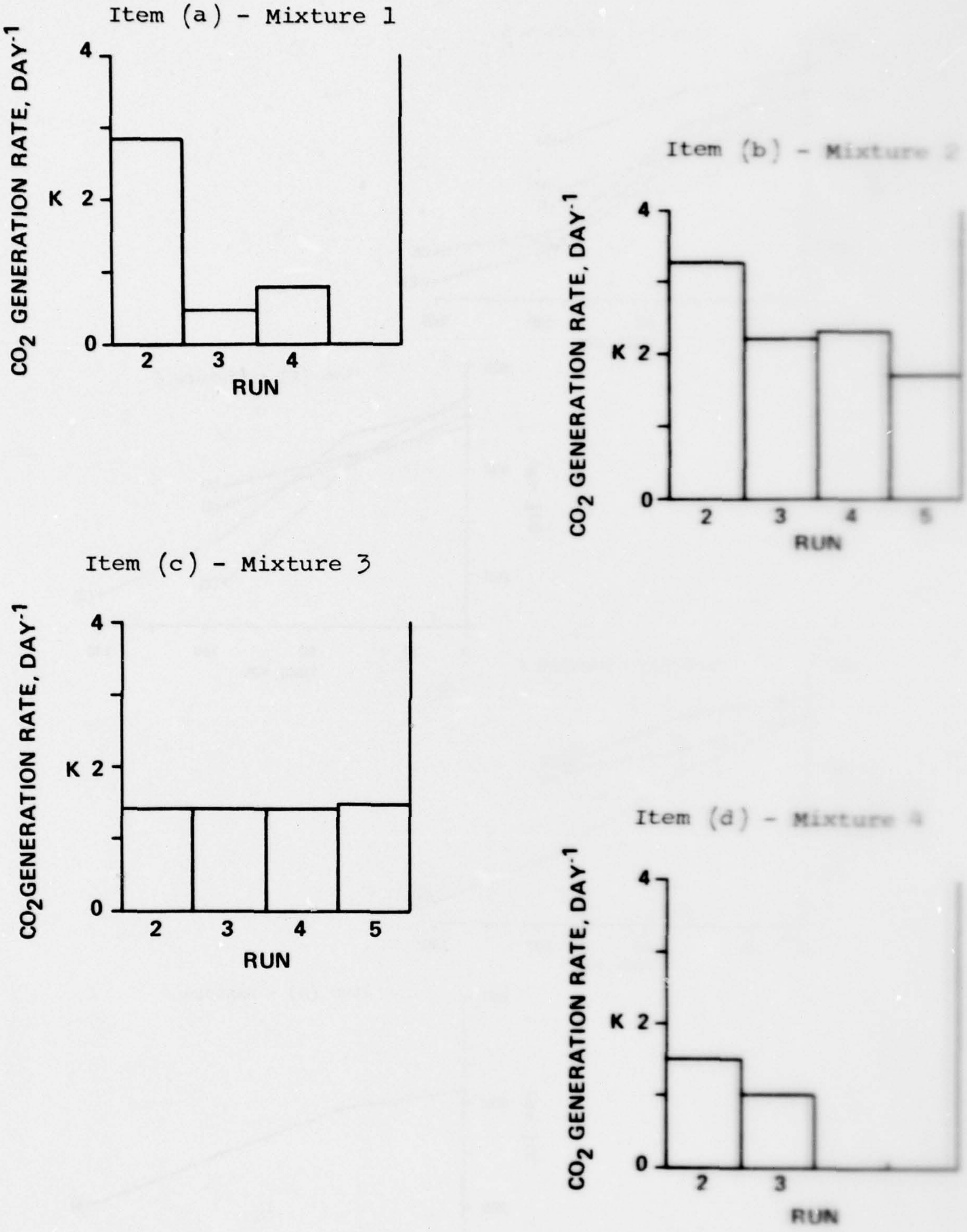
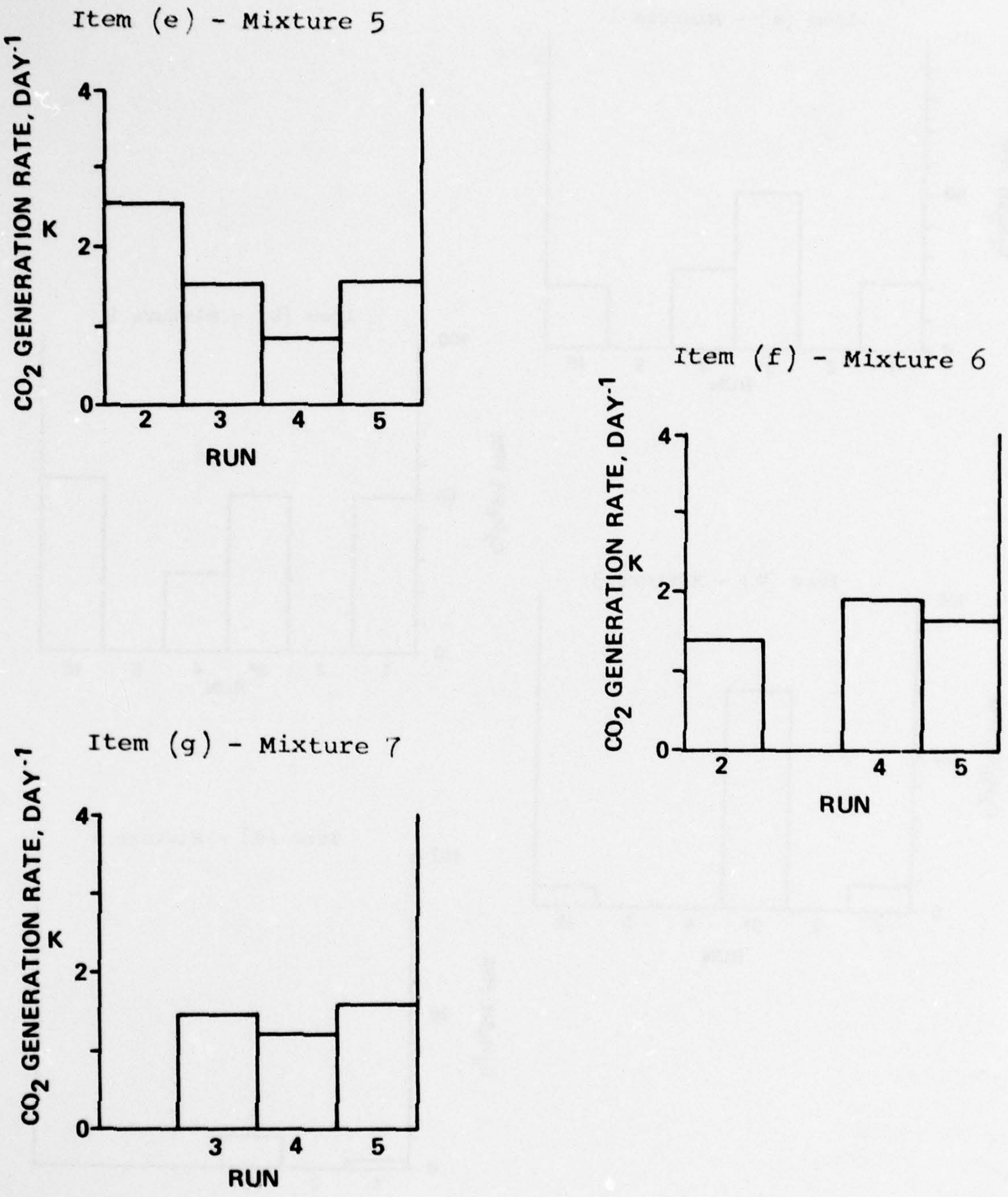
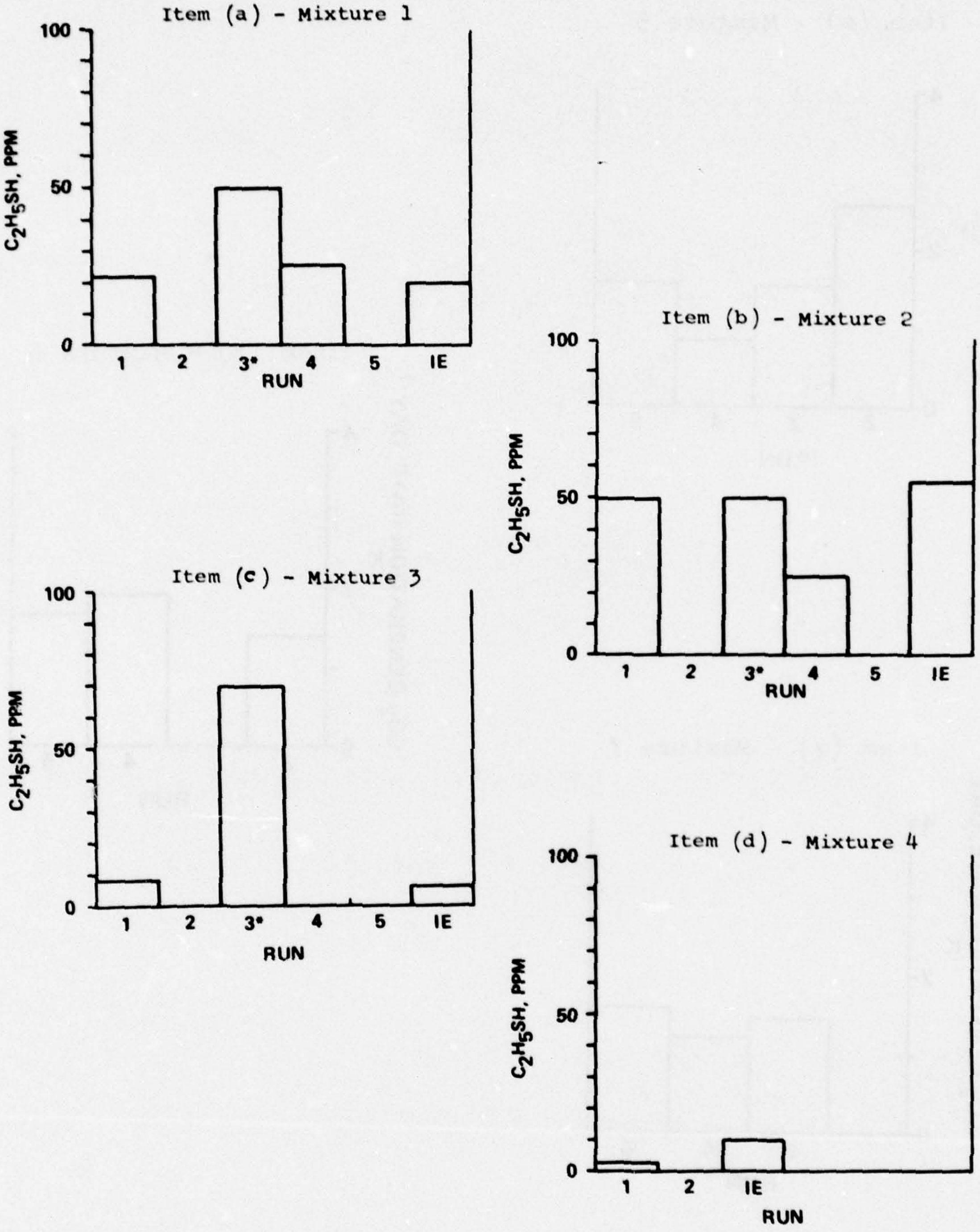


Figure 17
Comparison of CO_2 Rate Constants for Each Mixture
Under Various Environmental Conditions



NOTE: K = CO_2 RATE CONSTANT (DAY^{-1}) DERIVED BY LINEAR EXPRESSION $\ln y = k_t + \ln c$ (REFERENCE 11).

