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## GLOSSARY OF TERMS AND SYMBOLS

Unless otherwise stated, all terms and symbols used in this report are as defined below.

Chemical symbols other than those listed below are defined in standard chemical texts.

### ALPHABETIC

AFB	Air Force Base
AFLC	Air Force Logistics Command
AF-MJL	Air Force-Marquardt Jet Laboratory
ATL	Aero Thermo Laboratory
Cal	calories
cc	cubic centimeters
(Cl)	monatomic chlorine
cm	centimeter
dbA	decibels - "A", weighted octave band
dbC	decibels - "C", weighted octave band
DGF	dry gas fraction
EHL(K)	USAF Environmental Health Laboratory, Kelly AFB
EHL(M)	USAF Environmental Health Laboratory, McClellan AFB
EPA	Environmental Protection Agency
F/A	fuel/air mass ratio
FSN	Federal Stock Number
ft/sec	feet per second
gal	gallon
gm	gram
GN <sub>2</sub>	gaseous nitrogen
gpm	gallons per minute
gr/scf	grains per standard cubic foot corrected to 12% carbon dioxide
HC	hydrocarbons
Hg	mercury
hp	horsepower
ID	inside diameter
JP-4	jet engine fuel grade
Kg	kilogram
l	liter
lbs	pounds
m	meter
mg	milligram
mg/kg	milligram per kilogram
mg/l	milligrams per liter
min	minute
ml	milliliters
mm	millimeters
mph	miles per hour
MSA	Mine Safety Appliances



## GLOSSARY OF TERMS AND SYMBOLS (Cont'd)

mw	molecular weight
NA	not applicable
NaOH	sodium hydroxide
nb	normal butyl
ND	none detected
NE	not evaluated
no	number
NO <sub>x</sub>	nitrogen oxides (NO and NO <sub>2</sub> )
$\frac{N_U}{N_T}$	ratio of applied NaOH to theoretical amount of NaOH required
"Orange" Herbicide	A chlorinated-phenoxy hydrocarbon herbicide procured by the USAF to contain, by volume, 50% ( $\pm$ 1.5%) 2,4-D and 50% ( $\pm$ 1.5%) 2,4,5-T
P/N	part number
ppm	parts per million by volume in gases, parts per million by weight in liquids
pps	pounds per second
psid	pressure differential, pounds per square inch delta
psig	pounds per square inch gauge
RPE	relative pyrolysis efficiency
s or $\sigma$	standard deviation of sample population
SAAMA	San Antonio Air Materiel Area
sample codes	See Appendix C
SSW	spent scrubber water
STP	standard temperature (70°F) and pressure (29.92 inches Hg)
SUE <sup>®</sup>	"Sudden Expansion" Burner, Registered Trade Mark, The Marquardt Company
TBC	total burn composite
TC	thermocouple - subscript number denotes location
TC <sub>AVG</sub>	average of theoretical combustion temperature (TC <sub>THEO</sub> ) and reading of TC <sub>7</sub>
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
TC <sub>THEO</sub>	theoretical temperature of combustion
TMC	The Marquardt Company
USAF	United States Air Force
vs	versus
W	mass flow rate in pounds per second
WCTS	West Coast Technical Service, Inc. of Cerritos, California
$\bar{x}$	mean or average value of samples
<b><u>NUMERIC</u></b>	
2,4-D	normal butyl 2,4-dichlorophenoxyacetate
2,4,5-T	normal butyl 2,4,5-trichlorophenoxyacetate
40 CFR 76	Code of Federal Regulations, Title 40, Part 76

## GLOSSARY OF TERMS AND SYMBOLS (Cont'd)

### GREEK

$\Delta P$	pressure differential in pounds per square inch
$\mu$	micro or micron
$\mu g$	microgram
$\mu g/l$	microgram per liter
$\mu l$	microliter
$\mu l/l$	microliter per liter
$\mu mho/cm$	micro mho/centimeter

### SYMBOLS

$^{\circ}C$	degrees Centigrade
$^{\circ}F$	degrees Fahrenheit
$^{\circ}R$	degrees Rankine
$<$	less than
$\leq$	less or equal to
$>$	greater than
$\geq$	greater or equal to
$\#$	pounds
$"$	inches
$\approx$	approximately equal to
$\%$	percent

### SUBSCRIPTS

a	air
f	fuel
c	caustic solution
w	water

## 1.0 SUMMARY

This report describes a program conducted jointly by the United States Air Force and The Marquardt Company to investigate the destruction of "Orange" Herbicide by incineration in a commercial incineration system. Particular emphasis was placed on the destruction of ppm quantities (11-16 mg/kg) of 2,3,7,8-tetrachlorodibenzo-p-dioxin present in the herbicide. Other objectives were to obtain engineering data relative to controlling and monitoring the incineration process, to evaluate noise produced by the incineration system, to evaluate long term effects of "Orange" Herbicide combustion on incinerator materials, to evaluate the effectiveness of proposed drum cleaning operations, and to assess the toxicity of scrubber water and scrubbed gas effluents to several aquatic organisms and plants, respectively.

The program was conducted at the Air Force-Marquardt Jet Laboratory, Van Nuys, California between 8 October 1973 and 21 December 1973 utilizing a Marquardt incineration system. A total of 30.5 hours of burn time on undiluted "Orange" Herbicide fuel was accumulated during eight record burn periods. Average combustion temperatures varied from 2273°F to 2772°F, "Orange" Herbicide destruction rates ranged from 0.123 to 0.185 pps, and excess air ranged from 34 to 89%. In addition, 7.1 hours of burn time was accumulated during which drum rinse solutions of "Orange" Herbicide and JP-4 were incinerated.

Extensive sampling and analyses were conducted to quantitate the constituents of the unscrubbed combustion gases, the liquid used to cool and scrub the combustion gases, scrubbed effluent gases, drum cleaning samples, and any solid residues deposited in the system. Samples were analyzed by mass spectroscopy, flame ionization gas chromatography, and atomic absorption. Process system parameters and noise data were observed and recorded.

No significant problems were encountered in the storage, transfer, steady state or transient combustion of "Orange" Herbicide. Likewise, no significant problems were encountered in the structural integrity (safety) or deterioration of the incinerator or related process flow systems. Problems due to high viscosity of the "Orange" Herbicide were remedied by preheating to 95°F ( $\pm$  5).

Test data demonstrated that the "Orange" Herbicide was effectively and safely destroyed by incineration; no herbicide feed compounds were found (within the limits of detectability) in any combustion gas, scrubbed effluent gas, spent scrubber water or combustion chamber deposit sample resulting from incinerator operation (four test burns) while using slot type fuel injection nozzles. Likewise, no herbicide feed compounds were found in samples resulting from incineration operations (four test burns) while using a central poppet type fuel nozzle except for one combustion chamber

deposit sample and one spent scrubber water sample. This anomaly was attributed to the characteristics of poppet nozzle fuel injection. From sample analyses data, conclusions were made regarding possible undetectable discharge mass rates of herbicide constituents, effluent biological impact, formation of pyrolyzates and hydrolyzates, and possible criteria for drum cleaning operations. Criteria were also established regarding incinerator noise generation and incinerator process system functions.

## 2.0 INTRODUCTION

### 2.1 Program History

The United States Air Force is investigating the disposal of excess "Orange" Herbicide by incineration. Two bench scale incineration studies and a previous Marquardt small scale pilot study have provided basic understandings of the "Orange" Herbicide incineration process and have shown incineration to be a feasible disposal method.<sup>(1)(2)(3)</sup> The current program was initiated to obtain data on the herbicide's destruction in a commercial incinerator as required for evaluation and use in an environmental statement.

### 2.2 Description of "Orange" Herbicide

"Orange" Herbicide is a chlorinated phenoxy hydrocarbon compound procured under specifications to contain 50% (+ 1.5%) by volume of normal butyl 2,4-dichlorophenoxyacetate (2,4-D) and 50% (+ 1.5%) by volume of normal butyl 2,4,5-trichlorophenoxyacetate (2,4,5-T). The herbicide "Orange II" was procured under the same specifications except that iso-octyl 2,4,5-trichlorophenoxyacetate (IO 2,4,5-T) was substituted for normal butyl 2,4,5-T. The subject program was conducted exclusively with "Orange" Herbicide.

Both "Orange" and "Orange II" Herbicides contain trace amounts of a toxic contaminant 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The Air Force has analyzed its "Orange" Herbicide stocks and found TCDD concentrations ranging from <0.05 to 47.0 mg/kg. Statistical evaluation of these data indicated that pooled stocks would have an estimated average TCDD concentration of 1.9 mg/kg ( $\pm$  0.7 mg/kg) at a 95% confidence level.

### 2.3 Test Objectives

The objectives of the contract effort, as listed in the Statement of Work, were as follows with agencies of prime responsibility noted:

- a. Determine the capability of an incinerator system to destruct the "Orange" Herbicide over a range of selected incineration conditions (TMC and EHLs).
- b. Obtain the necessary engineering data to adequately monitor, control, and document the incinerator operation during the project (TMC).
- c. Evaluate the test burns' effects and project the long term effects of the combustion gases on the material of the incinerator unit (TMC).
- d. Determine the combustion gas, scrubbed effluent gas, and "spent" scrubber water discharge mass rates of herbicide constituents and any other organic compounds which may be detected (EHLs)

e. Determine the presence of herbicidal pyrolyzates and hydrolyzates, if any, in the combustion gases, scrubbed effluent gases, and "spent" scrubber water (EHLs and Analytical Chemistry Laboratory).

f. Determine the toxicity of "spent" scrubber water to several aquatic indicator organisms (EHL/K).

g. Evaluate the noise produced by an incineration system and assess its occupational hazard to operators (EHL/K).

h. Evaluate the effectiveness of a proposed drum cleaning procedure (EHL/K).

#### 2.4 Program Scope

Twenty-eight 55-gallon drums (1540 gallons) of "Orange" Herbicide were supplied by the Air Force for use in conducting this program. Program scope was defined as follows:

a. Take all appropriate measures to ensure safe storage, handling, transfer and combustion of the "Orange" Herbicide.

b. Conduct a minimum of six documented incinerator test burns of at least 3 to 4 hours duration each.

c. Conduct and duplicate the test burns at theoretical combustion temperatures of 2100°F, 2500°F and 2900°F burning undiluted "Orange" Herbicide with a minimum of 30% excess air.

d. Control within  $\pm 5\%$ , measure and record all system operating parameters.

e. Collect gas and particulate samples from combustion gases and scrubbed effluent gases and collect spent scrubber water from each burn period for analyses of chemical quality and toxicity.

f. Utilize on-line gas analyses equipment for monitoring combustion gas and scrubbed effluent gas quality during testing.

g. Retain spent scrubber water in holding tanks to measure toxicity before disposal.

h. Record noise intensities around the incinerator system and in the control room during test burns.

i. Rinse emptied "Orange" Herbicide drums in a specified manner with JP-4 and analyze the rinse samples.

j. Perform a final rinse of the entire system and incinerate all collected rinses and spillage at conditions similar to those used during test burns of "Orange" Herbicide.

## 2.5 Program Task Organization

The efforts described herein were conducted in the Aero Thermo Laboratory (ATL) of the Air Force-Marquardt Jet Laboratory at Van Nuys, California. Test activities were conducted, monitored, and evaluated by a team consisting of The Marquardt Company; the USAF Environmental Health Laboratory, Kelly AFB (EHL/K); and the USAF Environmental Health Laboratory, McClellan AFB (EHL/M). EHL/K monitored the project, provided liaison of all military activities, performed scrubber water sampling and inorganic analyses of these samples, conducted the bioassays, and collected noise measurements. EHL/M collected the gas and particulate samples from the combustion and scrubbed effluent gases and performed inorganic analyses of these samples. West Coast Technical Service (WCTS) of Cerritos, California, under subcontract to The Marquardt Company, performed organic analyses of all EHL test burn samples. The test burn schedule was arranged so that WCTS analyses of samples could commence on the day following sample collection.

## 2.6 Theoretical Combustion Data

Computer analysis of the combustion process was performed as detailed in Appendix A. Theoretically expected combustion products included CO, N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, HCl, O<sub>2</sub>, NO and monatomic chlorine. Figure A-1 presents theoretical combustion temperatures as a function of "Orange" Herbicide/air mass ratios assuming inlet air at 537°R and 1000°R. The equilibrium composition of these combustion products are presented in Figure A-2 as a function of "Orange" Herbicide combustion temperatures in air. The theoretical prediction of HCl and monatomic chlorine in the combustion gases indicated a need for caustic scrubbing for the neutralization and removal of these elements from the combustion gases.

Theoretical computer analysis was also conducted to predict the effects of incomplete combustion or pyrolysis in the event of incinerator failure, particularly regarding the formation of phosgene. Gases were analyzed for "Orange" Herbicide/air mass ratios up to 1.5 times stoichiometric. See Figure A-3 and A-4. Although these studies did not indicate the formation of phosgene or any other gaseous products of incomplete pyrolysis, precautions were nevertheless taken during test operations as described in paragraph 5.

### 3.0 TEST FACILITIES

A schematic diagram of the test system is presented in Figure 1. A pictorial of the installed system components is shown in Figure 2. The major components of the system consisted of a SUE® Burner incinerator and reaction tailpipe, venturi scrubber, scrubber collection tank, natural gas and "Orange" Herbicide fuel supply systems, air supply system, caustic solution supply system, scrubber water collection system, and scrubbed effluent stack and sampling platform. Operating personnel, controls, and instrumentation were housed in a concrete block control room which was adjacent to the test setup and provided visibility of the test cell. A detailed description of the test setup and control system is described in Appendix B. The following paragraphs present a brief description of the system components and facilities utilized.

#### 3.1 Incinerator and Reaction Tailpipe

The basic air-cooled SUE® incinerator and uncooled reaction tailpipe are shown in Figure 3. Natural gas was used for system ignition and temperature stabilization. "Orange" Herbicide was injected either via slot nozzles (configuration shown) or with a single central poppet type nozzle. The incinerator/reaction tailpipe was 12 inches in diameter with a combined length of 19 feet.

#### 3.2 Venturi Scrubber and Scrubber Tank

Combustion gas leaving the reaction tailpipe passed through the venturi scrubber and into the scrubber tank. Scrubbing water or a caustic solution (NaOH/water) was injected at the venturi inlet and mixed with the combustion gas at velocities up to 400 ft/sec. in the venturi throat. Spent scrubber water was pumped from the scrubber tank to holding tanks for disposal. The water saturated, scrubbed effluent gases were discharged through the scrubber stack. See Figures 6 and 16.

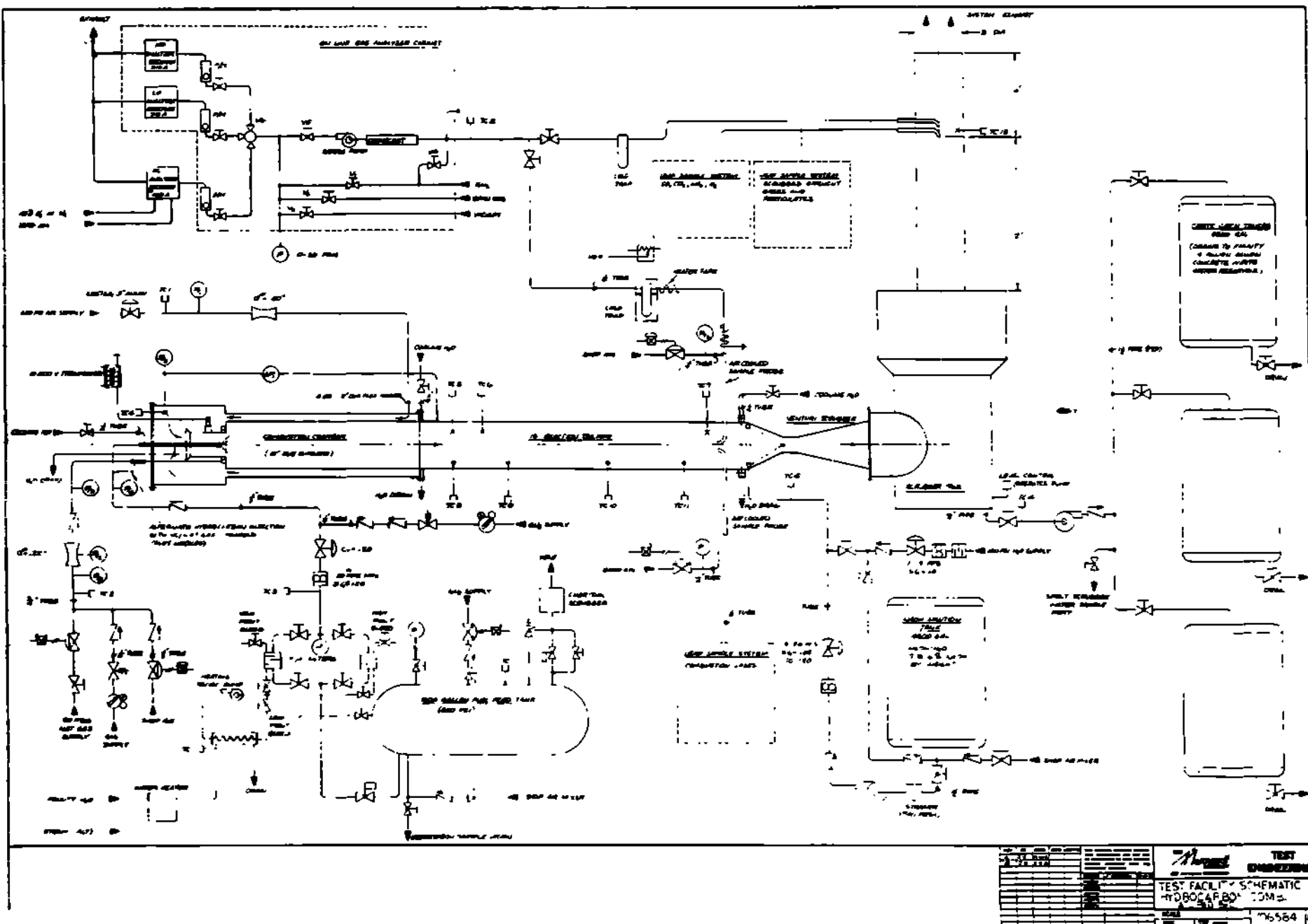
#### 3.3 Air Supply System

Combustion air was supplied from the facility air storage system via a remotely operated control valve and a choked venturi meter. See Figure 3.