Figure 17 (Cont)



*RUN 3 SHOWS CONCENTRATION AFTER 142 HOURS OF INCUBATION. AFTER 92 HOURS, CONCENTRATION WAS 0.

Figure 18
Comparison of Ethyl Mercaptan Concentrations After 92 Hours of Incubation

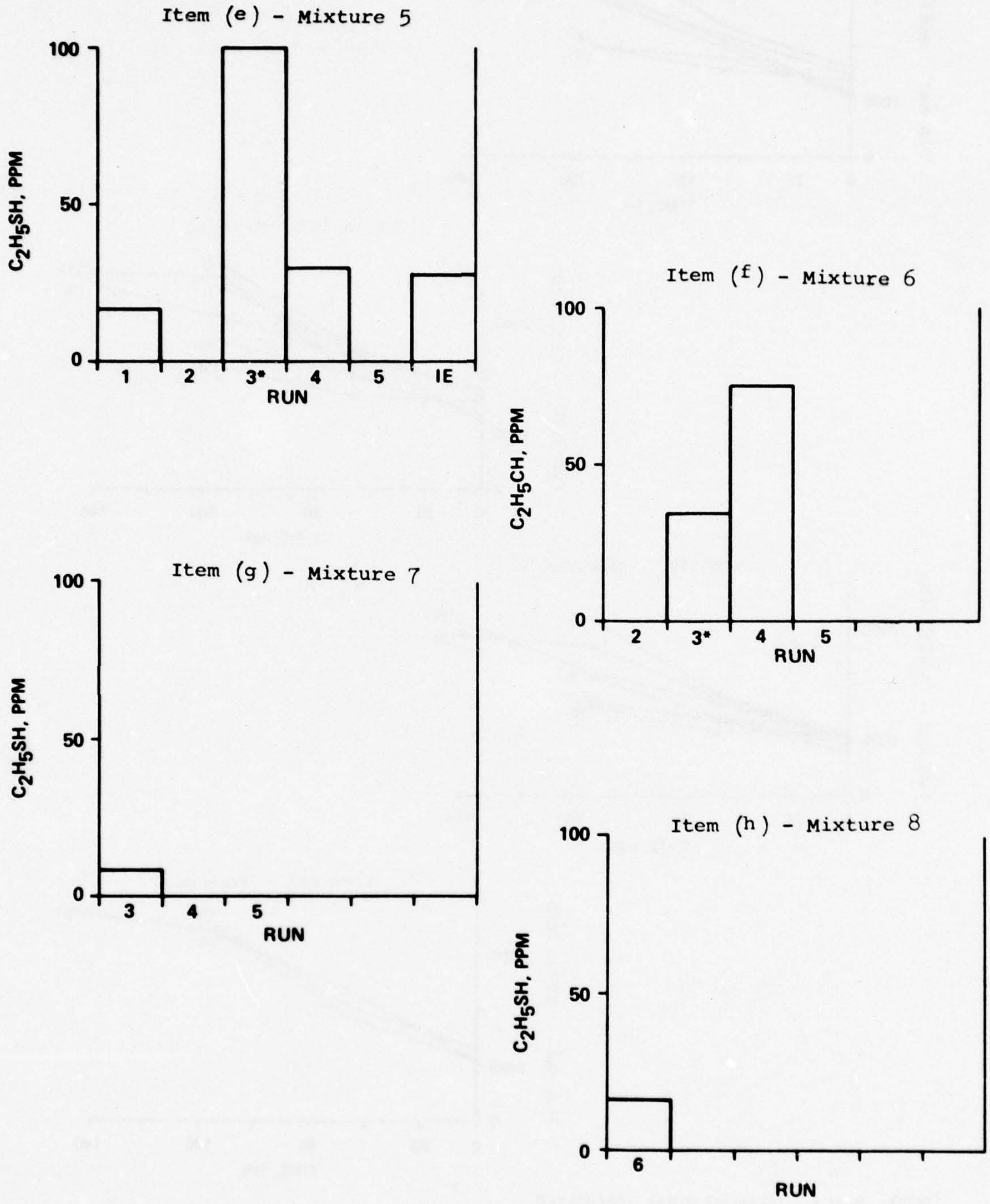
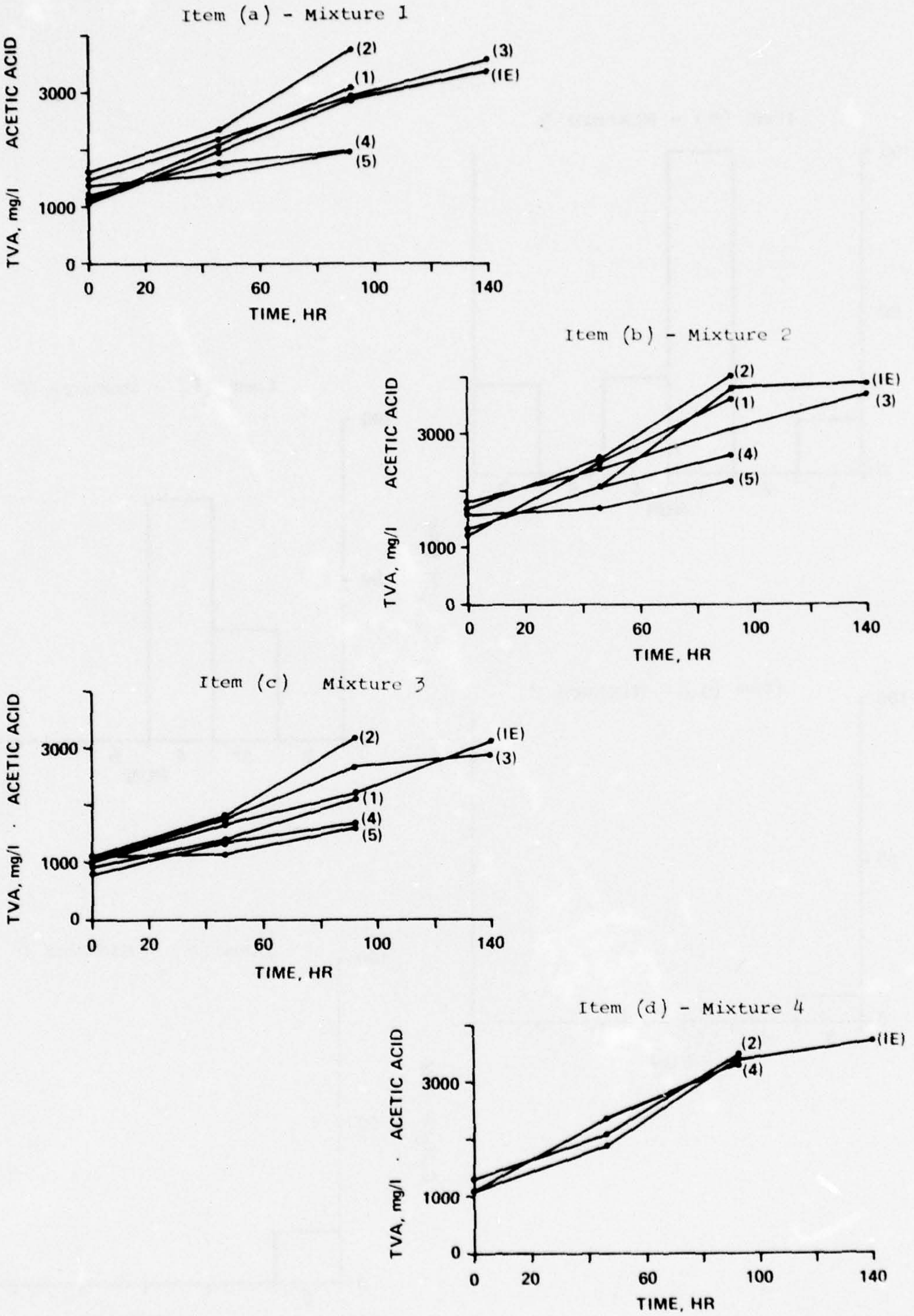
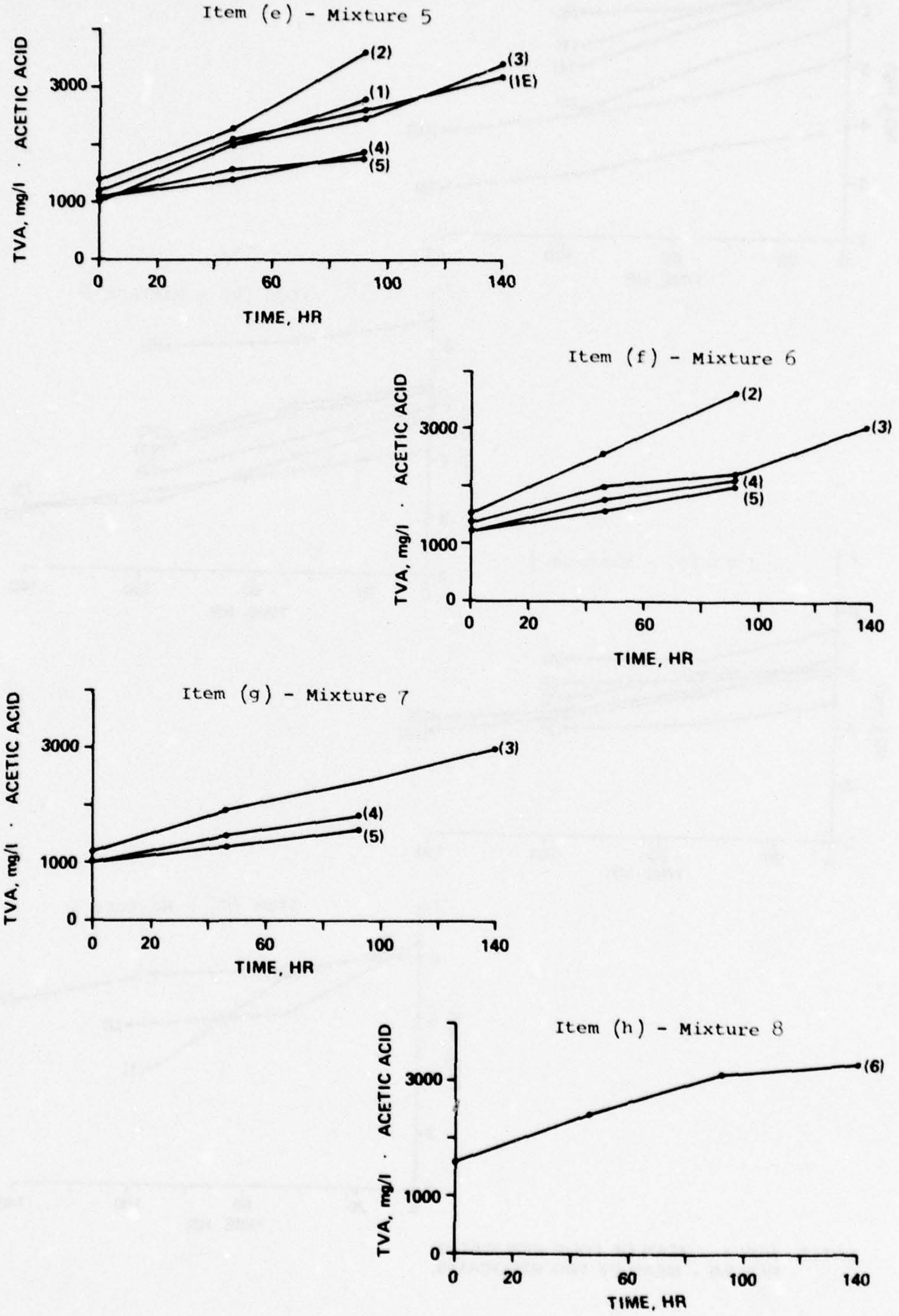


Figure 18 (Cont)



NOTE: RUN 1 – MEAN OF FOUR REPLICATES.
RUN 2-6 – MEAN OF TWO REPLICATES.

Figure 19
Variation of TVA Concentration with Time for Each Mixture
(Numbers in Parentheses Indicate Runs)

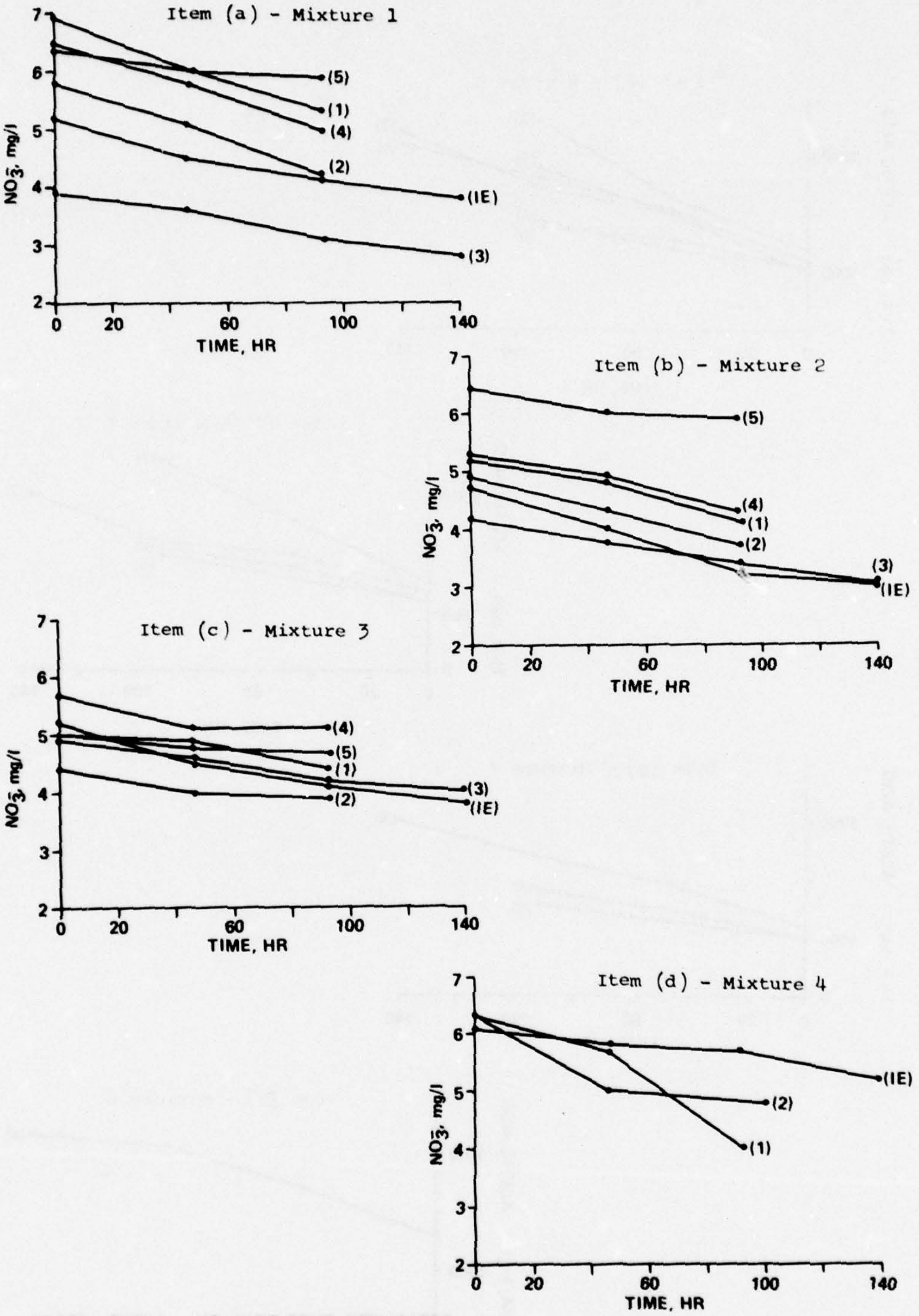

Item (e) - Mixture 5

Item (f) - Mixture 6

Item (g) - Mixture 7

Item (h) - Mixture 8

Figure 19 (Cont)



NOTES: RUN 1 – MEAN OF FOUR REPLICATES.
RUN 2-6 – MEAN OF TWO REPLICATES.

Figure 20
Variation of NO$_3^-$ Concentration with Time for Each Mixture
(Numbers in Parentheses Indicate Runs)

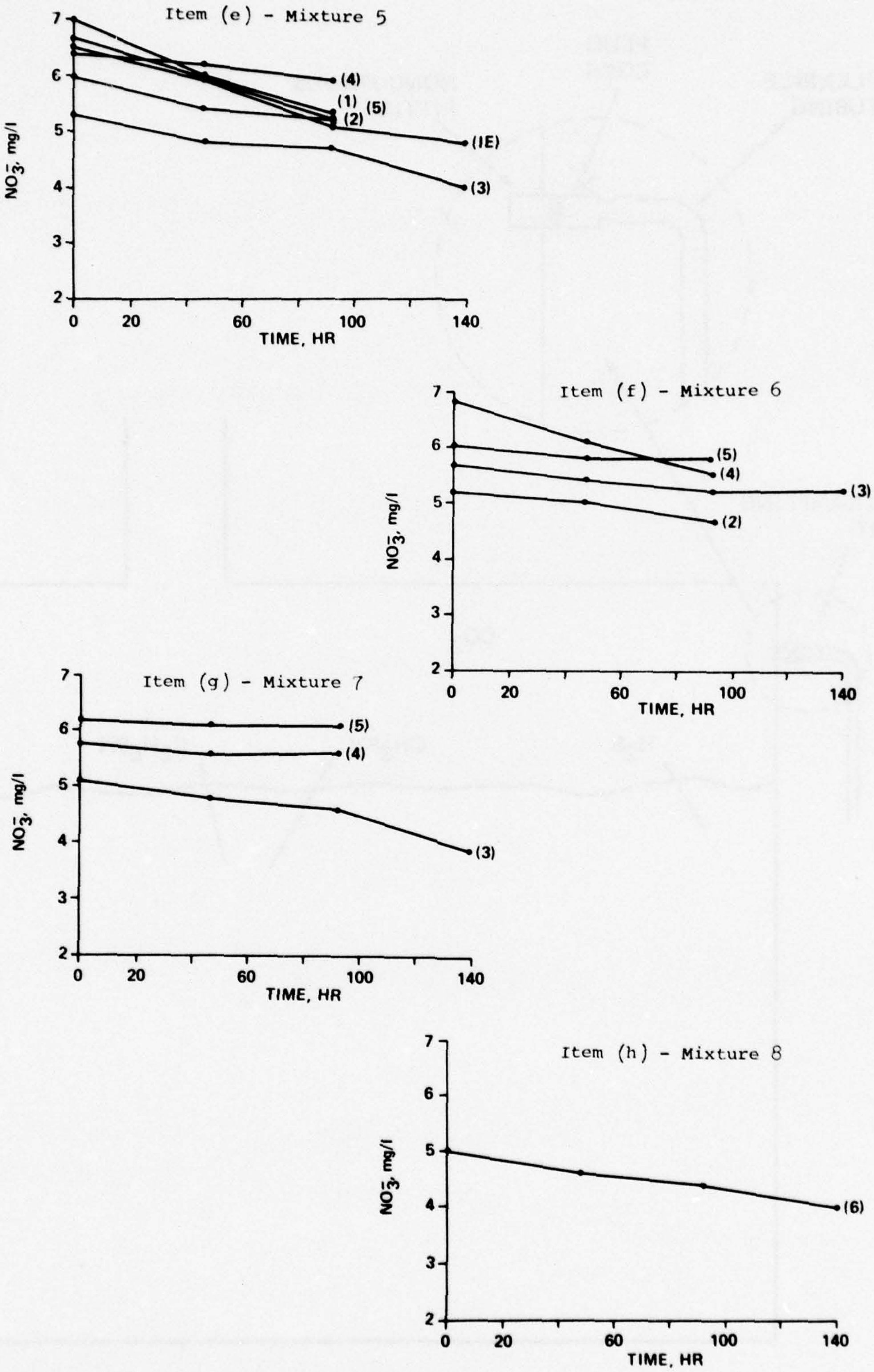


Figure 20 (Cont)

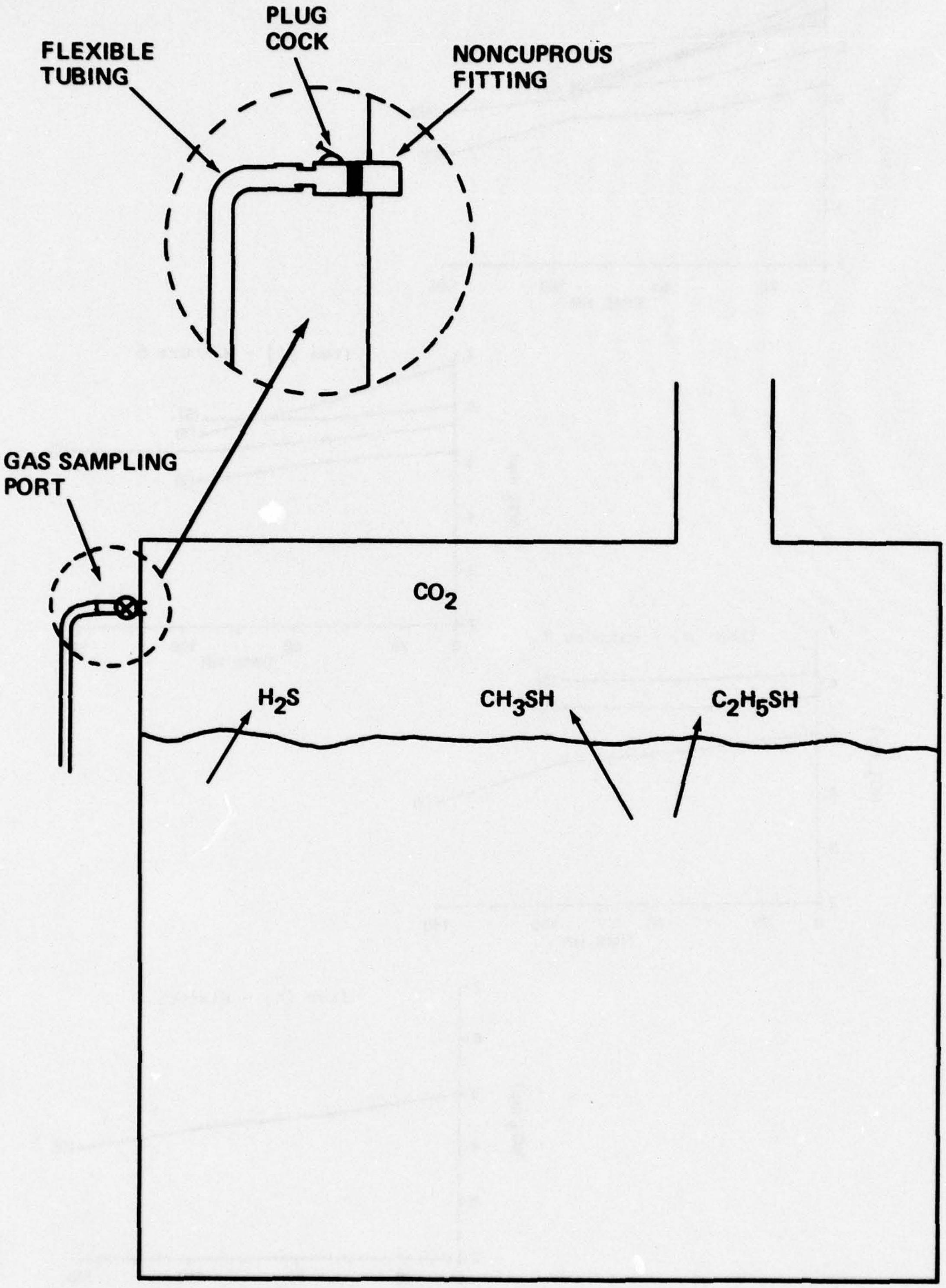


Figure 21
Gas Sampling Port

APPENDIX A
CHT GAS-GENERATION COMPUTER PROGRAM USER'S GUIDE

I. <u>PROGRAM DESCRIPTION</u>

Program Name: GASGEN

<u>Description</u>: This program uses a mathematical model to predict gas concentrations in the gas phase above the liquid in Navy CHT tanks. Predictions are made for carbon dioxide and hydrogen sulfide. Gas concentrations are given in parts per million for 0 to 10 days at 1-day intervals for tank temperatures of 25°, 35°, and 45° C and for both 30% and 60% of total tank capacity.