#### 3.4 Natural Gas System

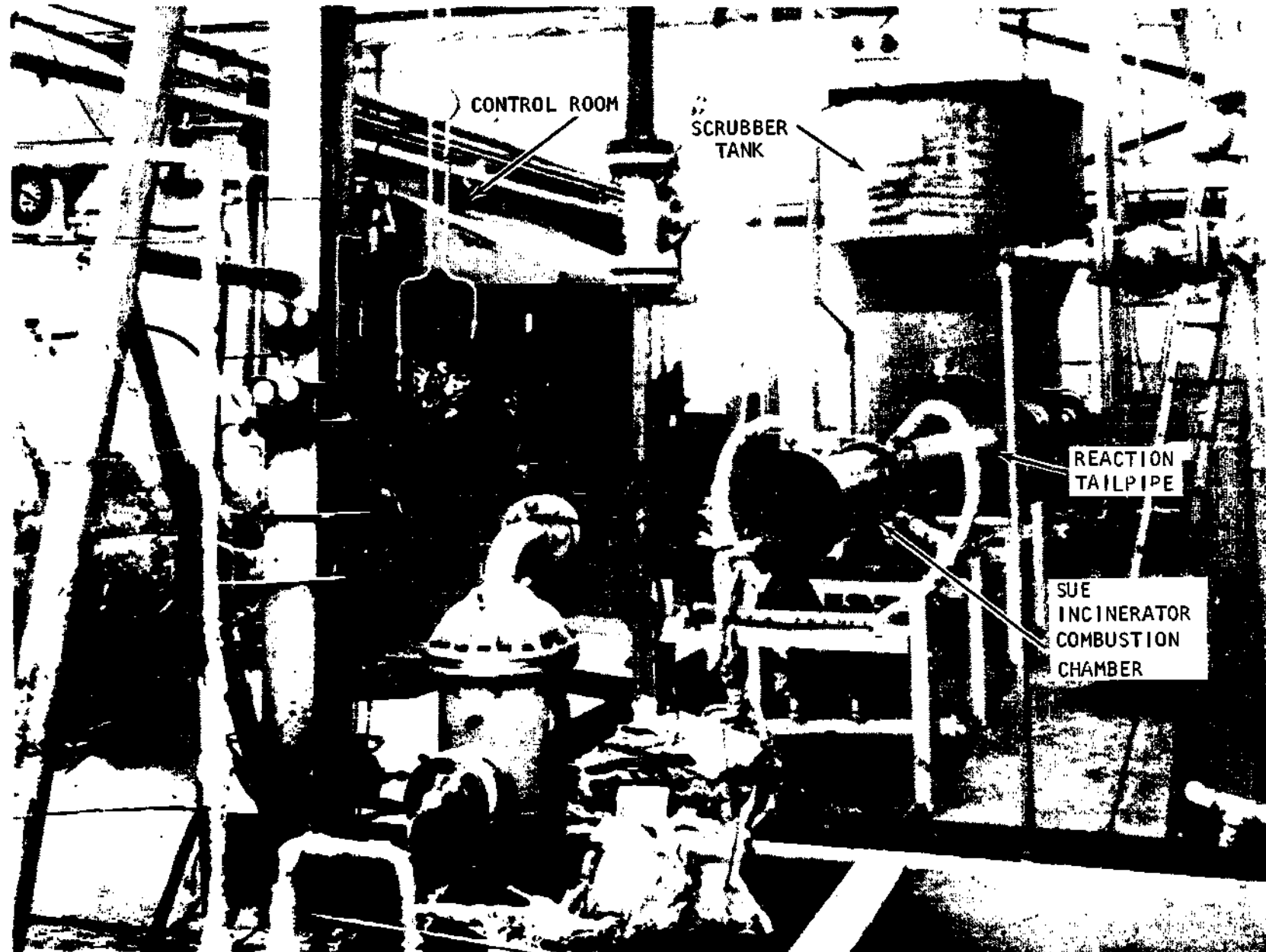
Natural gas was used to preheat the incinerator system to an equilibrium temperature (approximately 800°F) prior to introduction of the herbicide. Upon ignition of the herbicide, the natural gas was turned off and a small air flow was supplied through the natural gas system to cool the gas injection nozzles during sustained herbicide combustion. Both natural gas and cooling air mass flow were measured with a choked venturi meter. Cooling air





**FIGURE 1**

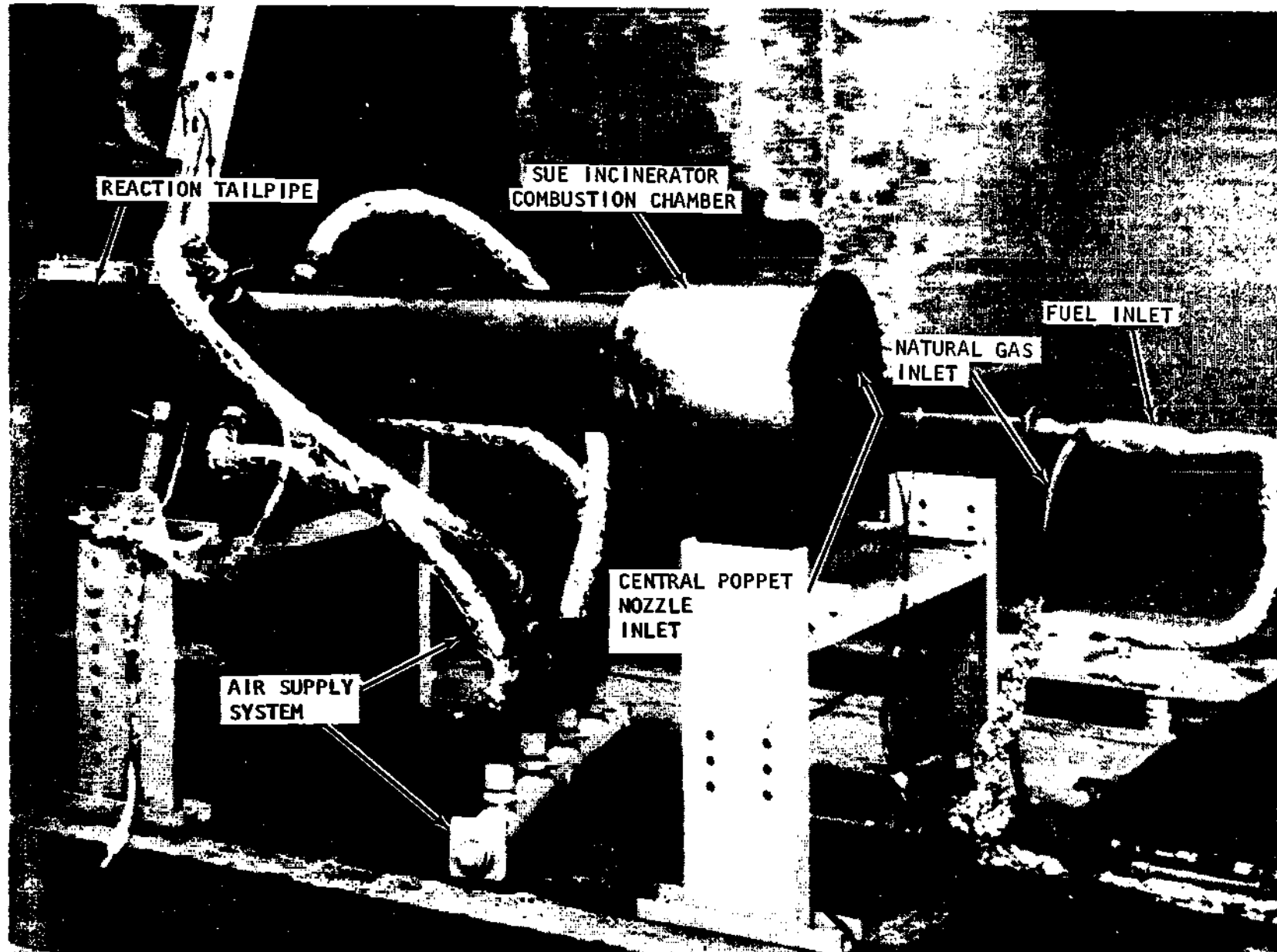
# GENERAL TEST SET-UP - ATL PAD B



8-1

FIGURE 2

# SUE INCINERATOR UNIT (SLOT NOZZLE MANIFOLD SET-UP)



NI-G 72-256-21

A71-12-565-11

flow was added to primary air flow in calculating total incinerator mass flow and fuel/air ratio. Flow was regulated by a remotely operated control regulator. A gaseous nitrogen ( $\text{GN}_2$ ) purge system was included to clean the system during shutdowns.

### 3.5 Primary Fuel ("Orange" Herbicide or JP-4) System

Fuel was supplied from a 300 gallon, 500 psig feed tank through either of two parallel 5 micron filter pots, a remotely operated control valve, and a turbine type flowmeter. This system is shown in Figure 4. The feed tank was pressurized with nitrogen which was vented to atmosphere through a charcoal bed. A herbicide fuel tank preheater was used to permit heating of the "Orange" Herbicide to 90 to 180°F prior to incineration. The fuel line to the incinerator was purged with a  $\text{GN}_2$  system. Fuel injection in the incinerator was either by a single central poppet type nozzle or a series of radial injection slot nozzles as discussed in Appendix B. A shop air bubbler was used to mix the fuel tank contents prior to test.

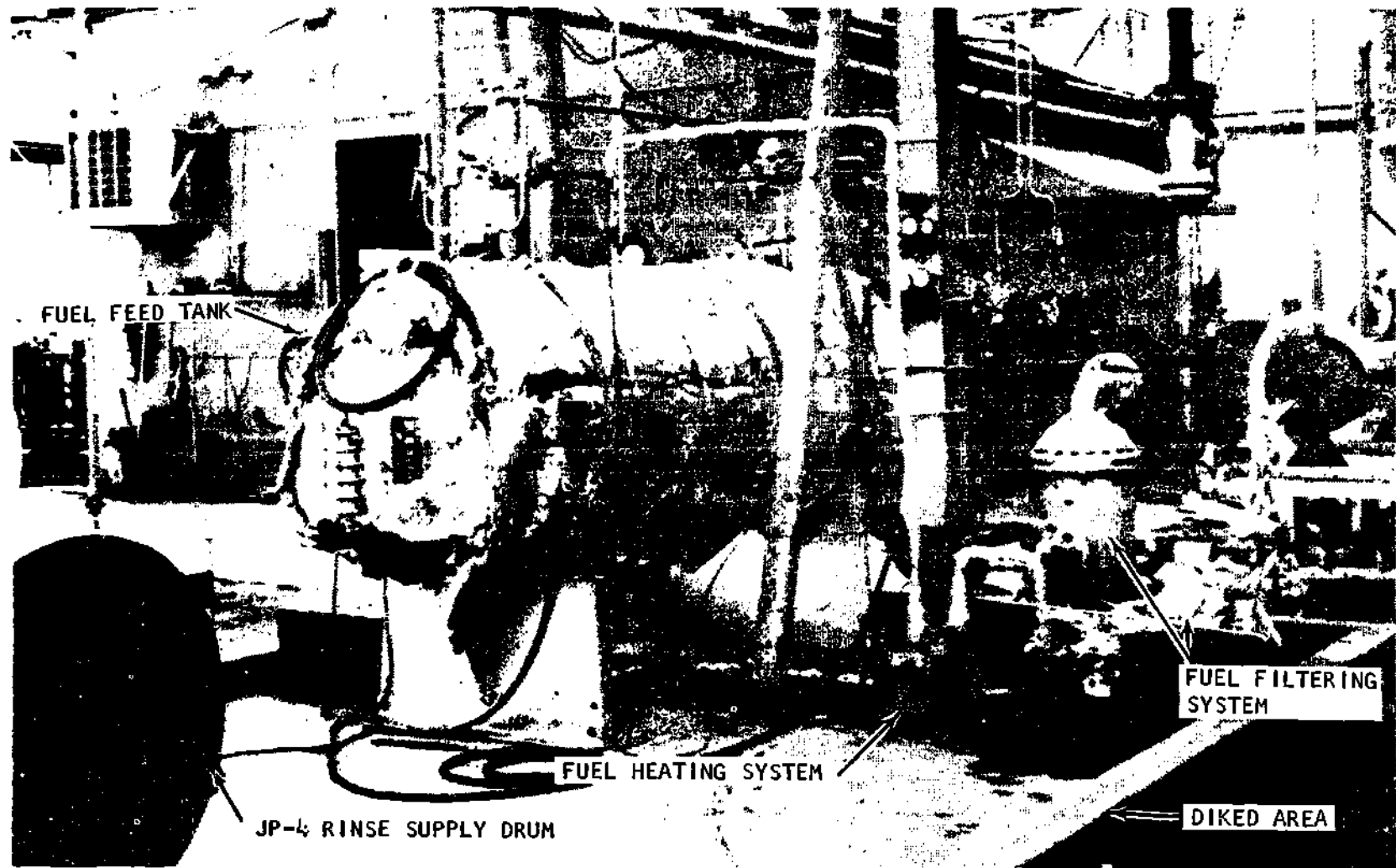
### 3.6 Caustic Solution and Water Supply Systems

A solution of NaOH and water was injected into the system at the venturi scrubber inlet to neutralize the HCl and  $\text{Cl}_2$  resulting from combustion of "Orange" Herbicide. The solution was approximately 12% by weight of NaOH and was injected at a rate to provide 1.1 to 3.1 times the amount required to neutralize the theoretically expected amounts of HCl. Fresh water was also injected at the same location to cool the combustion gases to saturation temperature, and to provide a total liquid flow of approximately 5 gpm per 1000 cubic feet of gas flow. The caustic solution was stored in a 4500 gallon tank and supplied to the control valve by a pump. See Figure 5. Caustic solution (50% by weight of NaOH) was loaded from drums into the caustic supply tank and tap water added to obtain the desired strength solution. Provisions were included to bubble shop air through the solution to ensure thorough mixing. Fresh water was supplied from the 140 psig facility system. Both flows were controlled by remotely operated control valves and metered with turbine type flowmeters. See Figure 14 foreground.

### 3.7 Scrubber Liquid Collection System

Spent scrubber water was collected in the scrubber tank and periodically pumped, by a float actuated switch, from the scrubber tank to one of three 5500 gallon holding tanks. See Figure 6. All spent scrubber water from an entire burn was thus collected and held until the results of the Air Force bioassay testing for that burn indicated that the water could be safely drained into the facility's 1.4 million gallon concrete waste water tank (also referred to as a holding pond). The system included a sample tap for the collection of spent scrubber water samples for chemical analyses and bioassay testing. Scrubber water samples were also drawn from the bottoms and sides of the holding tanks.

# FUEL STORAGE AND SUPPLY SYSTEM



NE-12 756-23

AJ-17-56-10

E-11

FIGURE 4

# CAUSTIC SOLUTION SUPPLY SYSTEM

CAUSTIC SUPPLY TANK

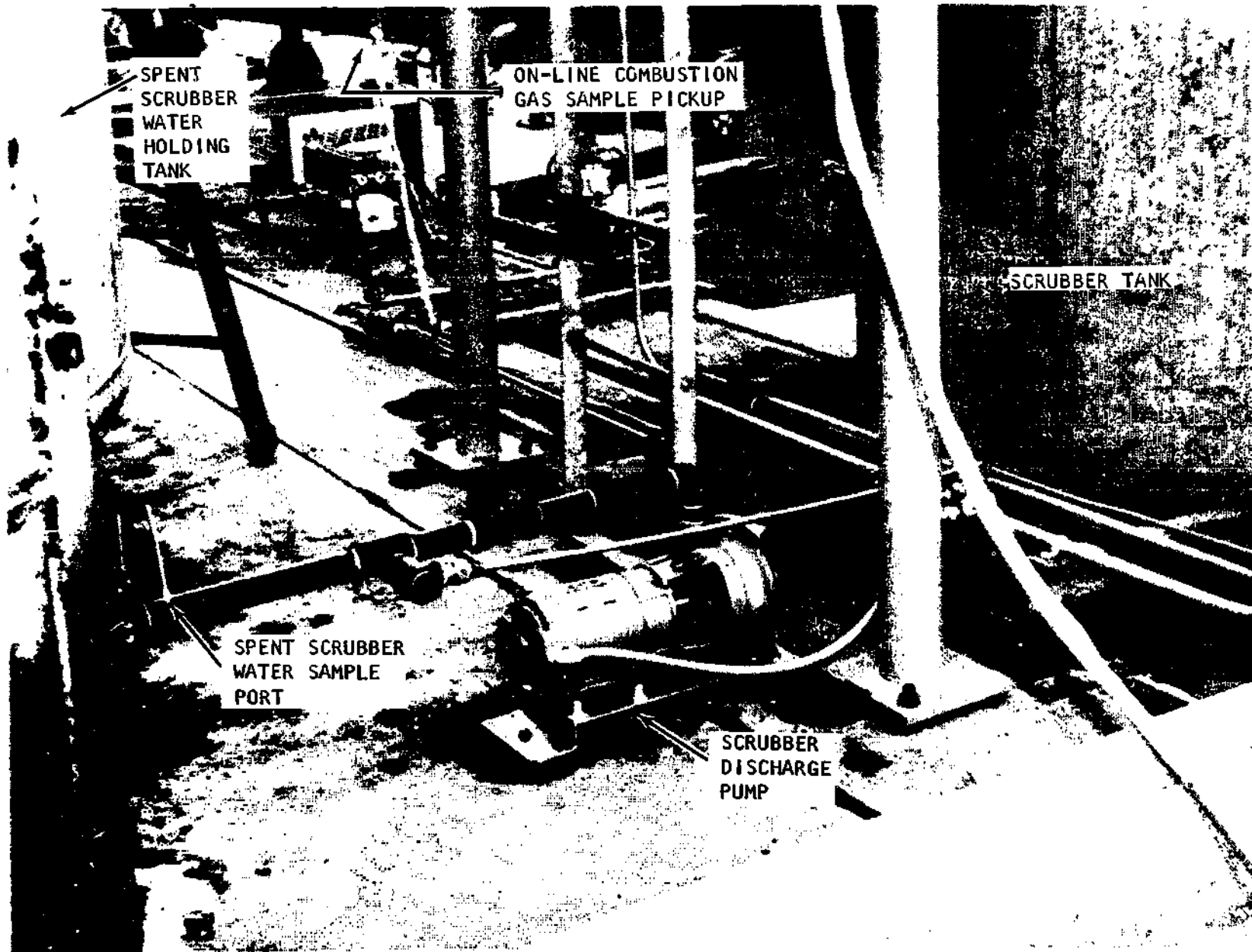
CAUSTIC SUPPLY PUMP

E-12

FIGURE 5

A73-12-505-3

# SCRUBBER DISCHARGE SYSTEM



### 3.8 Control Room

System controls were provided from the control room console. See Figure 7. Direct reading instrumentation was mounted outside the control room window. Remote reading instrumentation was located in the control room as shown in Figure 8. A complete listing of all measured parameters is included in Appendix B. All instrumentation was calibrated and certified by the Marquardt Standards Lab prior to use.