GASGEN is very flexible and can be used to predict gas concentrations in <u>any</u> CHT tank. The program has on file, tank volumes and influent characteristics for several ship classes and tanks. If the desired ship or tank is not on file, the program allows the user to input the necessary data manually.

II. <u>USING THE PROGRAM</u>

The program is stored in the PDP11 digital computer located at DTNSRDC, Building 182-1-F. After hookup to the computer, the lastoutput printed by the teletype will be:

```
.
RT - 11SJ         V02C - 02B
Date              Day-Month-Year
.
```

To run the program, follow this procedure:

1. After the period, type in R FORTRA and hit RETURN.

2. The computer will type A *. After it does, type in: GASGEN = GASGEN, hit return, and wait for the computer to come back with another *.

3. Now you are ready to "link" the program to the computer.

4. After the . simultaneously press CTRL and C. The computer will respond with *┌┐[* .

5. After the period, type in R Link, hit RETURN, and wait until the computer types another * before your next input. Now type GASGEN = GASGEN, SYSLIB/F and hit RETURN. The response to this will be another *.

6. After the *, again type CTRL and C. The computer will respond with a period.

7. Now we are ready to run the program. Type after the . , R GASGEN and hit RETURN. The program takes it from there.

III. VARIABLE LIST

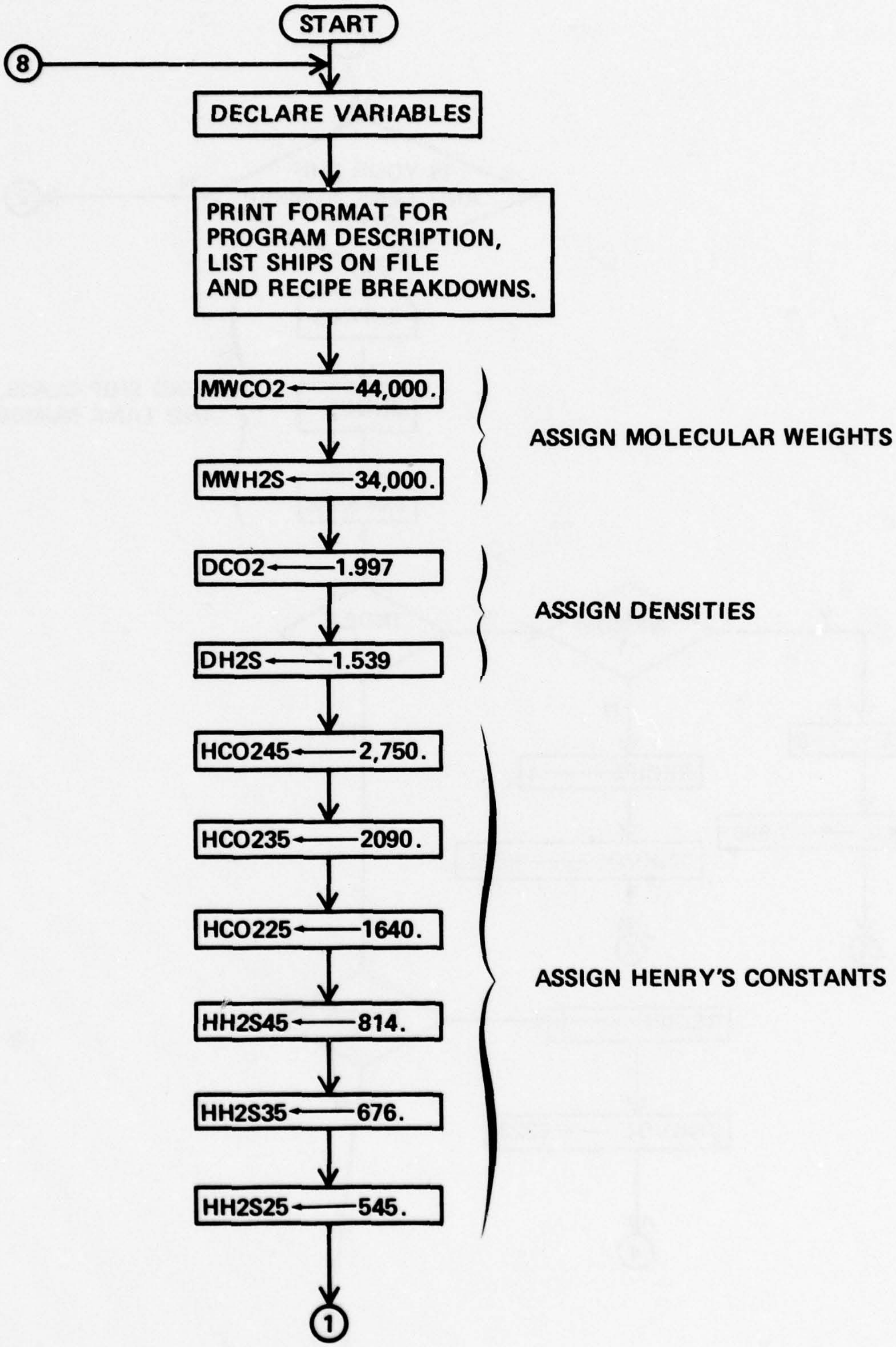
Variable Name	Type	Description	Value (If Constant)
MWC02	Real	Molecular weight of carbon dioxide	44,000
MWH2S	Real	Molecular weight of hydrogen sulfide	34,000
DC02	Real	Density of carbon dioxide at 0° C	1.977
DH25	Real	Density of hydrogen sulfide at 0° C	1.539
HC0245	Real	Henry's constant for carbon dioxide at 45° C	2,570
HC0235	Real	Henry's constant for carbon dioxide at 35° C	2,090
HC0225	Real	Henry's constant for carbon dioxide at 25° C	1,640
HH2S45	Real	Henry's constant for hydrogen sulfide at 45° C	814
HH2S35	Real	Henry's constant for hydrogen sulfide at 35° C	676
HH2S25	Real	Henry's constant for hydrogen sulfide at 25° C	545
KC0245	Real	Gas-generation rate constant for carbon dioxide at 45° C	
KC0235	Real	Gas-generation rate constant for carbon dioxide at 35° C	
KC0225	Real	Gas-generation rate constant for carbon dioxide at 25° C	
KH2S45	Real	Gas-generation rate constant for hydrogen sulfide at 45° C	
KH2S35	Real	Gas-generation rate constant for hydrogen sulfide at 35° C	
KH2S25	Real	Gas-generation rate constant for hydrogen sulfide at 25° C	
K45	Real	Gas-generation rate constant at 45° C used in the prediction equation and depends on the gas in question	
K35	Real	Gas-generation rate constant at 35° C used in the prediction equation and depends on the gas in question	

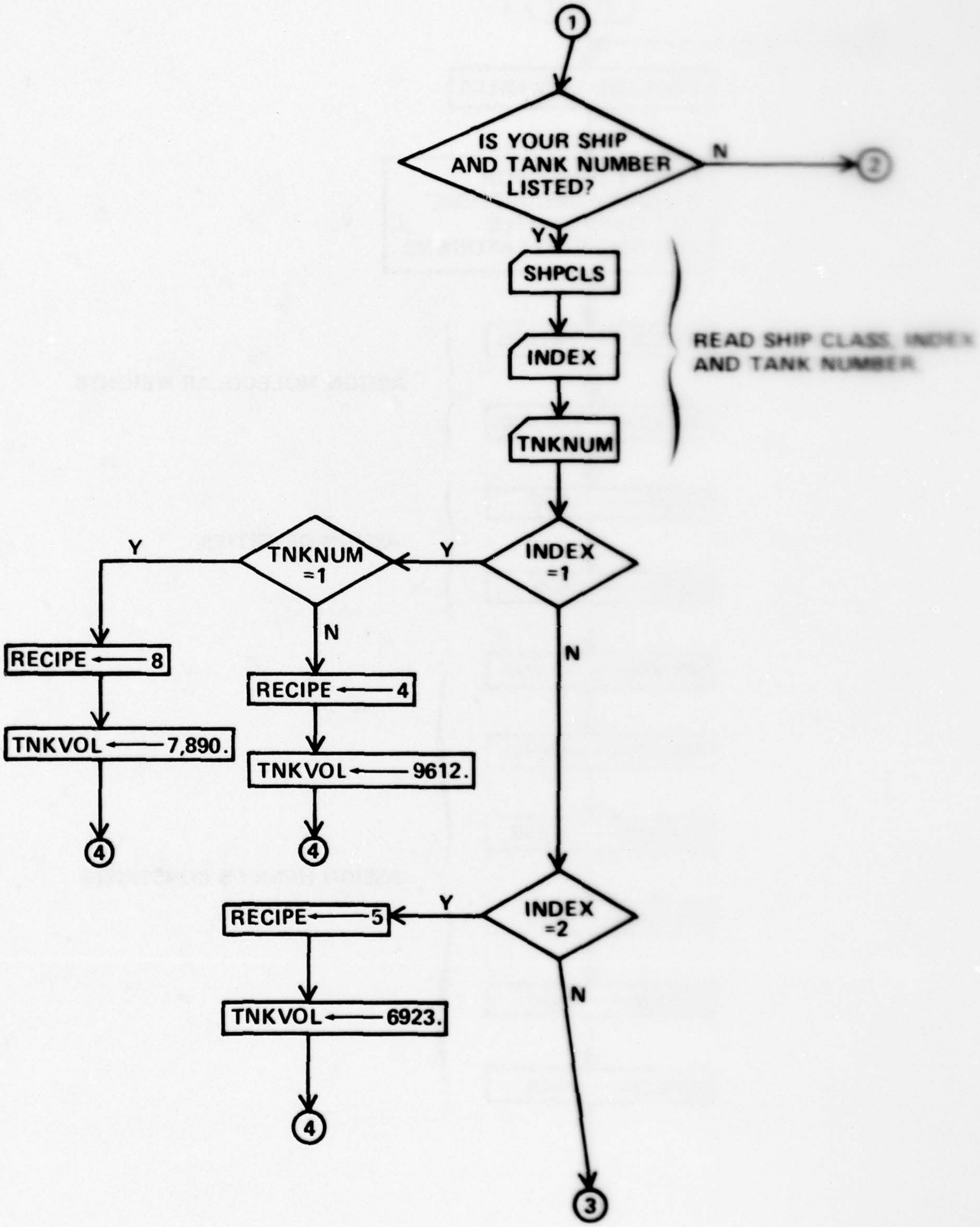
VARIABLE LIST (Cont)

Variable Name	Type	Description	Value (If Constant)
D	Real	Density used in ppm calculation depends on the gas in question	
K25	Real	Gas-generation rate constant at 25° C used in the prediction equation and depends on the gas in question	
PPM45	Real	Total increase in gas concentration for a gas at 45° C	
PPM35	Real	Total increase in gas concentration for a gas at 35° C	
PPM25	Real	Total increase in gas concentration for a gas at 25° C	
VOLTNK	Real	Volume of sewage in the tank in liters, equals either 30% or 60% of total tank volume	
MW	Real	Molecular weight of the gas in mg used in the ppm prediction equation	
H	Real	Henry's constant for the gas used in the ppm prediction equation	
X45	Real	Has no physical meaning; is defined X45 = VOLTNK* EXP (K35*T)	
X35	Real	Has no physical meaning; is defined X35 = VOLTNK* EXP (K35*T)	
X25	Real	Has no physical meaning; is defined X25 = VOLTNK* EXP (K25*T)	
W	Real	Has no physical meaning; is defined W = VSTT* MW* 55.6E-6	
Z	Real	Has no physical meaning; is defined Z = VFTT* D* DTC	
DTC	Real	Density temperature correction, depends on the reference temperature for the density of gas	
VSTT	Real	Volume of sewage in DTNSRDC test tank in liters	227
VFTT	Real	Volume of Freeboard in DTNSRDC test tank in liters	59
MIXTURE	Integer	Each mixture corresponds to a different combination of head, galley, and laundry wastes	1 → 8

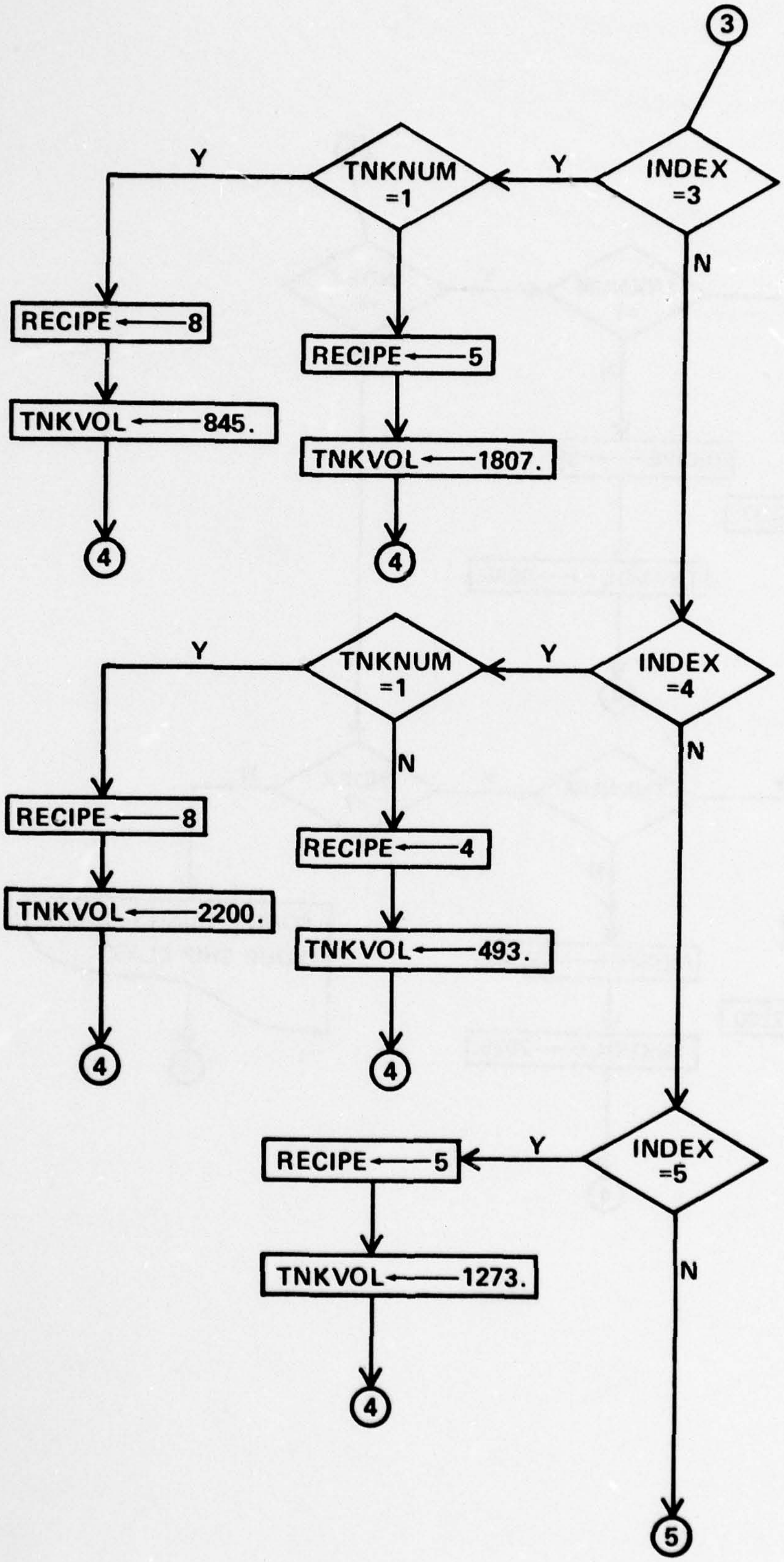
VARIABLE LIST (Cont)

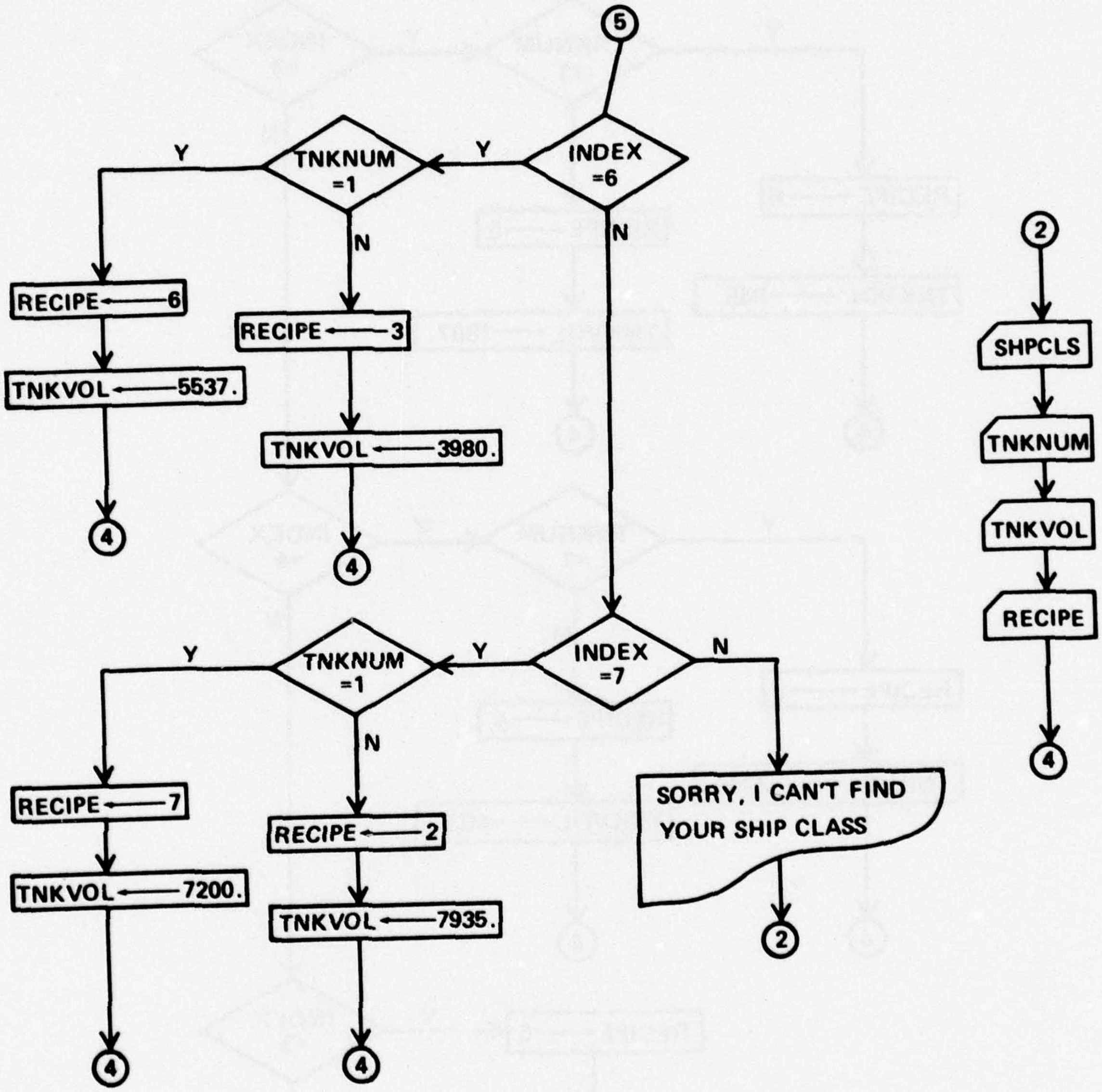
Variable Name	Type	Description	Value (If Constant)
TNKNUM	Integer	Number of the CHT tank in question; i.e., AD14 tank 1	
I	Integer	Loop counter which varies the gas under consideration	1, 2
J	Integer	Loop counter which varies the volume of sewage in the tank	30, 60
K	Integer	Loop counter which varies the time equals time in days plus 1	1 → 11
T	Integer	Time in days; T = K - 1	0 → 10
A	Integer	Corresponds to the gas in question, controls heading formats	1, 2
B	Integer	Answer to the question, "Is your ship listed?"	1 = yes 2 = no
C	Integer	Answer to the question, "Would you like to run again?"	1 = yes 2 = no
DD	Integer	Answer to the question, "Do you still want to run even though your ship is not listed?"	1 = yes 2 = no
INDEX	Integer	Corresponds to ship class	
TNKVOL	Integer	Corresponds to total tank capacity in gallons	
SHPCLS	Real	Holds alpha-numeric information corresponding to ship class	
H45	Real	Henry's constant used in prediction equation, depends on gas in question	
H35	Real	Henry's constant used in prediction equation, depends on gas in question	
H25	Real	Henry's constant used in prediction equation, depends on gas in question	