### 3.9 Test Cell

The Aero Thermo Lab, Pad B, is shown in Figure 2. This area was modified for the program by adding curbs around the cell pad, and by plugging the trench drains, to contain any possible herbicide spillage.

### 3.10 Herbicide Storage and Drum Rinsing

All "Orange" Herbicide drums, full or empty, were received and stored in a partially enclosed area north of Building 57 (about 50 yards from the test cell). See Figure 9. This area was prepared for drum storage with a resurfaced, sloping floor and completely curbed to contain a total herbicide spill. Additional protection was supplied by an existing water deluge system. The drums were transported individually to the fuel run tank area for transfer to the run tank and immediately returned to the storage area. All drum rinsing and rinse sampling was done within this diked drum storage area. A supply of JP-4 was maintained in the area for possible rinsing of herbicide spillage. All drums were kept covered with plastic sheeting as shown in Figure 9.

### 3.11 Bioassay/Inorganic Chemistry Test Area

An area was provided in Building 65 for use by EHL/K for conducting bioassays and inorganic chemical testing of the spent scrubber water. Part of the bioassay test setup is shown in Figure 10. The results and discussion of the bioassay portion of the program will be published by EHL/K at a later date under separate cover.

### 3.12 Air Sample Preparation Area

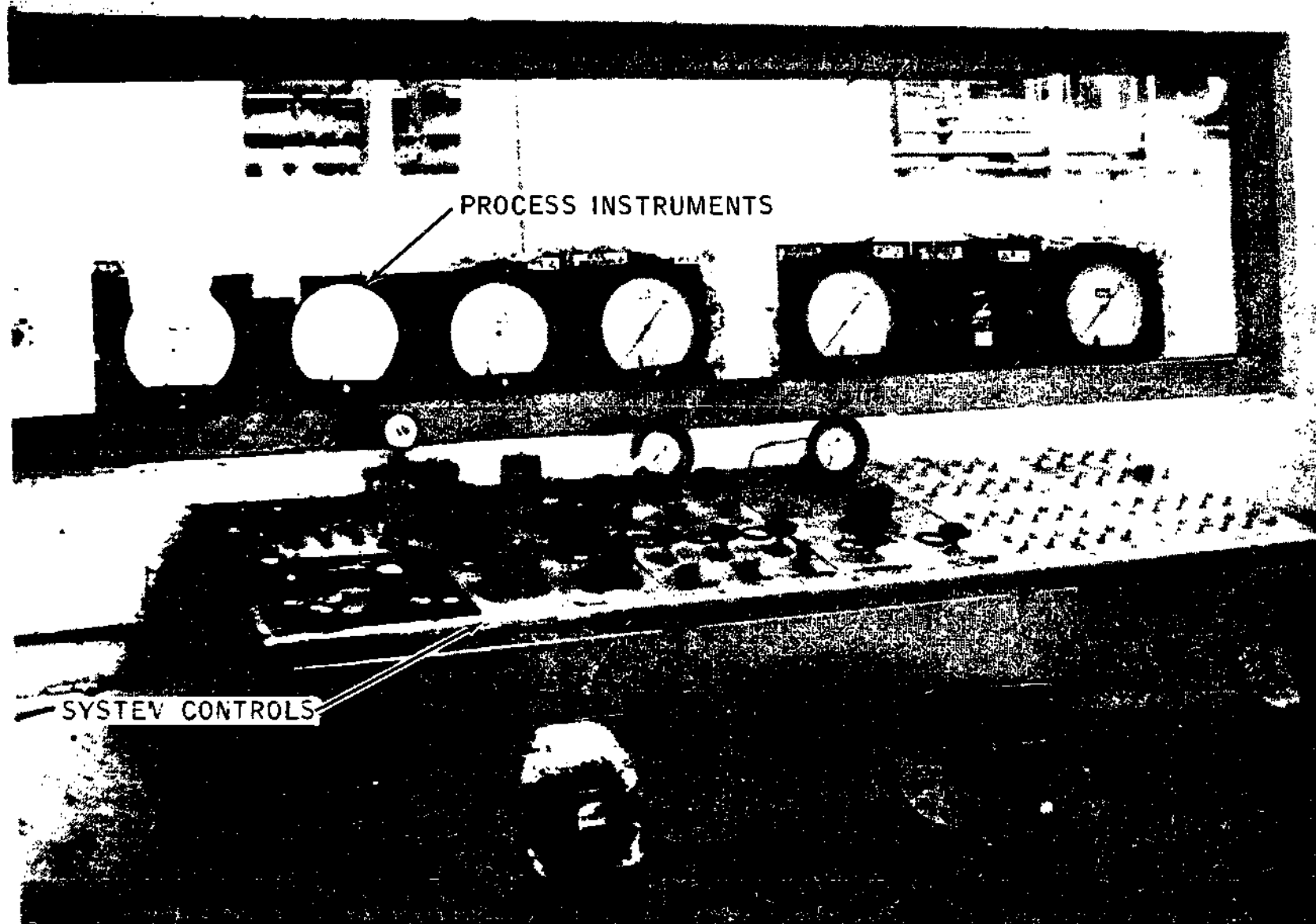
An area was provided in Building 84 for use by EHL/M in preparing the air sampling apparatus for testing. Part of this area is shown in Figure 11.

### 3.13 Other Facilities

Office space was provided for Air Force personnel in Building 26 (Engineering Building). Other facilities were used in support of testing activities, particularly the Standards Lab for weighing of residue samples.



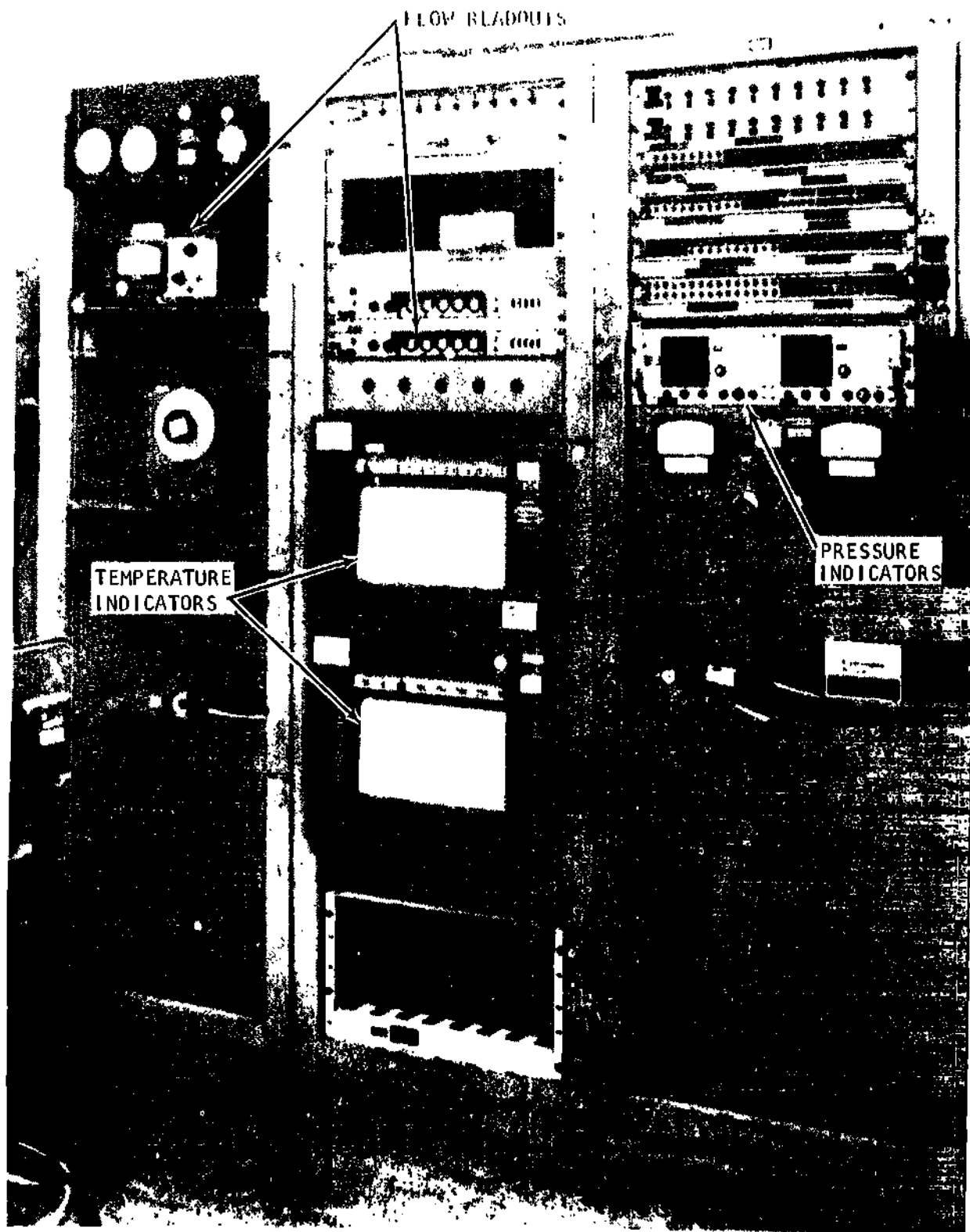
# CONTROL CONSOLE AND DIRECT INSTRUMENTATION



SYSTEM CONTROLS

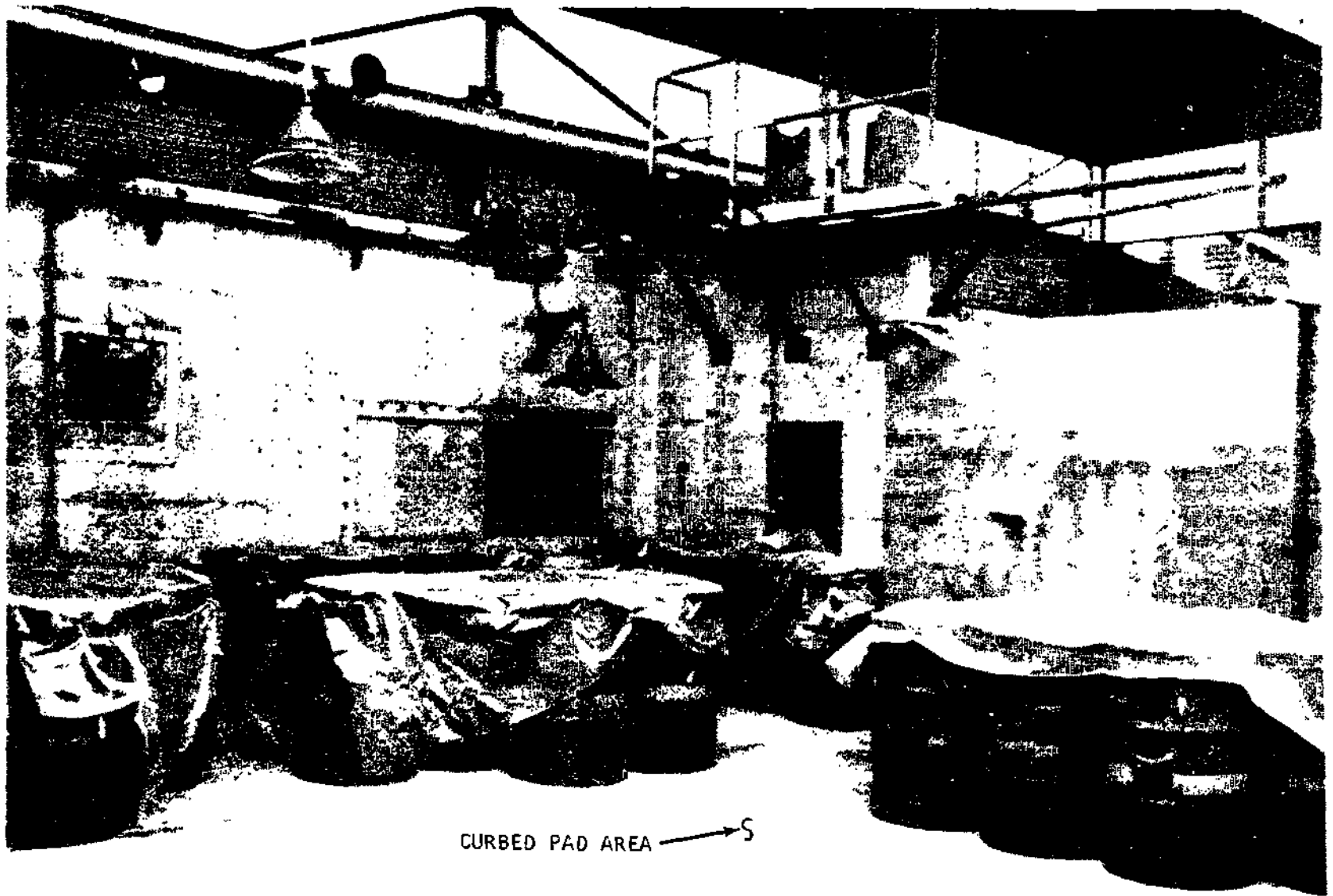
PROCESS INSTRUMENTS

## REMOTE INSTRUMENTATION AND RECORDERS



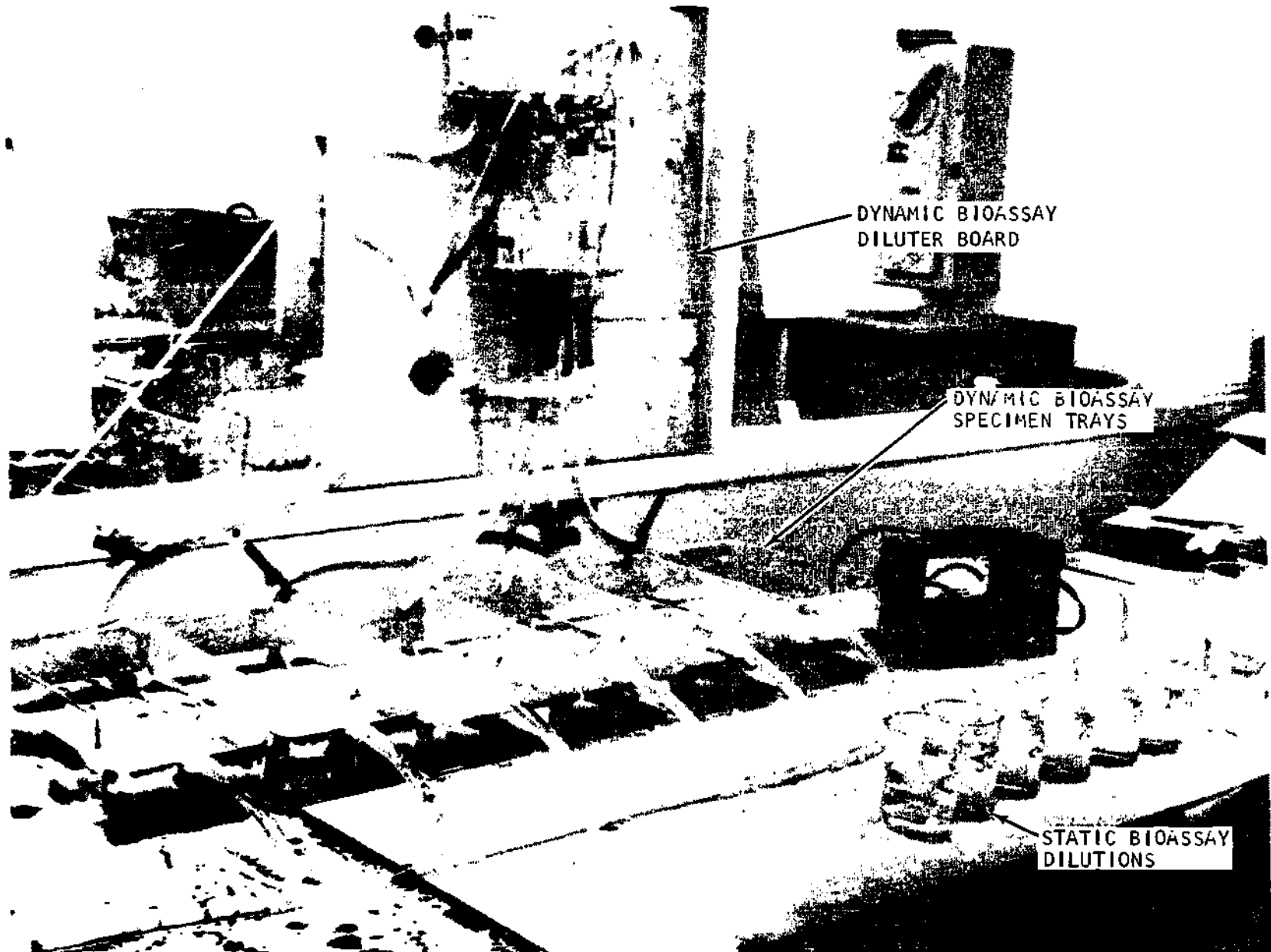
NFC 72 246 13

# DRUM STORAGE AREA



CURBED PAD AREA → S

# BIO ASSAY TEST APPARATUS - BLDG. 65



E-18

FIGURE 10

N-C 77-256-24

77-12-510-4

# GAS SAMPLING PREPARATION AREA - BLDG. 84



E-19

FIGURE 11

NE-G 12-25626

A 7-1-12-765 /

## 4.0 GAS AND LIQUID SAMPLING SYSTEMS

Analyses of combustion gas, scrubbed effluent gas, spent scrubber water, and system residue was of prime importance in this program. A considerable portion of pre-test effort was devoted to preparation of these systems by EHL/K, EHL/M, and The Marquardt Company. A pre-test meeting was held on 9 November 1973 between these parties and Dr. Fisher of West Coast Technical Service, Inc. to finalize plans for sample analyses and to establish procedures for Air Force monitoring of sample analyses, sample deliveries and data feedback. A detailed description of the sample collection and analyses procedures is presented in Appendices C through G and I. The following paragraphs provide a brief description of sampling system elements.

### 4.1 On-Line Equipment

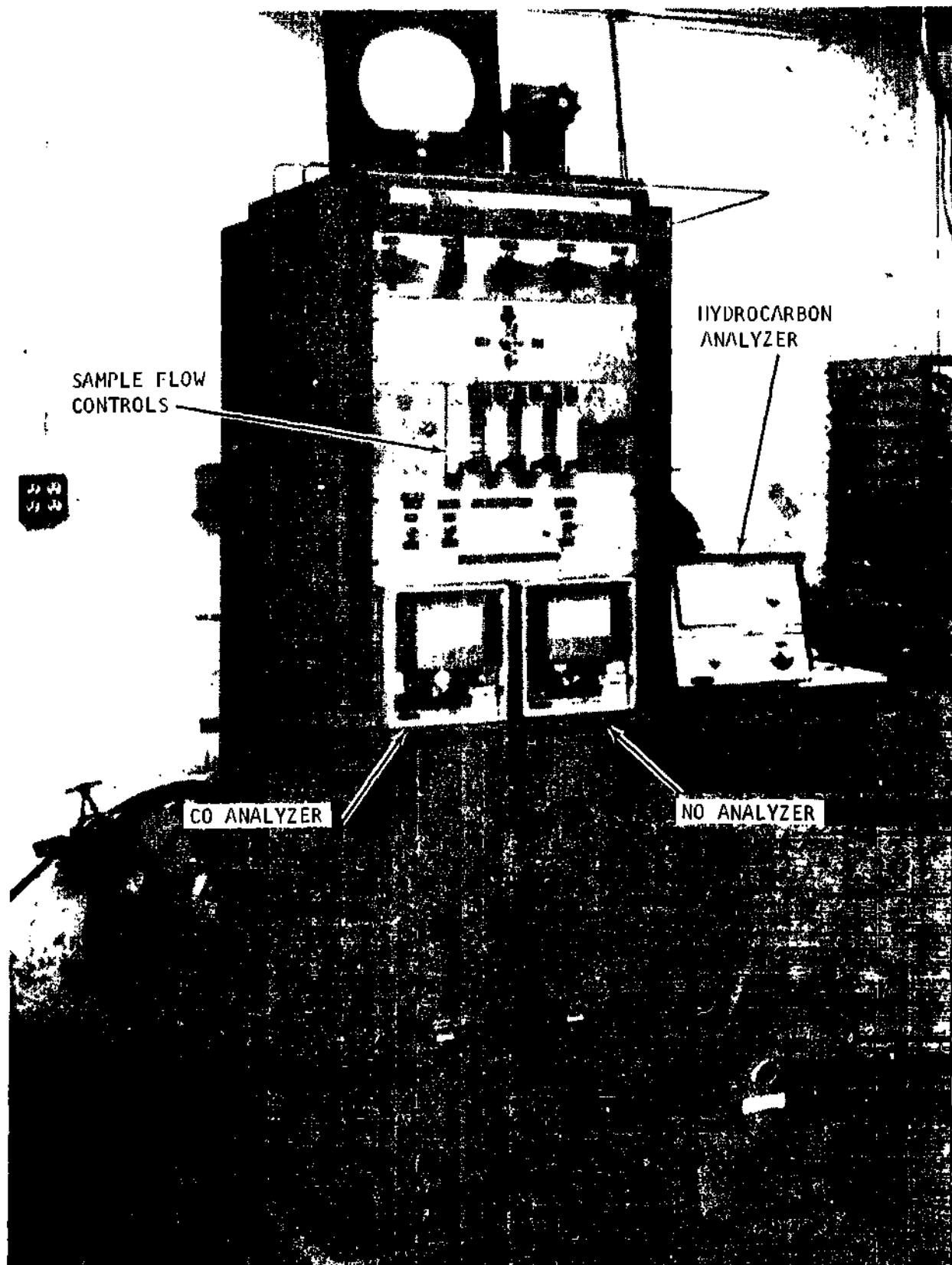
An on-line system using Beckman gas analyzers was used during testing for quick determination of CO, NO, and hydrocarbon (HC) concentrations produced. This system permitted determination of the effects of variations to test parameters and a relative indication of combustion efficiency. The system was used to sample combustion or scrubbed effluent gases. This equipment was located in the control room and is shown pictorially in Figure 12. Combustion gases were extracted from the reaction tailpipe with an air cooled probe. See Figure 13. This probe, with a 1/8 inch inner gas tube, extended into the gas stream about 5 inches and faced upstream. Combustion gases extracted through the probe were maintained at approximately 300°F in heated tubing before passage through a cold trap and into the analyzer system. Scrubbed effluent gases were extracted with a plain tube probe and passed through unheated tubing and a cold trap before entry into the analyzer system.

Calibrations were performed on the Beckmans before each test and sometimes during or after testing. Pertinent analyzer data were:

- The NO analyzer was a Beckman Model 315A infrared analyzer, span 0 to 2000 ppm. Nitrogen was used as a "zero" calibration gas. A 205 ppm NO/balance N<sub>2</sub> gas was used for "span" calibration.
- The CO analyzer was a Beckman Model 315A infrared analyzer, span 0 to 5000 ppm. Nitrogen was used as a "zero" calibration gas. A 415 ppm CO/balance N<sub>2</sub> gas was used for "span" calibration.
- The HC analyzer was a Beckman Model 109A hydrocarbon analyzer which used the flame ionization method of detection. Process gases were 40% H<sub>2</sub> in N<sub>2</sub> and "zero" air. The "zero" air was also used as a "zero" calibration gas. A 390 ppm C<sub>3</sub>H<sub>8</sub>/balance N<sub>2</sub> gas was used for "span" calibration.

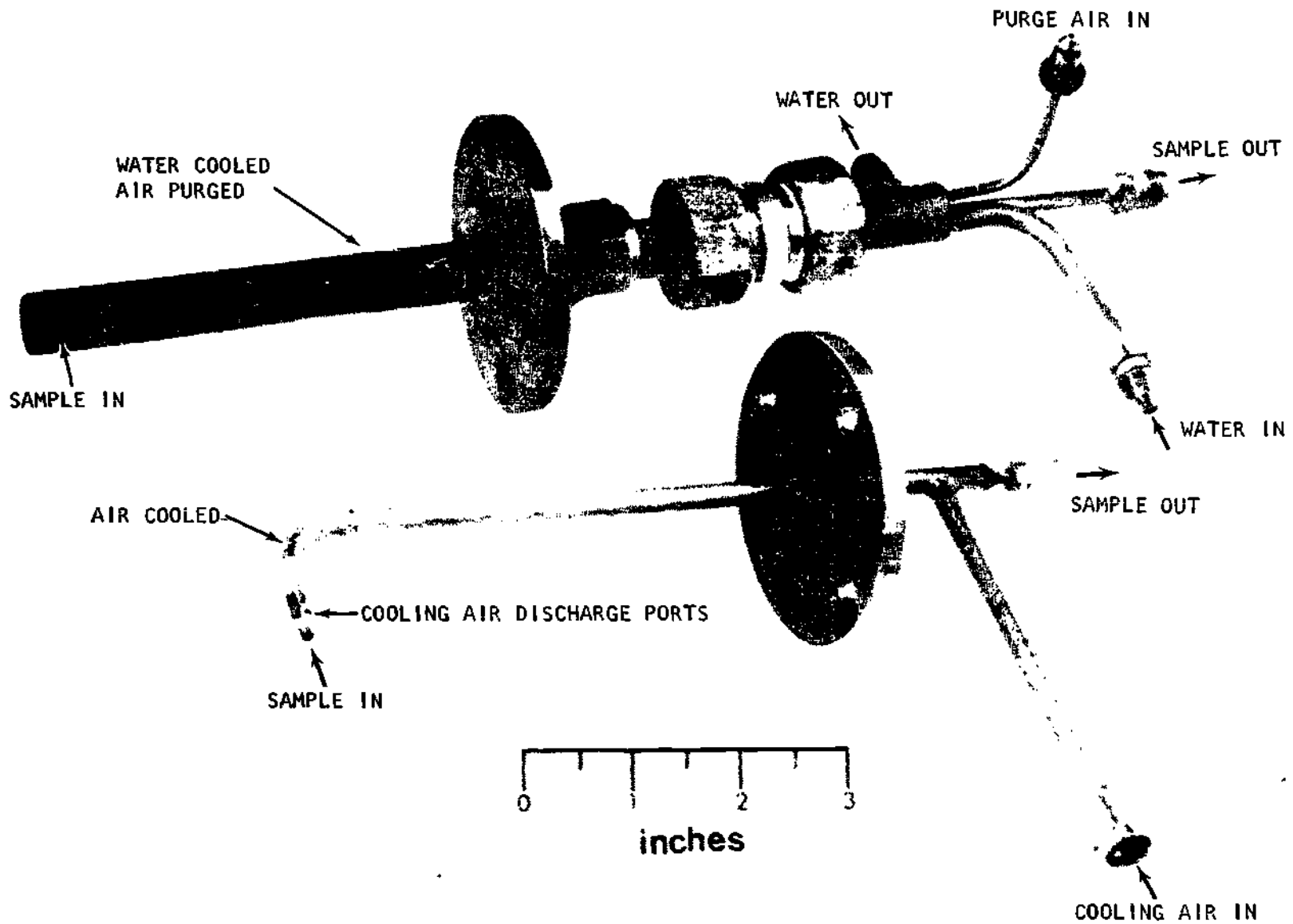
# ON-LINE GAS ANALYSES EQUIPMENT

AFS 12 565 10



AFS 12 565 10

# COMBUSTION GAS SAMPLING PROBES



E-22

FIGURE 15

NF-G 77-256-29

473-12-565-17



#### 4.2 Combustion Gas Sampling

The combustion gas sampling apparatus was supplied and operated by EHL/M. The combustion sampling train setup is shown in position at the exit of the reaction tailpipe in Figure 14. This apparatus was connected by the umbilical to the remotely stationed flow control apparatus shown in Figure 15. The sampling train extracted gas through either an air cooled probe identical to that described in paragraph 4.1, or from the water cooled probe shown in Figure 13. The water cooled probe incorporated a purge air bleed feature to keep combustion gas out of the probe until sampling was initiated. A detailed description of the combustion gas sampling equipment and procedures is presented in Appendix D.

#### 4.3 Scrubbed Effluent Gas Sampling

Scrubbed effluent gas and particulate sampling was also performed by EHL/M. The sampling equipment with integral probes were operated from a platform and withdrew gases 6 feet below the top of the stack exit. The setup is shown in Figure 16. Figure 17 depicts the apparatus in use during actual testing. A remotely stationed flow control station was also used in this system (Figure 15). See Appendix D for details of this equipment.

#### 4.4 Spent Scrubber Water Sampling

Spent scrubber water samples were collected during the scrubber water pumping cycles of each test burn. These samples were composited for chemical analyses and bioassay tests. The sample tap was located just downstream of the discharge pump as shown in Figure 6. A detailed description of scrubber water sampling is included in Appendix E.

#### 4.5 Herbicide Sampling

Samples of undiluted herbicide were drawn from the mixed fuel supply tank prior to each test burn. Sample analyses provided characterization of the composite herbicide mix from the various drums used to load the tank.

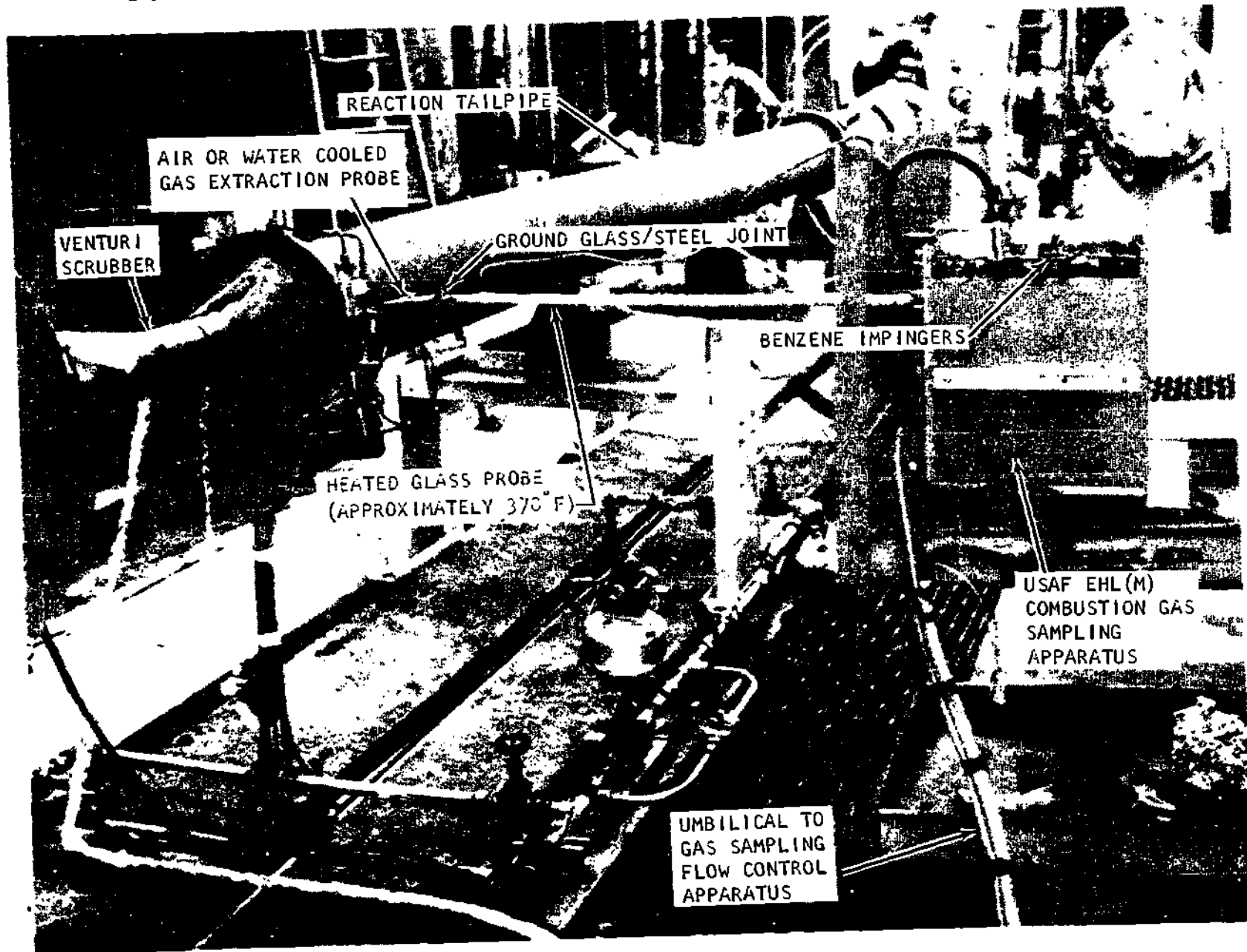
#### 4.6 Drum Rinse Sampling

Each supplied "Orange" Herbicide drum was allowed to free drain until empty and then rinsed three times with specified quantities of JP-4. These rinse solutions were sampled and analyzed by EHL/K to determine the effectiveness of rinse operations. See Appendix F for detailed description of drum cleaning procedures.

#### 4.7 System Residue Sampling

Residue samples were manually collected from the combustion chamber at various times between test burns. These samples were placed in new aluminum foil and given to EHL/K to weigh and forward to WCTS for organic analyses.