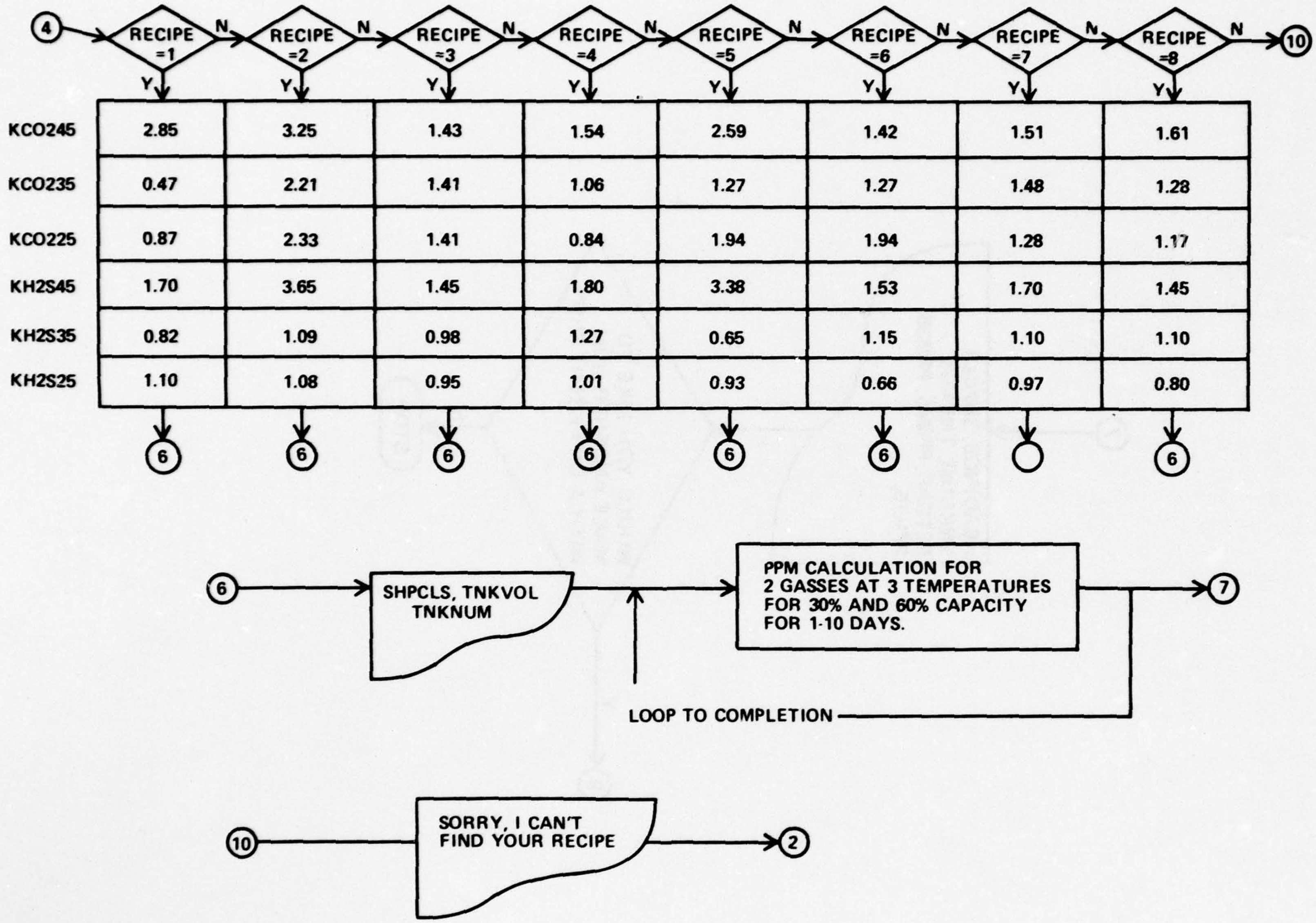

START
8
DECLARE VARIABLES
PRINT FORMAT FOR PROGRAM DESCRIPTION, LIST SHIPS ON FILE AND RECIPE BREAKDOWNS.
MWCO2 ← 44,000.
MWH2S ← 34,000.
ASSIGN MOLECULAR WEIGHTS
DCO2 ← 1.997
DH2S ← 1.539
ASSIGN DENSITIES
HCO245 ← 2,750.
HCO235 ← 2090.
HCO225 ← 1640.
HH2S45 ← 814.
HH2S35 ← 676.
HH2S25 ← 545.
ASSIGN HENRY'S CONSTANTS
1



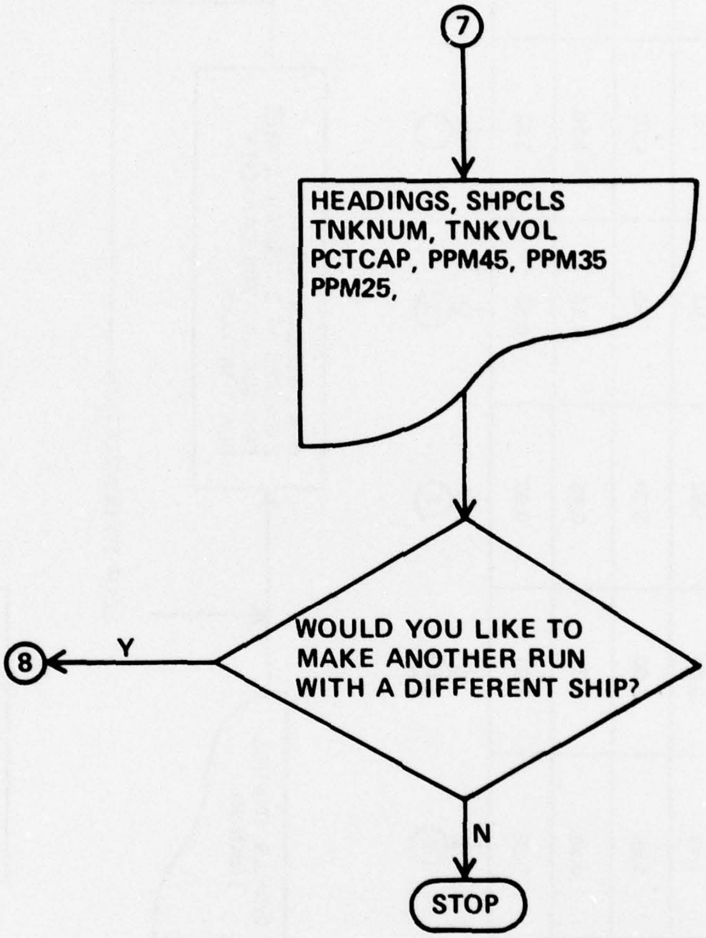
1
IS YOUR SHIP AND TANK NUMBER LISTED?
N
2
Y
SHPCLS
INDEX
TNKNUM
READ SHIP CLASS, INDEX AND TANK NUMBER.
INDEX =1
Y
TNKNUM =1
Y
RECIPE ← 8
TNKVOL ← 7,890.
4
N
RECIPE ← 4
TNKVOL ← 9612.
4
N
INDEX =2
Y
RECIPE ← 5
TNKVOL ← 6923.
4
N
3


3
INDEX =3
Y
TNKNUM =1
Y
RECIPE ← 8
TNKVOL ← 845.
4
RECIPE ← 5
TNKVOL ← 1807.
4
N
INDEX =4
Y
TNKNUM =1
Y
RECIPE ← 8
TNKVOL ← 2200.
4
N
RECIPE ← 4
TNKVOL ← 493.
4
N
INDEX =5
Y
RECIPE ← 5
TNKVOL ← 1273.
4
N
5


5
INDEX =6
Y
N
TNKNUM =1
Y
N
RECIPE ← 6
TNKVOL ← 5537.
4
RECIPE ← 3
TNKVOL ← 3980.
4
INDEX =7
Y
N
TNKNUM =1
Y
N
RECIPE ← 7
TNKVOL ← 7200.
4
RECIPE ← 2
TNKVOL ← 7935.
4
SORRY, I CAN'T FIND YOUR SHIP CLASS
2
2
SHPCLS
TNKNUM
TNKVOL
RECIPE
4



	RECIPE =1	RECIPE =2	RECIPE =3	RECIPE =4	RECIPE =5	RECIPE =6	RECIPE =7	RECIPE =8
KCO245	2.85	3.25	1.43	1.54	2.59	1.42	1.51	1.61
KCO235	0.47	2.21	1.41	1.06	1.27	1.27	1.48	1.28
KCO225	0.87	2.33	1.41	0.84	1.94	1.94	1.28	1.17
KH2S45	1.70	3.65	1.45	1.80	3.38	1.53	1.70	1.45
KH2S35	0.82	1.09	0.98	1.27	0.65	1.15	1.10	1.10
KH2S25	1.10	1.08	0.95	1.01	0.93	0.66	0.97	0.80