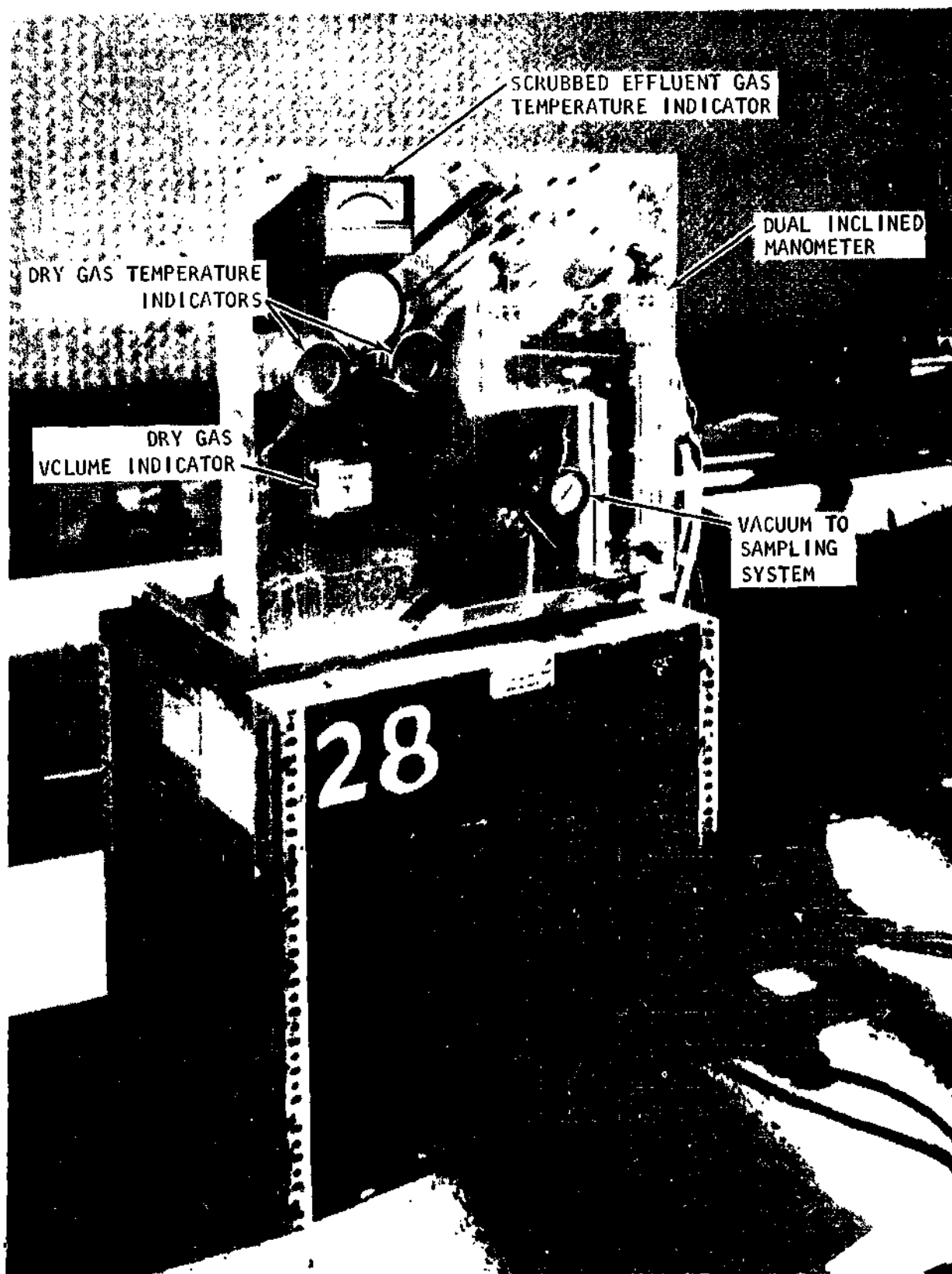
# USAF EHL/M COMBUSTION GAS SAMPLING APPARATUS



E-24

FIGURE 11

## USAF EHL(M) GAS SAMPLE FLOW CONTROL APPARATUS



NEG 72-256-16

FIGURE 15

# GAS EFFLUENT STACK

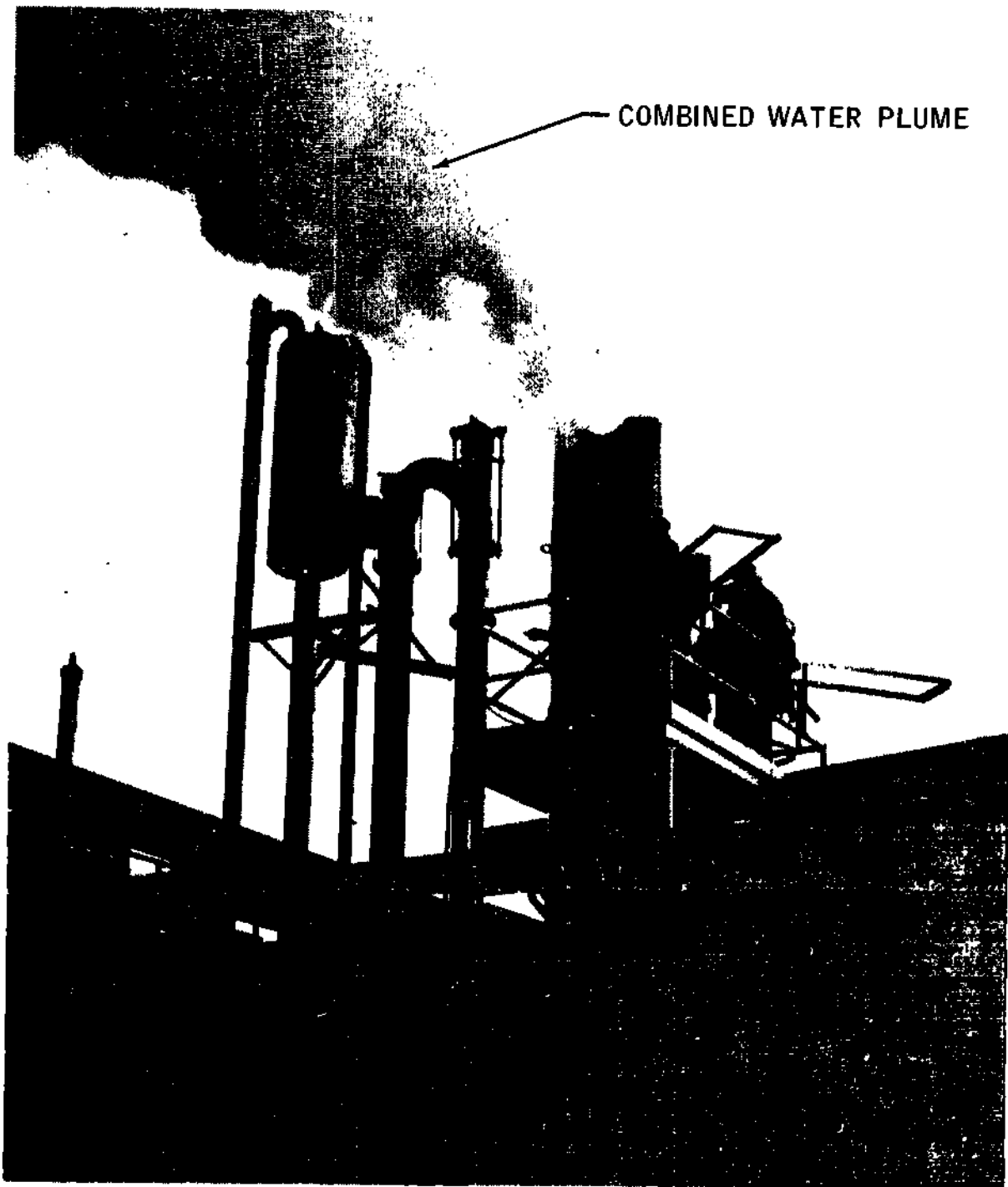
A73-12-565-9



NEG 72-258-19

FIGURE 16

# SCRUBBED EFFLUENT SAMPLING DURING TEST



NEG 72-256-11

FIGURE 17

## 5.0 SAFETY AND HANDLING

Due to the potential hazards of this program, certain facilities and operations were established to ensure safe storage, handling and disposition of "Orange" Herbicide. In addition, requirements were established regarding monitoring inspection, personnel physical examinations, special equipment usage, herbicide handling, and general procedures which are discussed in detail in Appendix H. Since The Marquardt Company has a long history of activities involved in use of toxic propellants, safety considerations were guided by established procedures regarding such materials. Other comments relative to the handling of "Orange" Herbicide during this program have been incorporated into Sections 7 and 13.

## 6.0 INCINERATOR TEST BURN PROCEDURES

This section outlines the general preparations and procedures used throughout the program.

### 6.1 Systems Preparation

The test system was assembled as shown in Figure 1 and as discussed in Section 3.0 and in Appendix B. Some modifications were made to the system during the program as operating experience developed. These changes are discussed later. Considerable effort was expended to ensure the operational reliability of this system, such as:

- All flow systems, particularly fuel, were thoroughly flushed and cleaned.
- Most system elements (valves) were overhauled. Seals and wearable components were replaced.
- Completed systems were pressure and flow checked.

These efforts were dictated by the nature of the herbicide and by the contract test schedule. Also, these efforts paid off in that no significant systems problems were encountered throughout the test sequence.

### 6.2 Preliminary Testing

Preliminary tests were conducted using JP-4 as the primary fuel to check out the entire system and obtain operating experience. Test and operating conditions expected to be used for herbicide combustion were simulated and the system was found to operate satisfactorily.

### 6.3 Herbicide Loading and Preheating

Herbicide was loaded prior to each test as required to give a full fuel feed tank for each burn. "Orange" Herbicide drums were picked at random. Once loaded, the tank's contents were agitated with shop air to ensure complete mixing. A sample was then withdrawn for WCTS organic analysis of the blended herbicide feed. After the first test burn with "Orange" Herbicide (Test Number 4), it was concluded that preheating of the blended herbicide was required to obtain the fluid properties necessary to achieve rated fuel mass flow rates. For all subsequent tests, the "Orange" Herbicide was preheated utilizing a hot water heat exchanger. Fluid temperatures were elevated to approximately 90 to 110°F except for a single test where preheat to approximately 180°F was utilized.

### 6.4 Typical Burn Sequence of Events

A detailed incinerator burn procedure was generated to prescribe the steps required to place the system in operation, to conduct the test, to shut down, and to provide safety verifications. A generalized burn consisted of the following sequential steps:

- a. Prepare all systems for incinerator testing.
- b. Establish pad area isolation and personnel accountability.
- c. Establish the desired air mass flow rate through the incinerator.
- d. Turn on the tap water to the desired flow rate for combustion gas cooling and scrubbing and to adjust the caustic to the desired strength.
- e. Turn on natural gas, ignite it, and allow the incinerator to stabilize at 800 - 1000°F (10 - 20 minutes).
- f. Turn on caustic solution flow to the desired flow rate.
- g. Introduce herbicide and establish combustion. Turn off natural gas.
- h. Adjust herbicide flow to the rate desired to produce the required average theoretical combustion temperature.
- i. Initiate phosgene gas monitoring in the pad area.
- j. Record data parameters periodically.

- k. Establish scrubber water sampling routine.
- l. Establish noise data collection.
- m. Initiate combustion and scrubbed effluent gas sampling after about one hour of burning on condition.
- n. Continue test burn until fuel feed tank empties or a desired total burn time has elapsed.
- o. Reestablish natural gas flow and combustion.
- p. Terminate herbicide flow and purge line with GN<sub>2</sub>.
- q. Terminate caustic solution flow.
- r. After system stabilization, terminate natural gas flow, scrubber cooling tap water flow, and air cool the system.
- s. Terminate air flow.
- t. Secure all systems.

## 7.0 INCINERATOR TEST PROGRAM

### 7.1 General

A total of 16 test runs were made during the program as summarized on Table 1. Tests were grouped as follows:

- Tests 1, 2, 3 - Preliminary tests on JP-4
- Tests 4, 5 - Preliminary tests on "Orange" Herbicide
- Tests 6 through 13 (AF Record Burns I through VIII) - Record tests on "Orange" Herbicide
- Tests 14, 15 - Incineration of JP-4/"Orange" Herbicide rinsings
- Test 16 - Final system flush with JP-4

Table 1 also summarizes loading of "Orange" drums in time sequence of the program. All "Orange" Herbicide supplied by the Air Force was destroyed (1540 gallons).

### 7.2 Combustion Temperatures

The contract specified that a minimum of two record burns be made at each of three different theoretical combustion temperatures: specifically, 2100°F, 2500°F, and 2900°F. Because the temperature in the combustion chamber could not be measured



TABLE 1

## GENERAL TEST PROGRAM EVENT SUMMARY - "ORANGE" HERBICIDE INCINERATION

Date (1973)	Drums Loaded (EHL/K No.)	Test No.		Start Time	Dura- tion (Min.)	Fuel	Orange Used (Gal.)	Remarks
		TMC	AF Burn No.					
11-1		1	-	14:20	60	JP-4	-	Initial systems checkout. 1.5 pps air, exit temp to 2200°F. Poppet nozzle.
11-2		2	-	13:15	135	JP-4	-	Systems check. 1.5 pps air, TCAVG of 2100, 2500, 2900°F
11-8		3	-	15:15	60	JP-4	-	Systems check. AF sampling. 1.5 pps, TCAVG to 2900°F
11-10	62,63 64,65							No transfer problems
11-12		4	-	11:45	15	Orange	6	Initial Orange combustion. System mods required.
11-13		5	-	11:44	15	Orange	14	Satisfactory systems check.
11-13		6	I	14:01	191	Orange	143	Satisfactory low temp burn. 1.5 pps air. Poppet nozzle.
11-15	76,77, 91							No transfer problems.
11-16		7	II	15:05	218	Orange	165	Satisfactory low temp burn. 1.5 pps air. Poppet nozzle.
11-17	78,80 89,92							No transfer problems.
11-19	86,87, 90	8	III	13:41	235	Orange	216	Satisfactory med temp burn. 1.5 pps air. Poppet nozzle.

TABLE 1 (Cont'd)

Date (1973)	Drums Loaded (EHL/K No.)	Test No.		Start Time	Dura- tion (Min.)	Fuel	Orange Used (Gal.)	Remarks
		TMC	AF Burn No.					
11-20		9	IV	13:10	236	Orange	216	Satisfactory med temp burn. 1.5 pps air. Poppet nozzle.
11-26	71,81, 82,84							No transfer problems.
11-27		10	V	12:45	213	Orange	221	Satisfactory high temp burn. 1.5 pps air. Slot nozzles.
11-28	69,73, 66,83, 85,88	11	VI	10:32	136	Orange	124	Short medium temp burn. 1.5 pps air. Slot nozzles.
11-29	68,70, 74,75	12	VII	9:13	213	Orange	222	Satisfactory high temp burn. 1.5 pps air. Slot nozzles.
11-30		13	VIII	8:56	356	Orange	245	Satisfactory high temp burn. 1.0 pps air. Slot nozzles. All Orange burned.
12-5		14	-	11:00	296	JP-4 Orange	~17	Rinse solution burn.
12-6		15	-	13:30	130	JP-4 Orange	~4	Final rinse solution burn.
12-7		16	-	13:54	127	JP-4	-	Final system rinse burn. All program burns completed.

directly and this temperature was not representative of the gas temperature throughout the incinerator, the contractually specified combustion temperature was defined as the "average theoretical combustion gas temperature" (TC<sub>AVE</sub>). This value was calculated as the average of the "theoretical temperature of combustion" (TC<sub>THEO</sub>) as determined by computer analysis, and the measured combustion gas temperature at the reaction tailpipe exit (TC<sub>7</sub>). The computer program calculations were based on least entropy considerations to predict the equilibrium chemical products of combustion, the theoretical combustion temperature (TC<sub>THEO</sub>), and the thermodynamic properties of the combustion gas. The computer program inputs included "Orange" Herbicide/air mass ratios, ambient "Orange" Herbicide and air temperatures, and combustion chamber pressure. See Appendix A. The predicted TC<sub>THEO</sub> values were considered to be the temperatures achieved within the combustion chamber at a point half way between the "flameholder" and the entry into the reaction tailpipe.

Prior to the initiation of "Orange" Herbicide testing, a range of possible incinerator conditions was analyzed by the computer program. From this data the selection of "Orange" Herbicide/air mass ratios was made prior to each burn which would achieve the desired TC<sub>AVE</sub>. Upon testing completion, computer analysis was performed using actual recorded data for each burn condition to determine TC<sub>THEO</sub>, and therefore TC<sub>AVE</sub>, for each burn.

Achieved actual TC<sub>AVE</sub> values were about 1800° above the target of 2100°F, within about 700° of the target of 2500°F, and about 1450°F below the target of 2900°F. The differences at the high and low target conditions were attributed to:

- The selection of a nearly constant air mass flow rate (1.55 pps) for all burns except Burn VIII.
- The contract requirement that excess combustion air be greater than 30%.
- Increased radiation heat losses from the reaction tailpipe as combustion gas temperatures increased.

The increased reaction tailpipe skin temperatures supported the contention of increased radiation heat losses. These radiation losses kept TC<sub>7</sub> temperature at near constant values for all burns and this produced lower calculated TC<sub>AVE</sub> values than were targeted for the higher temperature burns.

### 7.3 Summary of Incinerator Functioning

The functioning of the incinerator and systems was very satisfactory and is summarized as follows:

- There were no structural failures or leaks of the incinerator system.
- There were no leaks, plugging, or filter flow problems in the herbicide supply system.
- There were no problems in supply or collection of caustic solution and spent scrubber water except for a plugged screen in the spent scrubber water discharge line which was cleaned.
- Transition to combustion of "Orange" Herbicide was very smooth and the herbicide burned smoothly over all the tested temperature ranges without visible (smoke or odor) or audible evidence of poor combustion.
- No blowouts were experienced when burning the undiluted herbicide.
- No emergency shutdowns were required and normal transition back to natural gas was accomplished without difficulties.
- There were no modifications made to the basic configuration except that slot nozzles were used on Test No. 10 (Record Burn V) and subsequent tests in place of the central poppet nozzle.

#### 7.4 Test Descriptions and Data

A summary of test data for the eight record burns is presented in Table 2. Process flow rates, pressures, and temperatures were recorded periodically throughout each test and the average or high/low values presented in Table 2. Calculated process parameters are presented and the basis for these calculations shown at the bottom of the table. The following items are noted:

- TCTHEO and TC<sub>AVE</sub> were calculated using the computer program as discussed in paragraph 7.2.
- The stoichiometric "Orange" Herbicide/air mass ratio was 0.162 from chemical equilibrium of a 50/50 by volume mixture of 2,4-D and 2,4,5-T in air.
- The required theoretical amount of NaOH was the product of 0.31 pound HCl generated per one pound of "Orange" Herbicide burned times 1.1 pounds NaOH to neutralize one pound of HCl.
- Excess air was defined as the weight of air not reacted divided by the weight of air actually reacted.
- "Orange" Herbicide mass flow (pps) recorded during test was corrected for actual viscosity and specific gravity as determined by the fluid temperature at the flowmeter.

TABLE 2

E-35Column  
No.

- 15  $TC_{THEO}$  = Theoretical max. combustion temperature based on fuel/air ratio,  $TC_4$ , and average  $PT_3$
- 16  $TC_{AVG}$  Defined = Average of  $TC_{THEO}$  and  $TC_7$
- 17  $TSKIN$  Avg = Average of reaction tailpipe skin temperatures  $TC_8$  and  $TC_{11}$
- 18 Combustion Chamber Velocity based on  $TC_{AVG}$ ,  $PT_3$  avg, total mass flow, and theoretical gas composition
- 19 Stay Time = Length/burn velocity for length = 19'
- 20 Applied Avg NaOH =  $w_c \times$  weight fraction of NaOH in caustic solution
- 21  $\frac{M}{M_T} = \frac{\text{Applied avg NaOH}}{NaOH \text{ theoretically required}} = \frac{\text{Applied avg NaOH}}{w_f \times .34}$
- 26 Excess Air =  $100 \left( \frac{1}{\phi} - 1 \right)$  where  $\phi = \frac{(F/A)_{actual}}{(F/A)_{stoic}} = \frac{(F/A)_{actual}}{.162}$
- 27 Nozzle Type Code: P - Central poppet nozzle  
S - Slot nozzles

## 7.5 Summary of Each Test and Record Burn

- Test 1. Initial test on JP-4. Satisfactory ignition on natural gas and transition to JP-4 using the central poppet nozzle. Held air flow to 1.0 pps at a burner exit temperature (TC5) of 2200°F.
- Test 2. Systems checkout on JP-4 at air flow to 1.5 pps and simulated TC<sub>AVE</sub> of 2100, 2500 and 2900°F per contract requirements.
  - Minor system corrections made. System ready for "Orange" Herbicide testing but modifications and additions required for Air Force gas sampling trains.
- Test 3. Systems checkout on JP-4 with Air Force sampling systems installed. Air flow to 1.5 pps and TC<sub>AVE</sub> of 2900°F.
  - Fuel system drained of JP-4 and loaded with four drums of "Orange" Herbicide. Loading was noticeably slower as ambient temperature decreased during the loadings.
- Test 4. This was intended as the first record burn. Combustion was initiated satisfactorily on undiluted "Orange" Herbicide but fuel system pressure losses were so excessive that the desired fuel mass flow rate could not be obtained.
  - It was obvious that the "Orange" Herbicide could not be injected into the combustion chamber at the desired mass flow rate at lower temperatures (60°F) due to its very steep viscosity/temperature characteristic. (See Figure B-7.) A temporary hot water heat exchanger was added to the fuel line and the trim was changed in the fuel control valve. The Beckman system was modified to include a cold trap about 5 feet from the sample probe and sample line heating between the cold trap and the analyzer was removed. The backup (Air Force) HC analyzer was installed.
- Test 5. A checkout burn to test system modifications after Test 4 and verify satisfactory flow of preheated (90 - 100°F) "Orange" Herbicide. Satisfactory results.
- Test 6 (Record Burn I). A satisfactory low temperature (TC<sub>AVG</sub> = 2273°F) record burn at a fuel/air ratio of 0.086, and applied caustic of 3.05 times theoretical. Gas and liquid sampling accomplished satisfactorily. The area was monitored for phosgene and none was detected. Testing terminated at darkness.
- Disassembly of the burner revealed an accumulation of about 7.9 pounds of carbon residue around the combustion chamber, about 15 inches from the step, in an annular pattern. The residue

was brittle and easily removed from the wall. A residue specimen was sent to West Coast Technical Service for analyses. Patterns of these residue deposits were repeated during Burns II, III, and IV and are discussed in paragraph 10.1. A permanent heat exchanger system was added to preheat the "Orange" Herbicide to at least 90°F as shown in Figure 1. Modifications were made to the combustion chamber to ensure better air cooling. It was also noted that corrections were required to fuel flowmeter readings for viscosity effects. The fuel flowmeter was recalibrated and numerical corrections applied to all prior fuel mass flow data. The TMC Beckman HC analyzer was reinstalled.

Test 7 (Record Burn II). A satisfactory duplicate low temperature ( $TC_{AVG} = 2286^{\circ}F$ ) record run at fuel/air ratio of 0.086 and applied caustic at 3.18 times theoretical. Scrubber exit gas and liquid sampling accomplished. The combustion gas sampling probe plugged part way into the test but an adequate sample was obtained. The new "Orange" preheating system performed well and fuel temperature was maintained at about 98°F.

- The burner was again disassembled. A carbon deposit similar to that from Burn I was again present and weighed about 9 pounds. The deposit was removed and a specimen sent to West Coast Technical Service for analyses. To lengthen the test time available with the caustic supply tank, it was loaded with a higher concentration of NaOH. Caustic solution mass flow rates could then be reduced and total scrubber water flow maintained by an increased flow of tap water.
- Test 8 (Record Burn III). A satisfactory medium temperature ( $TC_{AVG} = 2567^{\circ}F$ ) record burn at a fuel/air ratio of 0.106 and applied caustic at 2.06 times theoretical. Sampling accomplished satisfactorily.
- Burner disassembly revealed another carbon deposit of 12.9 pounds which was removed and analyzed by WCTS. It was decided to preheat the fuel much higher to see if increased fuel temperature affected the quantity, size or shape of the deposit.

Test 9 (Record Burn IV). A satisfactory replicate medium temperature ( $TC_{AVE} = 2508^{\circ}F$ ) record burn at a fuel/air ratio of 0.105 and applied caustic at 2.16 times theoretical. Herbicide fuel temperature was preheated to about 177°F for this burn. This test condition appeared to move the flame closer to the inlet (step) of the combustion chamber as evidenced by the increased temperature at the inlet to the reaction tailpipe. Sampling was accomplished satisfactorily and noise measurements were taken around the test pad and in the control room.

- Burner assembly again revealed a sizeable annular carbon deposit of 2.8 pounds which was removed and sent to WCTS for analyses. The poppet nozzle was removed and the slot nozzle manifold installed for subsequent testing. It was felt that the slot nozzles would provide improved high flow combustion, and that the slot nozzle fuel pattern in the incinerator would alleviate the carbon residue problem.
- Test 10 (Record Burn V). A very satisfactory high temperature ( $TC_{AVE} = 2734^{\circ}F$ ) record burn at a fuel/air ratio of 0.120 and applied caustic at 2.23 times theoretical. Combustion with the slot nozzles was very smooth and the temperature profile down the system indicated faster burning in the incinerator. Higher  $TC_{AVE}$  was limited by the requirement of 30 percent minimum excess air. Scrubbed effluent gas and water sampling was completed satisfactorily. The combustion gas sampling probe plugged part way into the run and only a partial sample was obtained.
- Examination of the burner revealed only four small carbon deposits, these deposits being of finer grain, more flaky, and much less brittle than earlier ones. It was decided to add another medium temperature burn with the slot nozzles for comparison to Tests 8 and 9 (Record Burns III and IV).
- Test 11 (Record Burn VI). A satisfactory, but shortened, medium temperature ( $TC_{AVE} = 2454^{\circ}F$ ) record burn at a fuel/air ratio of 0.106. Caustic solution flow was reduced to provide only 1.73 times theoretical. However, an acid smell was noticed by stack gas monitoring personnel and caustic solution flow was increased to 2.23 times theoretical about one-half hour into the burn. This return to prior applied caustic conditions corrected the acid odor problem. After about one and one-half hours of operation a buildup of chamber pressure, with corresponding decrease of burner  $\Delta P$ , was noted which indicated a restriction in the venturi scrubber. Testing was terminated to investigate the problem. Gas and liquid sampling had been completed.
- Examination of the system revealed no significant restriction or other problem. It was theorized that a restriction had built up in the venturi from condensed caustic (a condition present some what during all tests) which had broken loose during shutdown, or that a piece of carbon residue from the combustion chamber had likewise caused a temporary restriction. About 1.95 pounds of carbon residue was removed from the combustion chamber, which was not as much as deposited during similar burn conditions while using the poppet nozzle.
- Test 12 (Record Burn VII). A satisfactory replicate high temperature ( $TC_{AVE} = 2772^{\circ}F$ ) record burn at a fuel/air ratio of 0.120 and applied caustic at 2.26 times theoretical. This was the last of the required burns, although additional supplies of "Orange" Herbicide remained. Sampling was completed satisfactorily and noise measurements taken.



- Test 13 (Record Burn VIII). This burn was completed satisfactorily at replicate high temperatures ( $TC_{AVE} = 2759^{\circ}F$ ) and at a fuel/air ratio of 0.118. The applied caustic was 1.29 times theoretical and the  $HCl/Cl_2$  odor was again noticed from the stack gas monitoring personnel. The air mass flow was decreased to 1.0 pps to provide data comparisons with other high temperature runs which had higher combustion chamber velocities and lower stay time. Sampling was completed satisfactorily.
- Test 14. A satisfactory burn at an estimated  $TC_{AVG}$  of  $2700^{\circ}F$  as required to destroy the first batch of JP-4/"Orange" Herbicide rinse solution, which was calculated by specific gravity of the solution to contain approximately 11% "Orange" Herbicide by weight. Testing was conducted at a fuel/air ratio of 0.060 and applied caustic of approximately 3.4 times theoretical. On-line gas sampling only was utilized which indicated very satisfactory scrubbed effluent gas properties (hydrocarbon at 10 ppm).
- Test 15. A satisfactory burn at an estimated  $TC_{AVG}$  of  $2700^{\circ}F$  to complete the destruction of JP-4/"Orange" rinse solutions (less than 8% "Orange" by weight). Testing was conducted at a fuel/air ratio of 0.050. Satisfactory on-line sampling data were collected for both combustion chamber and scrubbed effluent gases.
  - The fuel tank was loaded with approximately 80 gallons of clean JP-4 and circulated through the system.
- Test 16. A final satisfactory burn at an estimated  $TC_{AVG}$  of  $2700^{\circ}F$  to complete the cleaning of the fuel system using undiluted JP-4. Testing was conducted at a fuel/air ratio of 0.050. This completed all contractual testing requirements.

## 8.0 GAS SAMPLING RESULTS AND COMMENTS

### 8.1 Combustion and Scrubbed Effluent Gas Sampling Results (Prepared by USAF EHL/M)

Gas sampling equipment and field sampling personnel were furnished by the USAF EHL/M. The combustion and scrubbed effluent gas monitoring program is presented in detail in Appendix D. Organic analyses of gas and particulate samples were performed by WCTS. (See Appendix G and results discussed in detail in Appendix I). The results below were summarized from the discussions in Appendices D and I. The gas sampling train used for "Orange" Herbicide and related herbicidal compounds was laboratory tested with nb esters of 2,4-D and 2,4,5-T, and the acids of 2,4-D and 2,4,5-T (Appendix D).

#### 8.1.1 Gas Sampling Results:

Combustion and scrubbed effluent gas sampling was conducted satisfactorily except during Burn V. During Burn V the

air cooled sampling probe (combustion gas) clogged during sampling and a small (6 liters) sample was obtained. Otherwise, all sample volumes provided a detection level  $\leq 0.65 \times 10^{-9}$  grams per liter of sample gas (STP) for each of five "Orange" Herbicide compounds: TCDD, nb-2,4-D and nb-2,4,5-T esters, and nb 2,4-D and 2,4,5-T acids. The detection level for related herbicidal compounds was  $\leq 1.3 \times 10^{-9}$  grams per liter (STP) (Appendix G and I).

No "Orange" Herbicide compound was detected in any combustion or scrubbed effluent gas sample. Monochlorophenol ( $1.06 \mu\text{g/l}$ ) was detected in the combustion gas of Burn I but not in the combustion gas of Burns II through VIII.

#### 8.1.2 Herbicidal Compounds in Related Sampling Equipment:

Microgram quantities ( $0.7$  and  $6.5 \mu\text{g}$ ) of the nb-2,4-D and nb-2,4,5-T esters were found in the rinse from a cold trap used during Burn I. The cold trap was used to condition sample gas for the Beckman 109A hydrocarbon analyzer. The cold trap was used during two "Orange" Herbicide checkout burns. It was not rinsed before use in the successful record Burn I. The nb-esters were not considered to have been deposited during record Burn I (see discussion, Appendix I).

Microgram quantities ( $1.38$  and  $0.7 \mu\text{g}$ ) of dichlorophenol were detected in the rinse of the combustion gas air cooled sampling probes from Burns II and III. This compound was concluded to have been formed in the probes by reaction of  $\text{Cl}_2$  and  $(\text{Cl})$  on the nonchlorinated aromatic hydrocarbons condensed by the probe (see discussion, Appendix I).

Microgram quantities ( $1.2$ ,  $0.1$  and  $0.1 \mu\text{g}$ ) of dichlorophenol were also detected in the rinses of the cold traps (Beckman 109A) from Burns I, II and III. This compound was concluded to have been formed as discussed in the preceding paragraph (see Appendix I).

Microgram quantities ( $1.3$  and  $0.1 \mu\text{g}$ ) of dichlorophenol were detected in the water from the scrubbed effluent gas particulate source sampling train impingers from Burns IV and VI. An evaluation of all available data indicated that this compound was not associated with "Orange" Herbicide incineration (Appendix I).

#### 8.1.3 Nonchlorinated Aliphatic and Aromatic Hydrocarbons and Biphenyl in Gas Samples:

Biphenyl was detected in all scrubbed effluent gas samples at an average mass concentration of  $46 \times 10^{-9}$  grams per liter (STP).

Aliphatic hydrocarbons in the combustion and scrubbed effluent gases centered around  $\text{C}_{10}$ , ranging from  $\text{C}_7$  through  $\text{C}_{15}$  (Appendix G).

Aromatic hydrocarbons in the combustion and scrubbed effluent gases centered around a C<sub>4</sub> benzene substituted side-chain (C<sub>6</sub>H<sub>5</sub> (C<sub>4</sub>H<sub>9</sub>)). The sidechain appeared saturated (Appendix G).

#### 8.1.4 Relative "Orange" Herbicide Pyrolysis Efficiencies and General Comments:

Relative "Orange" Herbicide pyrolysis efficiencies (RPE) were calculated (based on carbon mass collected in the TCDD sampling train and carbon mass feed into the incinerator) for each burn. These relative efficiencies ranged from 99.98% in Burn II to 99.999% in Burns VI, VII and VIII (Appendix I). The RPE was considered relative since the TCDD sampling train did not efficiently collect light, volatile pyrolyzates. See Appendix I for a thorough discussion of RPE.

Additional preheat of "Orange" Herbicide fuel from ~90°F to 175°F significantly improved the RPE.

Hydrocarbon penetration through the caustic scrubber (relative to penetration through the TCDD sampling trains) increased significantly as the RPE improved (Appendix I).

Beckman 109A hydrocarbon data were not relatable to RPE's (Appendix I).

#### 8.1.5 Particulate, NO<sub>x</sub> and CO<sub>2</sub> Emissions:

Particulate emissions from the eight burns averaged 0.076 grains per standard cubic foot of scrubbed effluent gas and had a standard deviation of 0.035. The particulate matter, by visual observation, appeared to be mostly sodium salts. No aromatic hydrocarbons were detected in the particulate mass. An average 6 µg of unchlorinated aliphatic hydrocarbons was detected in an average particulate mass of 105 mg (filter maintained at 320°F).

Nitrogen oxide (NO<sub>x</sub>) emissions from all eight burns averaged 53.4 ppm with a standard deviation of 18.9 ppm. The emissions increased to about 100 ppm in Burns VII and VIII when the theoretical combustion temperature (TC<sub>THEO</sub>) increased from ~3000°F to above 3200°F.

The CO<sub>2</sub> concentration (% by volume) averaged 12.1% in Burns IV, V, VI and VII. An average 9.9% of the CO<sub>2</sub> was absorbed in the caustic scrubber (see Appendices D and E).

#### 8.2 On-Line Gas Sampling (Prepared by TMC)

The Beckman analyzer data for CO, NO<sub>x</sub>, and HC for the record burns are presented in Table 2. These were readings from the scrubbed effluent gas only. Both the high and low values observed

during the burn are presented. During temperature stabilization using natural gas at the beginning of each burn, hydrocarbon readings were high due to inefficient, low temperature combustion. Once combustion on "Orange" Herbicide was established, the hydrocarbon data took some time to stabilize at lower values due to the time required to sweep the analyzer input lines and traps. The low values presented were representative of the stabilized incineration process.

Considerable difficulty was experienced in trying to analyze combustion chamber gases. The system was initially set to maintain the sample gas temperature at 300°F into the analyzer, but condensation of acid and H<sub>2</sub>O within the analyzer was experienced. Consequently, a cold trap was installed in the sample line and the heating tape removed from the sample line between the cold trap and analyzer. Sample line heating was maintained from the sample probe to the cold trap. Heavy hydrocarbons were condensed and collected in the cold trap. Therefore, the cold trap was rinsed after each run and the rinse was analyzed for hydrocarbons.

Beckman sampling analyses were used throughout the program to sample scrubbed effluent gas since this was the final system effluent. This type of analyses was intended only to provide an operational indicator of system combustion stability. Scrubbed effluent gas hydrocarbon data were generally higher than noted during combustion of JP-4 which could be expected considering the potential products of "Orange" Herbicide combustion. In the Beckman 109A analyzer, the magnitude of instrument response caused by a given carbon atom depends on the chemical environment of the atom in the molecule. The data presented from the Beckman indicated the hydrocarbon content of the sample in ppm of carbon, and must be divided by an "effective carbon number" (proportional to carbon count) of the sample compounds to obtain the true ppm. Therefore true data values would be proportionally reduced for compounds of high carbon count. Also, in some compounds certain other atoms will change the analyzer's sensitivity to carbon. As noted in paragraph 8.1, these data could not be used to provide comparisons of relative pyrolysis efficiencies for the system.

The NO<sub>x</sub> readings generally followed the expected tendency to increase at higher combustion temperatures, remaining below 62 ppm for TCAVG up to 2500°F and rising to 168 ppm at a TCAVG of 2759°F.

## 9.0 SCRUBBER WATER SAMPLING RESULTS (Prepared by USAF EHL/K)

All water sampling and inorganic analyses were conducted by USAF EHL/K using their own equipment and specially prepared sample containers. The water monitoring program and discussion of inorganic analyses are presented in Appendix E. Organic analyses of scrubber water samples were performed by WCTS, see Appendix G, and the results are discussed in detail in Appendix I. Results below were summarized from the discussions in Appendices E and I.

## 9.1 Inorganic Quality of Spent Scrubber Water (SSW)

The consistency of SSW inorganic parameters throughout a given burn agreed with the smoothness with which burn operation parameters were maintained. The only exceptions occurred when the applied caustic was increased during Burn VI. Of all measured SSW physical and inorganic parameters, only temperature, specific gravity, and chlorides remained relatively constant between burns. All other measured parameters were acceptably correlated by least squares regression analyses to only one incinerator operating parameter; the ratio of applied NaOH to that required to neutralize the theoretically expected HCl ( $N_u/N_T$ ). Table 3 summarizes the range of measured parameters in SSW for all burns.

All loadings in Table 3 except chlorides, suspended solids, total iron, and hydroxyl alkalinity increased or decreased linearly about 30% as  $N_u/N_T$  increased to three or decreased to two, respectively. The exceptions varied non-linearly with  $N_u/N_T$  and were dependent upon complete neutralization of HCl and the adsorption of  $CO_2$  into the scrubber water. Approximately 10% ( $s = 4$ ) of the combustion gas  $CO_2$  was absorbed by the scrubber water.

Evaluations of scrubber water flow rates showed that, dependent on fuel to air mass ratios, about 1350 gallons ( $s = 175$ ) of scrubber water were needed for each drum of herbicide burned. About 1000 gallons ( $s = 200$ ) or 75% of this water was not volatilized and was therefore recovered as spent scrubber water.