7
HEADINGS, SHPCLS
TNKNUM, TNKVOL
PCTCAP, PPM45, PPM35
PPM25,
WOULD YOU LIKE TO
MAKE ANOTHER RUN
WITH A DIFFERENT SHIP?
Y
8
N
STOP

```
C         DECLARE ALL VARIABLES INTEGER OR REAL
C
          REAL MWCO2,MWH2S,DCO2,DH2S,D,HCO245,
     .    HCO235,HCO225,HH2S45,HH2S35,HH2S25,
     .    KCO245,KCO235,KCO225,KH2S45,
     .    KH2S35,KH2S25,
     .    K45,K35,K25,PPM45,PPM35,PPM25,VOLTNK,MW,H,X45,X35,X25,
     .    W,Z,
     .    WCO2,HH2S,DTC,VSTT,VFTT
C
          INTEGER RECIPE,TNKNUM,I,J,K,T,A,B,C,INDEX,TNKVOL,DD
          DOUBLE PRECISION SHPCLS
C
C         PRINT THE PROGRAM DESCRIPTION
          WRITE(7,200)
          WRITE(7,201)
          WRITE(7,202)
          WRITE(7,203)
          WRITE(7,204)
          WRITE(7,205)
          WRITE(7,206)
          WRITE(7,207)
          WRITE(7,208)
          WRITE(7,209)
          WRITE(7,216)
          WRITE(7,217)
          WRITE(7,211)
          WRITE(7,212)
          WRITE(7,213)
          WRITE(7,214)
          WRITE(7,215)
          WRITE(7,218)
          WRITE(7,219)
          WRITE(7,222)
          WRITE(7,223)
200       FORMAT(1H ,' THIS PROGRAM WILL CALCULATE THE GAS GENERATION IN'
     .,/,' PARTS PER MILLIOM IN NAVY CHT TANKS DURING STAGNANT
     .    CONDITIONS.')
201      FORMAT(1H ,'CONCENTRATIONS FOR CO2, AND HYDROGEN SULFIDE ARE
     .',/,' CALCULATED.  GENERATION RATES DEPEND ON GAS,TANK VOLUME
     .',/,',TEMPREATURE, AND TANK CONTENTS. TANK CONTENTS (PERCENTAGES')
202       FORMAT(1H ,'OF HEAD, GALLEY AND LAUNDRY WASTES) WILL VARY FROM
     .',/,' TANK TO TANK.  EIGHT DIFFERENT RECIPIES HAVE BEEN CHOSEN TO
     .',/,' APPROXIMATE THE CONTENTS OF ALL NAVY CHT TANKS.',//)
203       FORMAT(1H ,' THE RECIPIES ARE LISTED BELOW.
     .',//,' ************************************************
     .',/,' RECIPE     PCT HEAD     PCT GALLEY     PCT LAUNDRY')
204       FORMAT(1H ,'------     --------     ----------     ----------
     .',/,'     1         30             70              --
     .',/,'     2         59             41              --')
205       FORMAT(1H ,'  3           --          54               46
     .',/,'     4         34             36              30
     .',/,'     5         45             32              24')
206       FORMAT(1H ,'  6                65          19          16
     .',/,'     7         29             20              51
     .',/,'     8         100            --              --')
207       FORMAT(1H ,'                                                  .
     .',/,' ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
     .',//,' IN ORDER TO RUN THIS PROGRAM YOU MUST HAVE THE FOLLOWING')
208       FORMAT(1H ,'DATA AVAILABLE .  1. THE SHIP CLASS  2. THE TOTAL
     .',/,' TANK VOLUME IN GALLONS FOR THE TANK YOU WISH TO CONSIDER
     .',/,' AND 3. THE RECIPE WHICH APPROXIMATES THE TANK CONTENTS')
209       FORMAT(/,1H ,'BELOW IS SOME AVAILABLE DATA
```

```
     .','/','---------------------------------------------------------
     .','/',' SHIP CLASS   INDEX NUMBER   TANKNO.    VOLUME   RECIPE')
216     FORMAT(1H ,' AD14             1         1         7890       8
     .','/','  AD14           1         2         9612       4
     .','/','  AE26           2         1         6923       5')
217     FORMAT(1H ,' .
     .','/','  AOG50          3         1         845        8
     .','/','  AOG50          3         2         1807       5')
211     FORMAT(1H ,' .
     .','/','  AS11           4         1         2200       8
     .','/','  AS11           4         2         493        4')
212     FORMAT(1H ,' .
     .','/','  ATF76          5         1         1273       5')
213     FORMAT(1H ,' .
     .','/','  LST1179        6         1         5537       6
     .','/','  LST1179        6         2         3980       3')
214     FORMAT(1H ,' .
     .','/','  LPD4           7         1         7200       7
     .','/','  LPD4           7         2         7935       2')
215     FORMAT(1H ,' LPD4             7         3         7935       2')
218     FORMAT(1H ,'.
     .','//',' IF THE CHT TANK YOU WISH TO CONSIDER IS NOT LISTED ABOVE
     .','/',' THEN THE COMPUTER WILL INSTRUCT YOU TO INPUT THE PROPER')
219     FORMAT(1H ,'SHIP CLASS, INDEX NUMBER, AND TANK NO. YOU WILL ALSO
     .','/',' NEED TO INPUT  THE APPROPRIATE TANK VOLUME AND RECIPE.
     .','///',' AFTER RUNNING, THE PROGRAM  RETURNS THE CONCENTRATIONS')
222     FORMAT(1H ,'OF CO2 AND H2S AT 25, 35, AND 45 DEGREES CENTEGRADE
     .','/',' AT INTERVALS OF ONE DAY FOR 0 TO 10 DAYS. CONCENTRATIONS ARE
     .','/',' CALCULATED FOR 30% AND 60% OF THE TANKS FULL CAPACITY.')
223     FORMAT(///,1H ,'                            HERE WE GO!!!!!!!',//)
C
C
8000    CONTINUE
C
C       ASSIGN THE MOLECULAR WEIGHTS TO THE APPROPRIATE VARIABLES
C
        MWCO2=44000.
        MWH2S=34000.
C
C       ASSIGN THE APPROPRIATE DENSITIES TO EACH GAS
C
        DCO2=1.977
        DH2S=1.539
C
C       ASSIGN THE APPROPRIATE HENRYS CONSTANTS TO THE GASES
C
        HCO245=2570.
        HCO235=2090.
        HCO225=1640.
        HH2S45=814.
        HH2S35=676.
        HH2S25=545.
C
C       ASK WEATHER SHIPCLASS AND TANK NUMBER ARE LISTED.
C
1000    WRITE(7,210)
210     FORMAT(1H ,5X,'IS YOUR SHIP CLASS AND TANK NUMBER LISTED ABOVE ?
        TYPE IN 1=YES OR 2=NO')
C
C       READ THE REPLY AND SEND CONTROL TO THE PROPER STATMENT
C
        READ(5,100)B
100     FORMAT(I1)
        IF(B.EQ.1) GO TO 1030
        WRITE(7,226)
226     FORMAT(1H ,' IF YOU HAVE TANK VOLUMEIN GALLONS AND THE RECIPE
     .','/',' WHICH MOST CLOSELY APPROXIMATES THE CONTENTS OF YOUR TANK
     .','/',' YOU CAN STILL RUN THE PROGRAM.
     .','//',' DO YOU STILL WANT TO RUN ?  TYPE 1= YES OR 2= NO')
```

```
        READ(5,112)DD
112     FORMAT(I1)
        IF(D.EQ.2) GO TO 7001
C
C       READ SHIP CLASS ,INDEX AND TANK NUMBER
C
1030    WRITE(7,220)
220     FORMAT(1H ,5X,'TYPE IN SHIP CLASS')
        READ(5,110)SHPCLS
        WRITE(7,225)
225     FORMAT(1H ,5X,'TYPE IN INDEX NUMBER.  IF THE SHIP IS NOT
       LISTED THEN INDEX=0')
        READ(5,111)INDEX
110     FORMAT(A6)
111     FORMAT(I3)
        WRITE(7,230)
230     FORMAT(1H ,5X,'TYPE IN TANK NUMBER')
        READ(5,120)TNKNUM
120     FORMAT(I2)
C
C       THIS CONDITIONAL IF WILL BYPASS READS FOR TANK VOLUME AND
C       RECIPE IF THE SHIP IS LISTED IN THE PROGRAM.
C
        IF(B.EQ.1) GO TO 1010
C
C       IF SHIP CLASS AND TANK NUMBER ARE NOT LISTED THEN THE PROGRAM
C       REQUESTS THAT TANK VOLUME AND RECIPE NUMBER BE ENTERED.
C
        WRITE(7,240)
240     FORMAT(1H ,5X,'TYPE IN TANK VOLUME IN GALLONS')
        READ(5,130)TNKVOL
130     FORMAT(I7)
        WRITE(7,250)
250     FORMAT(1H ,5X,'TYPE IN PROPER RECIPE NUMBER')
        READ(5,140)RECIPE
140     FORMAT(I1)
C
C       CONTROL IS SENT PAST A SEARCH FOR TANK VOLUME AND RECIPE
C
        GO TO 1020
1010    CONTINUE
C
C       NOW THE PROGRAM , GIVEN THE SHIP CLASS AND TANK NO. SEARCHES
C       THROUGH THE STORED DATA FOR THE PROPER TANK VOLUME AND RECIPE
C
        IF(INDEX.EQ.1) GO TO 2000
        IF(INDEX.EQ.2) GO TO 2010
        IF(INDEX.EQ.3) GO TO 2020
        IF(INDEX.EQ.4) GO TO 2030
        IF(INDEX.EQ.5) GO TO 2040
        IF(INDEX.EQ.6)  GO TO 2050
        IF(INDEX.EQ.7) GO TO 2060
C
C       IF SHIP CLASS IS NOT FOUND THEN PROGRAM ASKS FOR MANUAL INPUT
C
        WRITE(7,260)
260     FORMAT(1H ,5X,'SORRY BUT I CANNOT FIND YOUR SHIP PLEASE INPUT
         DATA MANUALLY AS INSTRUCTED')
        B=2
        GO TO 1030
C       NOW WE KNOW THE SHIP CLASS AND MUST FIND THE TANKNUMBER
C       WHICH WILL TELL US THE TANK VOLUME AND RECIPE
C
2000    CONTINUE
        IF(TNKNUM.EQ.1) GO TO 2001
```

```
      RECIPE=4
      TNKVOL=9612.
      GO TO 1020
2001  RECIPE=8
      TNKVOL=7890.
      GO TO 1020
2010  RECIPE=5
      TNKVOL=6923.
      GO TO 1020
2020  IF(TNKNUM.EQ.1) GO TO 2021
      RECIPE=5
      TNKVOL=1807.
      GO TO 1020
2021  RECIPE=8
      TNKVOL=845.
      GO TO 1020
2030  IF(TNKNUM.EQ.1) GO TO 2031
      RECIPE=4
      TNKVOL=493.
      GO TO 1020
2031  RECIPE=8
      TNKVOL=2200.
      GO TO 1020
2040  RECIPE=5
      TNKVOL=1273.
      GO TO 1020
2050  IF(TNKNUM.EQ.1)GO TO 2051
      RECIPE=3
      TNKVOL=3980.
      GO TO 1020
2051  RECIPE=6
      TNKVOL=5537.
      GO TO 1020
2060  IF(TNKNUM.EQ.1) GO TO 2061
      RECIPE=2
      TNKVOL=7935.
      GO TO 1020
2061  RECIPE=7
      TNKVOL=7200.
      GO TO 1020
C
C     NOW THAT THE RECIPE IS KNOWN  WE MUST ASSIGN THE GENERATION
C     RATES.
C
1020  CONTINUE
      IF(RECIPE.NE.1) GO TO 3010
      KCO245=2.85
      KCO235=0.47
C

      KCO225=0.87
      KH2S45=1.70
      KH2S35=0.82
      KH2S25=1.10
      GO TO 4000
3010  IF(RECIPE.NE.2) GO TO 3020
      KCO245=3.25
      KCO235=2.11
      KCO225=2.33
      KH2S45=3.65
      KH2S35=1.09
      KH2S25=1.08
      GO TO 4000
3020  IF(RECIPE.NE.3) GO TO 3030
      KCO245=1.43
      KCO235=1.41
      KCO225=1.41
```

```
        KH2S45=1.45
        KH2S35=0.98
        KH2S25=0.95
        GO TO 4000
3030    IF(RECIPE.NE.4) GO TO 3040
        KCO245=1.54
        KCO235=1.06
        KCO225=0.84
        KH2S45=1.80
        KH2S35=1.27
        KH2S25=1.01
        GO TO 4000
3040    IF(RECIPE.NE.5) GO TO 3050
        KCO245=2.59
        KCO235=1.27
        KCO225=1.94
        KH2S45=3.38
        KH2S35=0.65
        KH2S25=0.93
        GO TO 4000
3050    IF(RECIPE.NE.6) GO TO 3060
        KCO245=1.42
        KCO235=1.27
        KCO225=1.94
        KH2S45=1.53
        KH2S35=1.15
        KH2S25=0.66
        GO TO 4000
3060    IF(RECIPE.NE.7) GO TO 3070
        KCO245=1.51
        KCO235=1.48
        KCO225=1.28
        KH2S45=1.70
        KH2S35=1.10
        KH2S25=0.97
        GO TO 4000
3070    IF(RECIPE.NE.8) GO TO 3080
        KCO245=1.61
        KCO235=1.28
        KCO225=1.17
        KH2S45=1.45
        KH2S35=1.10
        KH2S25=0.80
        GO TO 4000
C
C       IF THE RECIPE IS NOT FOUND MANUAL INPUT IS REQUESTED
C       AND CONTROL IS SENT TO THE RECIPE SEARCH.
C
3080    WRITE(7,270)
270     FORMAT(1H ,5X,'SORRY, I CANT FIND YOUR RECIPE .  PLEASE TYPE
     .',/,'  IN THE RECIPE YOU DESIRE, PICK IT FROM THE LIST I GAVE
     .',/,' YOU BEFORE')
        READ(5,140)RECIPE
        GO TO 1020
C
C       ONCE THE RECIPE IS FOUND WE GO ON TO THE CALCULATION
C
4000    CONTINUE
C
C       THE THREE FOLLOWING DO LOOPS ENCLOSE OUR GAS INCREASE CAL-
C       CULATIONS.  THE FIRST LOOP VARIES THE GAS FROM CO2 TO H2S
C       .  THE SECOND LOOP VARIES THE TANK LEVEL
C        FROM 30% FULL CAPACITC TO 60% OF FULL CAPACITY.  THE THIRD
C       LOOP VARIES THE TIME FROM 0 TO 10 DAYS.
C
C       PRINT A HEADING
C
```

```
      WRITE(7,6000)SHPCLS,TNKNUM
6000  FORMAT('1',5X,'SHIP CLASS: ',A6,10X,'TANK NUMBER: ',I2,/)
      WRITE(7,6010)TNKVOL
6010  FORMAT(1H ,5X,'TANK VOLUME: ',I7)
      WRITE(7,6011)
6011  FORMAT(1H ,'   **************************************************')
C
C     BEGIN THE FIRST LOOP
C
      DO 4010 I=1,2,1
C
C     THESE CONDITIONAL IFS VARY THE GAS UNDER CONSIDERATION
C                       I=1  IMPLIES CO2
C                       I=2  IMPLIES H2S
C
      IF(I.EQ.1) GO TO 4040
      IF(I.EQ.2) GO TO 4050
C
C     DEPENDING ON THE GAS ;  GENERATION RATES , MOLECULAR WEIGHTS,
C     DENSITIES, DENSITY TEMPERATURE CORRECTIONS AND HENRYS
C     CONSTANTS ARE ASSIGNED.  THEN THE CALCULATION IS STARTED.
C
4040  CONTINUE
      A=1
      D=DCO2
      MW=MWCO2
      H45=HCO245
      H35=HCO235
      H25=HCO225
      DTC=0.273
      K45=KCO245
      K35=KCO235
      K25=KCO225
      GO TO 5000
4050  CONTINUE
      A=2
      MW=MWH2S
      D=DH2S
      DTC=0.273
      H45=HH2S45
      H35=HH2S35
      H25=HH2S25
      K45=KH2S45
      K35=KH2S35
      K25=KH2S25
      GO TO 5000
C
C     NOW THE INCREASES IN GAS CONSENTRATIONS ARE CALCULATED, AFTER
C     THE TANK VOLUME IS CONVERTED TO LITERS,  AFTER A SECOND
C     HEADING IS PRINTED.
C
5000  CONTINUE
      IF(A.EQ.1) GO TO 9001
      WRITE(7,6016)
      GO TO 9002
9001  WRITE(7,6015)
9002  CONTINUE
6016  FORMAT(//,1H ,5X,'GAS: H2S')
6015  FORMAT(//,1H ,5X,'GAS: CO2')
C
C     BEGIN THE SECOND LOOP TO VARY THE TANK LEVEL.
C
      DO 4020 J=30,60,30
      WRITE(7,6018)J
6018  FORMAT(1H ,//,5X,' PERCENTAGE FULL CAPACITY: ',I2,/)
```

```
        WRITE(7,6020)
6020    FORMAT(1H ,5X,'TIME',3X,'PPM 45 C',4X,'PPM 35 C',4X,'PPM 25 C',/)
C
C       BEGIN THE INSIDE LOOP WHICH DOES THE REPETITIVE CALCULATION
C
        DO 4030 K=1,11,1
C
C       K IS EQUAL TO ONE PLUS DAYS SO T EQUALS K MINUS ONE.
C
        T=K-1
        VOLTNK=(TNKVOL*3.875)
        VSTT=227.
        VFTT=59.
        X45=VOLTNK*EXP(K45*T)
        X35=VOLTNK*EXP(K35*T)
        X25=VOLTNK*EXP(K25*T)
        W=VOLTNK*J*0.01*MW*55.6E-6
        Z=VOLTNK*(1.-J*0.01)*D*DTC
        PPM45=X45/(VSTT*(W/H45+Z/318.))
        PPM35=X35/(VSTT*(W/H35+Z/308.))
        PPM25=X25/(VSTT*(W/H25+Z/298.))
C
C       WRITE THE CALCULATED VALUES FOR PARTS PER MILLION INCREASE.
C
        WRITE(7,6030)T,PPM45,PPM35,PPM25
6030    FORMAT(1H ,5X,I2,4X,E10.3,2X,E10.3,2X,E10.3)

C
C       DO LABLES
C
4030    CONTINUE
        WRITE(7,6031)
6031    FORMAT(1H ,'            ---------------------------------------------')
4020    CONTINUE
        WRITE(7,6032)
6032    FORMAT(1H ,'            =============================================')

4010    CONTINUE
C
C       NOW ASK THE OPERATOR IF HE WOULD LIKE TO MAKE ANOTHER RUN
C
7001    CONTINUE
        WRITE(7,7000)
7000    FORMAT(1H ,5X,'DO YOU WISH TO MAKE ANOTHER RUN WITH A DIFFERENT
     .',/,' SHIP OR A DIFFERENT TANK?  TYPE 1=YES OR 2=NO')
        READ(5,7012)C
7012    FORMAT(I1)
        IF(C.EQ.1) GO TO 8000
        CONTINUE
        STOP
        END
```

APPENDIX B

GASGEN PROGRAM EXAMPLE RUN
(USS DIXON (AS 37), CHT TANK 1)

```
 THIS PROGRAM WILL CALCULATE THE GAS GENERATION IN
PARTS PER MILLIOM IN NAVY CHT TANKS DURING STAGNANT  CONDITIONS.
CONCENTRATIONS FOR CO2, AND HYDROGEN SULFIDE ARE
CALCULATED.  GENERATION RATES DEPEND ON GAS,TANK VOLUME
TEMPREATURE, AND TANK CONTENTS. TANK CONTENTS (PERCENTAGES
OF HEAD, GALLEY AND LAUNDRY WASTES) WILL VARY FROM
TANK TO TANK.  EIGHT DIFFERENT RECIPIES HAVE BEEN CHOSEN TO
APPROXIMATE THE CONTENTS OF ALL NAVY CHT TANKS.


 THE RECIPIES ARE LISTED BELOW.

**************************************************
RECIPE     PCT HEAD     PCT GALLEY     PCT LAUNDRY
------     --------     ----------     ----------
   1          30            70             --
   2          59            41             --
   3          --            54             46
   4          34            36             30
   5          45            32             24
   6          65            19             16
   7          29            20             51
   8          100           --             --

++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

IN ORDER TO RUN THIS PROGRAM YOU MUST HAVE THE FOLLOWING
DATA AVAILABLE .  1. THE SHIP CLASS  2. THE TOTAL
TANK VOLUME IN GALLONS FOR THE TANK YOU WISH TO CONSIDER
AND 3. THE RECIPE WHICH APPROXIMATES THE TANK CONTENTS

BELOW IS SOME AVAILABLE DATA
------------------------------------------------------------
SHIP CLASS   INDEX NUMBER   TANKNO.     VOLUME    RECIPE
 AD14             1            1         7890       8
 AD14             1            2         9612       4
 AE26             2            1         6923       5
 .
 AOG50            3            1         845        8
 AOG50            3            2         1807       5
 .
 AS11             4            1         2200       8
 AS11             4            2         493        4
 .
 ATF76            5            1         1273       5
 .
 LST1179          6            1         5537       6
 LST1179          6            2         3980       3
 .
 LPD4             7            1         7200       7
 LPD4             7            2         7935       2
 LPD4             7            3         7935       2
.

IF THE CHT TANK YOU WISH TO CONSIDER IS NOT LISTED ABOVE
THEN THE COMPUTER WILL INSTRUCT YOU TO INPUT THE PROPER
SHIP CLASS, INDEX NUMBER, AND TANK NO. YOU WILL ALSO
NEED TO INPUT  THE APPROPRIATE TANK VOLUME AND RECIPE.


AFTER RUNNING, THE PROGRAM  RETURNS THE CONCENTRATIONS
OF CO2 AND H2S AT 25, 35, AND 45 DEGREES CENTEGRADE
AT INTERVALS OF ONE DAY FOR 0 TO 10 DAYS. CONCENTRATIONS ARE
CALCULATED FOR 30% AND 60% OF THE TANKS FULL CAPACITY.
```

```
                  HERE WE GO!!!!!!

IS YOUR SHIP CLASS AND TANK NUMBER LISTED ABOVE ?  TYPE IN 1=YES
                                                           2=NO
2

IF YOU HAVE TANK VOLUME IN GALLONS AND THE RECIPE WHICH MOST CLOSELY
APPROXIMATES THE CONTENTS OF YOUR TANK  YOU CAN STILL RUN THE PROGRAM.

DO YOU STILL WANT TO RUN ?  TYPE IN 1=YES  OR 2=NO

1

TYPE IN SHIP CLASS

AS37

TYPE IN INDEX NUMBER. IF THE SHIP IS NOT LISTED THEN INDEX=0

0

AS37
     TYPE IN TANK NUMBER

1

TYPE IN TANK VOLUME IN GALLONS

5500

TYPE IN PROPER RECIPE NUMBER

5
```

```
SHIP CLASS: AS37            TANK NUMBER:  1

TANK VOLUME:    5500
*************************************************

GAS: CO2

PERCENTAGE FULL CAPACITY: 30

TIME    PPM 45 C     PPM 35 C     PPM 25 C

 0      0.299E 01    0.279E 01    0.257E 01
 1      0.398E 02    0.994E 01    0.179E 02
 2      0.531E 03    0.354E 02    0.124E 03
 3      0.708E 04    0.126E 03    0.865E 03
 4      0.944E 05    0.449E 03    0.602E 04
 5      0.126E 07    0.160E 04    0.419E 05
 6      0.168E 08    0.569E 04    0.292E 06
 7      0.224E 09    0.203E 05    0.203E 07
 8      0.298E 10    0.722E 05    0.141E 08
 9      0.397E 11    0.257E 06    0.983E 08
10      0.529E 12    0.915E 06    0.684E 09
------------------------------------------------

PERCENTAGE FULL CAPACITY: 60

TIME    PPM 45 C     PPM 35 C     PPM 25 C

 0      0.352E 01    0.314E 01    0.272E 01
 1      0.470E 02    0.112E 02    0.189E 02
 2      0.626E 03    0.398E 02    0.132E 03
 3      0.835E 04    0.142E 03    0.917E 03
 4      0.111E 06    0.505E 03    0.638E 04
 5      0.148E 07    0.180E 04    0.444E 05
 6      0.198E 08    0.640E 04    0.309E 06
 7      0.264E 09    0.228E 05    0.215E 07
 8      0.351E 10    0.811E 05    0.150E 08
 9      0.468E 11    0.289E 06    0.104E 09
10      0.624E 12    0.103E 07    0.724E 09
------------------------------------------------
================================================

GAS: H2S

PERCENTAGE FULL CAPACITY: 30

TIME    PPM 45 C     PPM 35 C     PPM 25 C

 0      0.272E 01    0.246E 01    0.217E 01
 1      [illegible] 02    0.470E 01    0.551E 01
 2      0.234E 04    0.901E 01    0.140E 02
[illegible]
```

```
    PERCENTAGE FULL CAPACITY: 60

    TIME     PPM 45 C      PPM 35 C      PPM 25 C

     0       0.229E 01     0.198E 01     0.167E 01
     1       0.673E 02     0.380E 01     0.422E 01
     2       0.198E 04     0.727E 01     0.107E 02
     3       0.581E 05     0.139E 02     0.271E 02
     4       0.171E 07     0.267E 02     0.687E 02
     5       0.501E 08     0.511E 02     0.174E 03
     6       0.147E 10     0.979E 02     0.441E 03
     7       0.432E 11     0.187E 03     0.112E 04
     8       0.127E 13     0.359E 03     0.284E 04
     9       0.373E 14     0.688E 03     0.719E 04
    10       0.109E 16     0.132E 04     0.182E 05
  ------------------------------------------------
  ================================================
    DO YOU WISH TO MAKE ANOTHER RUN WITH A DIFFERENT
 SHIP OR A DIFFERENT TANK?  TYPE 1=YES OR 2=NO
 2
 STOP - -
```

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