Suspended solids were present in moderate concentrations (56-97 mg/l). However, there were finely sized black carbon particles which imparted a distinct grey color to the SSW. Elevated iron concentrations (160-400 mg/l) in Burns VI and VIII attributed intense rust colors to the water. These solids concentrations were reduced by 77% with primary settling.

Inorganically measured mass balances of sodium, hydroxide, and chlorine throughout the incinerator system were all accounted for within five percent of their theoretical or measured input values. These balances validated the overall accuracy of scrubber water collection and analyses.

After five drums of herbicide had been burned, about 5000 gallons of SSW were discharged into 1.4 million gallons of relatively excellent quality facility waste water. The waste water's quality changed significantly in pH, total and carbonate alkalinity, sodium, chlorides, specific conductance, and total dissolved solids but its specific gravity, total solids, chlorine residual (0.0 mg/l), hydroxyl alkalinity (0.0 mg/l), and bicarbonate alkalinity were unchanged. These chemical quality changes were, however, not detrimental to the waste water's intended industrial uses. The water's quality met industrial sewer ordinance codes after receiving nearly 25,000 gallons of SSW. Chemical quality changes of the final sample collected indicated that the waste water's quality had already begun to adjust back toward the carbonate equilibrium system. Such adjustment would naturally lower all measured parameters except conservative sodium and chlorides to near original conditions.

TABLE 3: INORGANIC LOADING AND RANGE OF QUALITY IN SPENT SCRUBBER WATER

Parameter (mg/l unless noted)	Range of Quality	Loading - Pounds Per Drum of Herbicide Burned @ $N_U/N_T = 2.0$
Temperature ( $^{\circ}\text{F}$ ) when collected	164	N/A
pH	10.5-11.8	N/A
Specific Gravity	1.057	N/A
Specific Conductances ( $\mu\text{mho/cm}$ )	11.3-15.8	N/A
Total Solids or Total Dissolved Solids ( $\times 10^3$ )	61-87	$\approx 590$
Suspended Solids	56-97*	0.66
Chlorides ( $\times 10^3$ )	16.5-28.0	166
Free and Total Chlorine Residuals	250-500	1.9
Sodium ( $\times 10^3$ )	32-38**	254
Iron, Total	3.0- 5.0***	0.03
Total Alkalinity ( $\times 10^3$ as $\text{CaCO}_3$ )	32.0-52.5+	278
Carbonate Alkalinity ( $\times 10^3$ as $\text{CaCO}_3$ )	22.4-36.4++	232
Hydroxyl Alkalinity ( $\times 10^3$ as $\text{CaCO}_3$ )	9.6-16.1+++	47
Bicarbonate Alkalinity ( $\times 10^3$ as $\text{CaCO}_3$ )	0*†	0.00
<p>* Increased to 500-800 when <math>N_U/N_T &lt; 2.0</math>.</p> <p>** Decreased to 25.0 when <math>N_U/N_T</math> decreased to 1.29.</p> <p>*** Increased to 400 when <math>N_U/N_T</math> decreased to 1.29.</p> <p>+ Decreased to 12.0 when <math>N_U/N_T</math> decreased to 1.29.</p> <p>++ Averaged 70 (<math>\pm 8</math>) % of Total Alkalinity but increased to 90 (<math>\pm 10</math>)% of Total Alkalinity when <math>N_U/N_T &lt; 2.0</math>.</p> <p>+++ Averaged 30 (<math>\pm 8</math>)% of Total Alkalinity but decreased toward zero when <math>N_U/N_T &lt; 2.0</math>.</p> <p>*† Was zero but increased to 8% of Total Alkalinity as <math>N_U/N_T</math> decreased to 1.29.</p>		

## 9.2 Organic Quality of SSW

Combustion gas hydrocarbons apparently condensed through the venturi, were impacted into the scrubber water, and were slightly dissolved into the warm (165°F) caustic. As discussed in Section 11 some pyrolyzates (unchlorinated aromatics) in the combustion gases reacted with the oxidants in the combustion gas (HCl, Cl<sub>2</sub>, and monatomic chlorine) and the caustic to produce hydrolyzates: monochlorophenol and dichlorobenzene. A detailed summary of these organic masses is presented in Table I-8. The average concentration of these pyrolyzates and hydrolyzates expressed as carbon in the spent scrubber water averaged 0.60 mg/l for Burns I, II, and III and decreased to an average of 0.02 mg/l for Burns IV through VIII. None of these hydrocarbon compounds were detected in suspended solids in the scrubber water. Comparison of both water and gas hydrocarbon analyses showed that improved combustion efficiency in the last five burns significantly reduced the hydrocarbons delivered into, and collected by, the scrubber.

No TCDD and none of the esters or acids of 2,4-D or 2,4,5-T were detected in any of the spent scrubber water samples or suspended solids except the total burn composite of Burn III. The detection limit of each compound averaged 0.045 µg/l for an overall average detection limit of 0.23 µg/l for the five compounds. A thorough discussion of this sample and the most probable source of its positive TCDD (0.25 µg/l) are presented in Appendix I. The source of the TCDD was concluded to have been combustor coke deposit which broke away from the combustion chamber, settled in the scrubber, and provided the TCDD to the scrubber water. This heavily contaminated combustor coke, found only in Burn III, was attributed to fuel flow conditions and the incinerator poppet nozzle which in this instance produced poorer combustion and mixing within the combustion chamber than was observed in any of the other burns. This situation is discussed in Section 10.

## 10.0 COMBUSTION CHAMBER COKE DEPOSIT RESULTS AND DISCUSSION

### 10.1 Quantity and Quality (Prepared by EHL/K)

The relationships regarding quantity and quality of the coke deposits removed from the combustion chamber are discussed in detail in Appendix I. A summary of results regarding coke deposits is presented below.

The central poppet nozzle was utilized for Burns I through IV. The deposits removed from the combustion chamber averaged 3.03 pounds of coke per drum of "Orange" Herbicide incinerated. These quantities of coke were twenty times the average produced in Burns V through VIII while utilizing the radial slot fuel nozzles. None of the coke samples lost weight until heated to 523°C and all left an ash content of <0.06% when heated to 725°C. The coke deposits

from Burns I, II, and IV had a steel gray color and were grainy, hard, and brittle. The deposits from Burns V - VIII were darker (like carbon black), of finer particle size, and much more easily crushed. Except for Burn III deposits, none of the coke had a herbicidal odor. Burn III coke also had "soft spots" which were not observed in coke from other poppet nozzle burns (I, II, and IV).

Except for Burn III, the total hydrocarbon contaminants in the coke deposits were small amounts of pyrolyzates per 100 gm of deposit: unchlorinated aromatics, <512 µg; unchlorinated aliphatics, <87 µg; and biphenyl, <17 µg. See Table G-9, Appendix G. Burn III coke deposit, however, contained these pyrolyzates in lesser amounts but also contained 1100.2 µg of herbicide esters and acids of 2,4-D and 2,4,5-T per 100 gm of deposit. Of these original herbicide compounds 551 µg was normal butyl 2,4-D ester and 542 µg was normal butyl 2,4,5-T ester. Although TCDD was not detected, the existence of these esters indicated TCDD presence--probably below the detection limit of 23 µg/100 gram of sample analyzed. Burn III's coke quantity, 3.28 pounds per drum of herbicide incinerated, was 10% greater than the other deposits encountered while using the central poppet nozzle. The coke's appearance, odor, and chemical quality indicated that lower than usual temperatures had existed around the coke. For these reasons, the coke was implicated as the source of TCDD found in the Burn III spent scrubber water samples. (See paragraph 12, Appendix I.)

The cause for coke deposits and their characteristics was attributed primarily to physical characteristics of the fuel injected and the injection nozzles. These relationships are discussed in the following paragraph.

## 10.2 Fuel Injection Characteristics Relative to Coke Depositing (Prepared by TMC)

Since the quantity and quality of the coke deposited in the combustion chamber was dependent primarily on the type of fuel injection nozzles utilized, the characteristics attributable to each nozzle type relative to observed data is discussed below.

### 10.2.1 Poppet Nozzle Injection:

Air entered the combustion chamber through the smaller diameter inlet and expanded into the larger diameter combustion chamber, hence the sudden expansion mechanism. See Figure B-3, Appendix B. Fuel and air mixing was obtained by mounting the poppet nozzle on the centerline of the inlet with the exit of the nozzle near the point of expansion. Mixing occurred somewhat as a result of the momentum of the fuel toward the walls of the chamber and primarily as a result of air recirculation into the region immediately downstream of the sudden expansion. The central poppet nozzle injects fuel into the air stream in a conical pattern and



should produce a finely atomized fuel spray immediately upon leaving the nozzle. It was apparent from the deposits in the combustion chamber from Burns I through IV that some portion of the unreacted "Orange" Herbicide spray was penetrating the air recirculation stream and was pyrolyzing on the chamber walls, thus developing deposits and generating a partial obstruction at about 1½ to 2 diameters from the inlet step. This situation was attributed to the extreme viscosity of the "Orange" Herbicide fuel (see Figure B-7) which required high fuel nozzle driving pressures, and likewise the lack of quick fuel spray atomization necessary for proper burning. This situation generally does not occur with conventional fuels of low viscosity (<1.0 centistoke). The deposition of coke deposits is quite common in conventional commercial incinerator/boilers using high viscosity fuel oils.

The partial obstruction deposited in the combustion chamber tended to limit recirculation of the air and also affected the fuel and air mixing mechanism of the poppet nozzle. The entering air anticipated the restriction thereby reducing the recirculation and changing the mixing characteristics of the zone around the nozzle. Burner performance was thus degraded. Also, as this restriction increased during the burn, it is certain that some of the deposits broke loose due to the increasing gas velocity and turbulence through the "orifice" and were propelled into the scrubber tank.

The poppet nozzle was selected for Burns I - IV on the basis of prior experience indicating satisfactory results at fuel/air mass ratios up to about two thirds of stoichiometric; approximately the ratio required for the middle temperature burns (2500°F). For Burns I and II, a fuel/air mass ratio (0.086) of approximately one half stoichiometric was utilized which, although causing coking of the combustion chamber, did not allow raw herbicide or TCDD to exit the reaction tailpipe. During Burn III, the fuel flow was increased to provide a fuel/air mass ratio (0.106) of approximately two thirds stoichiometric. Deposits increased some 10% over Burns I and II which was attributable to the increased momentum (penetration) of the fuel stream. The increased coking would have caused lower combustion efficiencies and more tendency to break deposits loose. It is apparent that the increased severity of the depositing situation occurring in Burn III resulted in the presence of herbicide in the Burn III deposit and the TCDD in the spent scrubber water which was composited during the later portion of the burn when combustion efficiency had decayed. It is probable that TCDD was present in the deposit but at an undetectable concentration. Likewise it is probable that herbicide broke loose from the deposits, or remained after initial combustion, but was thermally degraded before reaching the scrubber or reacted with the scrubbing solution, whereas TCDD passed unreacted into the scrubber. The fact that TCDD was not found in the combustion gas sample or the first hourly spent scrubber water composite sample indicated that it was produced during the last two hours of operation after these samples were collected.

Burn IV was a duplicate of Burn III except that the "Orange" Herbicide was preheated to approximately 175°F as compared to about 90°F for Burn III. No herbicide or TCDD was found in any effluent sample and the combustion chamber coking was reduced some 10% from Burn III. This increased temperature reduced the viscosity by a factor of 16, thus providing much faster atomization and combustion of the herbicide and a decrease in solid liquid penetration. Burn VI was a duplicate of Burn III also except that the poppet nozzle had been replaced by slot nozzles as discussed below.

#### 10.2.2 Slot Nozzle Injection:

The slot nozzle configuration is described in Appendix B. These nozzles, utilized in Burns V through VIII, injected the fuel radially toward the combustion chamber center-line at the sudden expansion step thereby mixing the fuel and air primarily by injection rather than by recirculation. This method of injection resulted in more efficient mixing near the burner inlet and more efficient combustion within the first diameters length of the combustion chamber. The deposits from Burns V through VIII were much smaller, sparsely distributed, of finer softer grain, and did not contain herbicide. This data indicated that carbon formation occurred in a well mixed combustion gas stream that did not permit significant penetration of liquid fuel to the chamber walls. Likewise, restrictions in the chamber which altered the air flow path did not affect the mixing and burning to the extent noted for poppet nozzle operation. The fuel temperature (viscosity) and fuel/air mass ratio were not as critical regarding combustion destruction efficiency as when using the poppet nozzle. None of the compounds identified in the herbicide feed were found in any of the effluent samples for Burns V through VIII.

#### 11.0 PYROLYZATE AND HYDROLYZATE RESULTS AND DISCUSSION (Prepared by USAF EHL/M and K)

Table 4 presents those detected organic compounds considered to have been pyrolyzates and hydrolyzates in the combustion gas, scrubbed effluent gas, spent scrubber water, spent scrubber water sediment and combustor coke deposit samples taken during "Orange" Herbicide incineration. Two values are given: the average values from Burns I, II and III; and the average values from Burns IV, V, VI, VII and VIII. These burns were so grouped to demonstrate the more efficient pyrolysis of "Orange" Herbicide in the last five burns (see discussion in Appendix I).

The nonchlorinated aliphatics, aromatics, and biphenyls were all considered pyrolyzates since they were undetected in the herbicide fuel and their formation was not dependent on hydrolysis. These aliphatics and aromatics were partially collected in the

TABLE 1: AVERAGE RANGE OF DETECTED HYDROCARBON MASSES CONSIDERED TO BE  
PYROLYZATES AND HYDROLYZATES OF ORANGE HERBICIDE INCINERATION

Organic Pyrolyzates/Hydrolyzates	Combustion Gas <sup>1</sup>		Spent Scrubber <sup>2</sup> Water		Scrubbed Effluent <sup>1</sup> Gas		Spent Scrubber <sup>3</sup> Water Sediment		Combustor <sup>3</sup> Coke Deposit		Average Weight Percent Present in Herbicide Feed
	P	H	P	H	P	H	P	H	P	H	
Unchlorinated Aliphatics (C <sub>10</sub> H <sub>22</sub> )	0.96-0.15	ND	105.8-7.9	ND	0.07-0.09	ND	ND	ND	51.0-22.0	ND	ND
Unchlorinated Aromatics (C <sub>6</sub> H <sub>6</sub> (C <sub>4</sub> H <sub>9</sub> ))	1.81-0.25	ND	125.8-4.6	ND	0.08-0.06	ND	ND	ND	105.0-126.0	ND	ND
Biphenyl (unchlorinated)	ND	ND	ND	ND	0.01-0.06	ND	ND	ND	8.75-4.86	ND	ND
Dichlorobenzene	ND	ND	ND	500.5-2.8	ND	ND	ND	ND	ND	ND	ND
Monochlorophenol	ND	1.0**	ND	22.2-0.1	ND	ND	ND	ND	ND	ND	ND
Dichlorophenol***	ND	ND	ND	ND	ND	ND	ND	ND	2.5-1.5	ND	1.46
2,4-D Dichlorophenoxy Acetic Acid***	ND	ND	ND	ND	ND	ND	ND	ND	2.5*	ND	0.73
2,4,5-T Trichlorophenoxy Acetic Acid*	ND	ND	ND	ND	ND	ND	ND	ND	2.1*	ND	0.52
Phenoxy Acetic Acid (unchlorinated)	ND	ND	ND	ND	ND	ND	ND	ND	0.5*	ND	ND

ND - Not detected. For detectable limits see Tables G-2 through G-9.

\* In Combustor Coke Deposit, Burn III only.

\*\* Burn I only.

\*\*\* These compounds were in "Orange" Herbicide - may not have been pyrolyzates.

Note: The first value in each column was an average of Burns I, II and III. Second value in each column was an average of Burns IV, V, VI, VII and VIII.

Reported as mass of compound

1.  $\mu\text{g}$  per liter of gas (STP)

2.  $\mu\text{g}$  per liter of spent scrubber water

3.  $\mu\text{g}$  per 100 grams

STP = 70°F, 29.92" Hg, and Dry

USAF EHL/M and K

scrubber while the biphenyls completely penetrated through the scrubber. The respective penetration of these pyrolyzates through the scrubber was probably due to their relative solubilities and vapor pressures in hot NaOH solution. (See Appendix I.) The biphenyl pyrolyzate undoubtedly existed in the combustion gases but its detection was considered to have been masked via gas chromatograph peak interference (see Comments section of Appendix G).

Monochlorophenol and dichlorobenzene were consistently detected in the spent scrubber water but never in the herbicide feed or in any of the combustion or scrubbed effluent gas samples except for the monochlorophenol in Burn I combustion gas. Since the precursor(s) (unchlorinated aromatics) of these compounds were present in the combustion gas along with HCl, Cl<sub>2</sub>, and monatomic chlorine, it was reasoned that condensation and hydrolyses of these combustion gas products occurred in the venturi scrubber to produce monochlorophenol and dichlorobenzene as hydrolyzates.

Since the 2,4-D and 2,4,5-T chlorophenoxy acetic acids and dichlorophenol averaged 2.71% by weight of the blended "Orange" Herbicide feed, these compounds may or may not have been pyrolyzates. These compounds were found only in the combustor coke deposit. The phenoxy acetic acid was however not detected in the blended herbicide feed samples. Thus this acid was considered a pyrolyzate formed when combustion chamber mixing was its poorest and combustor coke deposit was at its maximum (Burn III).

Ionol and didecylphthlate were detected in all combustion and scrubbed effluent gas samples and all spent scrubber water samples. However, as discussed in Appendices G and I, these compounds were considered environmental contaminants and not pyrolyzates or hydrolyzates.

## 12.0 BIOASSAY, NOISE TESTING, AND DRUM CLEANING/DISPOSAL RESULTS AND DISCUSSION (Prepared by USAF EHL/K)

### 12.1 Bioassays

Dynamic bioassays of up to 96 hours were conducted with three-spined stickleback fish (Gasterosteus aculeatus) in the spent scrubber water. Static bioassays were also conducted with brine shrimp (Artemia salina) in spent scrubber water for periods up to 24 hours. Plant biomonitoring was initiated several days prior to Burn I, during all burns, and five days after Burn VIII. Monitored flora consisted of the indigenous plants around TMC's perimeter and ten young tomato plants at each of sixteen locations evenly distributed around the incinerator facility. Results and discussion of these bioassays and plant biomonitoring will be published by EHL/K under separate cover.

[The EHL/K report on biological monitoring has been included as Appendix M to the Final Environmental Statement]

## 12.2 Noise Testing

Incinerator noises were predominately in the 2000-8000 Hertz bands and had an overall noise level of 91 (+ 2) dbA at a distance of twelve feet. A fifty-foot radius around the incinerator was a hazardous noise area to unprotected personnel occupationally exposed to the noise. The control room effectively attenuated incinerator noises so that no speech interference levels were observed in the control room. Calculations were made to determine the noise levels at various distances from one or more incinerators. See Appendix J.

## 12.3 Drum Cleaning Analyses and Comments

Appendix F presents and discusses the drum cleaning procedures, drum disposal, and analyses of rinse samples in detail. An abbreviated summary of these results is presented here.

During initial transfer of "Orange" Herbicide to the fuel feed tank, a drum pumping device was used which left usually less than two quarts of herbicide in each drum. Before the cleaning phase each drum was upended and allowed to free drain until steady dripping stopped. Each drum was then rinsed three times with various amounts of JP-4 for five minutes each on a barrel rolling device. Rinse quantities of clean JP-4 in each drum rinse set were 5/5/5, 3/3/3, 2/2/2, and 5/3/2 gallons. Each rinse was drained into a holding tank for subsequent incineration. Samples were taken of each rinse solution midway during the draining.

The cleaned drums were safely disposed of in an environmentally approved manner in the Los Angeles County "Class 1" Landfill Number 5 at Calabasas, CA.

Evaluation of drum rinse sample analyses provided an estimate of total herbicide mass left in a freshly drained drum: 450 (+ 25) grams. On a proportional basis, slightly more of the herbicide's 2,4,5-T nb ester was removed during rinsing than the 2,4-D nb ester. Smaller rinse volumes produced significantly more variable results. Nonetheless, a given total volume of rinse removed about the same amount of herbicide whether it was used in subdivided volumes or in a single volume with the restriction that a total volume was  $\leq 5$  gallons, from 6 to 10 gallons, or from 9 to 15 gallons. The percent efficiency of herbicide removed increased with total rinse volume applied: range 45% for 2/2 gallons to 79% for 5/5 gallons. A third drum rinse of  $\leq 5$  gallons did not improve the herbicide removal efficiency any more than 3%.

Analyses of TCDD in the rinse solutions was beyond the scope of this study. With TCDD solubilities similar to that of the herbicide esters, it was indicated that as much as 1.25 mg of TCDD may have been left in the best rinsed drums. This amount of TCDD in these drums represented the worst case, however, since these drums contained herbicide with the highest TCDD contamination known to exist in Air Force stocks.

All rinse samples have been stored at FHL/K should any further analyses of them be needed to select a drum disposal method.

### 13.0 OTHER TEST PROGRAM COMMENTS (Prepared by TMC)

#### 13.1 "Orange" Herbicide Properties

Problems were caused by the high viscosity of "Orange" Herbicide with the unexpectedly low ambient temperatures at the start of testing. Figure B-6 shows viscosity vs. temperature and indicates that even at 100°F the viscosity of "Orange" Herbicide is very high (16 centistokes) compared to other conventional fuels. At 65°F the viscosity rises to 48 centistokes. The temperature/viscosity characteristic was also quite evident during transfer operations. The flow problems in the incinerator system were alleviated by heating the herbicide feed to 90°F or higher. However, the herbicide remained quite difficult to atomize even at these elevated temperatures.

No filtration or plugging problems were noted in the fuel feed system during the program. Although a parallel filter system was available, a 5 micron filter pot selected for initial use was utilized without cleaning throughout the entire program. The maximum pressure loss noted during testing was about 20 psid across the filter. This absence of filtration problem was attributed to the complete flushing of the fuel feed tank during system assembly and the filtering of the "Orange" Herbicide during loading.

No slot nozzle plugging problems were experienced. All testing using slot nozzles was performed with herbicide temperatures about 90 to 110°F. The nozzle slots were 0.009 inch wide. Slot nozzle combustion was very smooth and no indications of plugging were noted. Removal of the manifold after testing revealed the slots had remained clean. The fuel slot nozzles were placed inside the natural gas nozzles as described in Appendix B. This arrangement kept the fuel slot nozzles cooled and precluded the possibility of "Orange" Herbicide being exposed to a hot metal surface during initial injection and thus prevented the formation of any deposits in the nozzle slot. This feature and the 5 micron filtering system was felt to have prevented any slot nozzle plugging problem.

#### 13.2 Herbicide Handling

The safety program established for this effort is described in Appendix H. There were no problems experienced in handling of the "Orange" Herbicide during the program. There was no spillage or other release of the herbicide to the environment, except for minor drips normally occurring during transfer or fuel system modifications. These drips were promptly absorbed with a

rag soaked in JP-4. Contaminated rags and other materials were kept in a sealed container and disposed of by the Air Force at test program completion. All contaminated utensils employed during transfer or systems operations (funnels, hoses, drip pans, etc.) were thoroughly rinsed in JP-4 after each use and the rinse solution incinerated.

### 13.3 Effect on Incinerator Materials

A total of 44 hours of operation, including 30.5 hours on undiluted herbicide, was accumulated during the program with 16 complete start/stop transients. During this period no structural problems were noted in the units themselves or at gasketed mating flanges. There were no emergency shutdowns or shortened runs due to physical incinerator problems. Examination of the incinerator during and after the program indicated no evidence of scaling or other physical deterioration indicating impending failure.

General experience with Type 310 stainless steel, and our specific experience with Marquardt incinerators made of 310 stainless, indicate long term durability at the temperatures experienced, particularly at the low stresses and creep rates created by near ambient pressure operation. Even at a chamber pressure as high as 16 psig, the creep rate is 1% per 100,000 hours at 1500°F. Also, the maximum skin temperature noted on the uncooled reaction tailpipe throughout the program was 1700°F which was below the temperature (2000°) at which oxidation scaling becomes appreciable.

## 14.0 CONCLUSIONS (Prepared by USAF EHL/K, EHL/M and TMC)

### 14.1 Destruction of "Orange" Herbicide by Incineration

"Orange" Herbicide was effectively and safely destroyed by incineration. No "Orange" Herbicide constituent was detected in any system effluent when operating with the slot nozzles or the poppet nozzles except for the combustor coke deposit and spent scrubber water sample of Burn III. Very favorable relative pyrolysis efficiencies were obtained, ranging from 99.98% to 99.999%. Chlorinated phenolic compounds were undetected in all of the scrubbed effluent gas samples and detected only in one combustion gas sample (monochlorophenol at  $1.06 \times 10^{-6}$  grams/liter in Burn I). The spent scrubber water from all burns contained monochlorophenol but at a level not exceeding  $0.14 \times 10^{-6}$  grams/liter in the last five burns or  $53 \times 10^{-6}$  grams/liter in any of the burns.

## 14.2 Engineering Data

Preheat of "Orange" Herbicide fuel prior to injection in the combustion chamber was an important combustion efficiency parameter. The RPE was improved significantly (from 99.99 to 99.999%) when the "Orange Herbicide fuel was preheated to between 90° and 175°F. Preheat of "Orange" Herbicide fuel to at least 90°F was required to accomplish acceptable fuel injection characteristics.

The method of fuel injection was an important combustion efficiency parameter. The radial slot nozzles produced a higher RPE (Appendix I) and only about 1/20 the mass of combustion chamber coke deposits produced when central poppet nozzles were used. The slot nozzles provided satisfactory results at higher fuel/air mass ratios and combustion temperatures and therefore permitted a higher destruction rate of the "Orange" Herbicide.

Basic flow control was quite simple in that only fuel and air mass flow regulation was required once steady state was achieved. Transients were performed without incident due to the ease of ignition of "Orange" Herbicide into an established flame. The manual control systems were quite satisfactory in these regards and the only real flow control monitoring needed was to correct for minor changes in flow caused by changes in facility air storage pressure or changing fuel properties. It was concluded that "Orange" flow regulation is no problem as long as temperature is maintained within a reasonable band as determined by system sizing and is properly filtered to prevent plugging of fuel nozzles. Basic incinerator control therefore consisted of fuel and air flow regulation with monitoring of the combustion gas temperature to verify the presence of combustion and provide a relative indication of combustion and consistency of operating parameters. Air and fuel mass flow depended on delivery system pressure. The burner system pressure provided an indication of combustion gas flow and downstream conditions. These control parameters were conventional and could be readily automated using existing process industry control components. Such systems quite routinely monitor and control flow and combustion processes and take appropriate corrective action in the event of system anomalies. From purely a combustion point of view, this incineration process was not much different than when using conventional fuels. However, the serious differences were in the structural integrity (safety) of the incinerator and the safety aspects of storage and delivery of the "Orange" Herbicide.

Scrubbing of the combustion gases and neutralization of acids was accomplished satisfactorily. Optimization of this system was not within the scope of this effort and it is recognized that other types of scrubbers may be more desirable.



The on-line gas analyses equipment used was adequate for CO and NO<sub>x</sub> monitoring of scrubbed effluent gas only. Gas analyses equipment incorporating additional features would be required for sampling of combustion gas and for representative hydrocarbon sampling of the scrubbed and combustion gases. Application of on-line sampling analyses to a production process would require additional study beyond the scope of this effort.

#### 14.3 Effects on Incinerator Materials

Considering the absence of structural or sealing problems in the physical combustion chamber enclosures, the lack of evidence indicating physical deterioration in the materials utilized, the qualities of the materials used, and prior experience in similar systems, it was concluded that the basic incinerator design would provide a unit of considerable longevity. There are design considerations that would be required, "external" to the basic combustion process, which could further ensure longevity and provide a reliable unit. Such design factors do not appear to be particularly unusual or exotic in nature. It was also concluded that durability would be enhanced by long term continuous operations where start-stop transients are minimized.

#### 14.4 Mass Discharge Rates of "Orange" Herbicide Constituents

TCDD was detected in the spent scrubber water from Burn III at  $0.25 \times 10^{-6}$  grams/liter. Otherwise, no "Orange" Herbicide constituent was detected in any scrubbed effluent gas sample or in any spent scrubber water sample. "Orange" Herbicide constituents were detected only in the combustion chamber coke deposit from Burn III but these deposits were contained and the mass of the "Orange" Herbicide constituents in the 12.9 pounds of coke was 64.4 mg.

Table 5 presents the maximum potentially undetected "Orange" Herbicide constituents that could have been discharged without being detected. The TCDD in the spent scrubber water from Burn III was included in the discharge. The average mass that could have been discharged in the scrubbed effluent gas during each burn was 9.3 mg ( $\sigma = 2.7$  mg). The average mass that could have been discharged in the spent scrubber water during each burn was 3.4 mg ( $\sigma = 1.4$  mg).

#### 14.5 Spent Scrubber Water Quality

Spent scrubber water inorganic quality was directly related to applied caustic. Mineral content of spent scrubber waters would be minimized and acid gases effectively scrubbed if applied caustic were 2.0 ( $\pm 0.1$ ) times that required to neutralize the theoretically expected amount of HCl. Primary settling, dechlorination, and adjustment of pH to about 9 may be required before discharging the spent scrubber water to natural

**TABLE 5: MAXIMUM POTENTIALLY UNDETECTED "ORANGE" HERBICIDE MASS DISCHARGE RATES FROM INCINERATION OF "ORANGE" HERBICIDE**  
(includes TCDD, nb 2,4-D and nb 2,4,5-T esters, and 2,4-D and 2,4,5-T acids)

Burn Number	I	II	III	IV	V	VI	VII	VIII
SCRUBBED EFFLUENT GAS								
Total Volume (STP) Produced During Burn ( $\times 10^6$ liters)	6.55	7.75	8.58	9.47	7.65	5.03	7.55	8.76
Undetectable Mass Concentration ( $\times 10^{-3}$ $\mu\text{g/l}$ ) <sup>+</sup>	1.05	0.90	1.15	0.80	1.00	3.00	1.30	1.20
Total Burn Undetectable Mass ( $\times 10^{-3}$ grams) <sup>+</sup>	6.88	6.98	9.87	7.58	7.65	15.09	9.82	10.51
Burn Time (minutes)	191	218	235	236	213	136	213	356
Undetectable Mass Discharge Rate ( $\mu\text{g/min}$ ) <sup>+</sup>	40	30	40	30	40	110	50	30
SPENT SCRUBBER WATER								
Total Volume Discharged During Burn ( $\times 10^3$ liters)	15.7	15.0	15.1	15.9	13.5	7.2	14.3	12.1
Undetectable Mass Concentration ( $\times 10^{-3}$ $\mu\text{g/l}$ ) <sup>+</sup>	225	225	430*	225	225	225	225	225
Total Burn Undetectable Mass ( $\times 10^{-3}$ grams) <sup>+</sup>	3.54	3.39	6.46*	3.57	3.05	1.62	3.22	2.74
Burn Time (minutes)	191	218	235	236	213	136	213	356
Undetectable Mass Discharge Rate ( $\mu\text{g/min}$ ) <sup>+</sup>	20	20	30*	20	10	10	20	10

\*Only gas or water sample in which any subject compounds were detected:  $0.25 \times 10^{-6}$  gm/l

+These values expressed as the total of the five herbicide constituents

USAF EHL/M and K

waterways. For burns using the slot nozzles, the total average hydrocarbons were less than 20 µg/l and no hydrocarbons were detected in the water's suspended carbon particles. Of the 20 µg/l total hydrocarbons, less than 1.5 percent of them could have been undetectable compounds of the original herbicide feed.

#### 14.6 Pyrolyzates and Hydrolyzates

All of the detected unchlorinated aliphatics, aromatics, and biphenyls were considered pyrolyzates. The total mass of these pyrolyzates in the scrubber water, combustor coke deposit, and scrubbed effluent gas averaged 1.32 gms as carbon per drum of herbicide incinerated in the less efficient burns (I, II, III) and was an order of magnitude less (0.42 gms as carbon per drum) in the more efficient burns (IV through VIII).

All of the detected monochlorophenol and dichlorobenzene were considered hydrolyzates. These compounds were detected in only one effluent from the incinerator (spent scrubber water). Their total effluent mass averaged 0.86 grams as carbon per drum of herbicide incinerated in the less efficient burns (I, II, and III) but decreased three orders of magnitude to an average of 0.006 grams as carbon per drum of herbicide incinerated during the more efficient burns (IV through VIII).

#### 14.7 Air Sampling

Data from the Beckman 109A hydrocarbon analyzer was not an indicator of RPE or combustion efficiency (Appendix I).

The formation of dichlorobenzene, dichlorophenol, and monochlorophenol by the reaction of nonchlorinated aromatic hydrocarbons with HCl, Cl<sub>2</sub> and (Cl) was indicated in locations of rapid combustion gas cooling. The quantity of these compounds that might be formed in other systems would not be expected to exceed the mass of aromatic hydrocarbons existing in the combustion gas.

#### 14.8 Bioassays

Conclusions about bioassay and plant biomonitoring data will be published under separate cover by USAF EHL/K.

#### 14.9 Noise Hazards

Unprotected personnel occupationally working within fifty feet of the incinerator(s) should be provided ear protection and be monitored via a hearing conservation program. The conventional masonry control room walls effectively protected the operators from the incinerator's hazardous noise levels (91 + 2 dbA) and provided them an area quiet enough for reliable communication. Masonry walls around the incinerator pad would preclude ambient incinerator noises from interfering with any adjacent operations.

#### 14.10 Drum Cleaning

Data of this study can be used to determine the volumetric rinses of used or contaminated JP-4 needed to meet any prescribed drum cleaning requirements. Under the following constraints, separate rinse procedures should be used to obtain maximal removal of the 450 ( $\pm$  25) grams of herbicide remaining in the drums after drainage:

a. Some cleaning required but  $\leq 5$  gallons of clean or contaminated JP-4 available per drum. Use the five gallons in a single rinse to obtain 70 percent herbicide removal.

b. Maximal cleaning required but  $\leq 10$  gallons of clean or contaminated JP-4 available per drum. Use two rinses of five gallons each to remove 79.1 percent of the herbicide.

c. Third rinses of less than five gallons of JP-4 did not improve overall herbicide removal by more than three percent.

Removing drum ends and spraying the rinse downward through the open drum would provide better rinse drainage. Depending on rinse volumes used, such a rinse application technique might improve herbicide removal efficiencies by 10 to 25 percent over the results of this study.

APPENDIX A  
(TO APPENDIX E)

THEORETICAL COMBUSTION TEMPERATURES AND PRODUCTS  
FOR "ORANGE" HERBICIDE AND AIR COMBUSTION

A computer program for the calculation of complex chemical equilibrium compositions was used to obtain theoretical combustion temperatures and products for "Orange" Herbicide/air mass ratios. This program is "NASA Report SP-273, Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations by Sanford Gordon and Bonnie J. McBride, 1971."

The chemical composition of the "Orange" Herbicide was assumed to consist of:

50% by volume of N-Butyl 2,4,5-T     $C_{12}H_{13}O_3Cl_3$

and

50% by volume of N-Butyl 2,4-D     $C_{12}H_{14}O_3Cl_2$

The heats of formation used for each fuel were as follows:

<u>Fuel</u>	<u>Heat of Formation</u> <u>Cal/Mole</u>
N-Butyl 2,4,5-T	-159,000
N-Butyl 2,4-D	-152,000

The heats of formation of these compounds were estimated by taking the heats of formation of similar compounds and adding/subtracting the heats of formation of similar/dissimilar groups.

The results of computer analysis are summarized in Figures A-1 through A-4. Figure A-1 presents the theoretical temperature of "Orange" Herbicide and air combustion plotted against "Orange" Herbicide/air mass ratios for ambient air temperatures of 537 and 1000°R. The mass ratios were those of interest in the understoichiometric range which would provide combustion temperatures spanning the 2100° to 2900°F range to meet program requirements. Figure A-2 presents equilibrium products of "Orange" Herbicide/air combustion plotted against theoretical combustion temperature for an ambient air temperature of 537°R. This data was used as a basis for prediction of incinerator combustion gas product composition.

Figures A-3 and A-4 present similar data for the over-stoichiometric combustion of 2,4,5-T herbicide in 537°R ambient air. This data was computed to predict the effects of incomplete combustion or pyrolysis at very fuel rich conditions which could be created by incinerator failure, particularly regarding the formation of phosgene. Mass ratios were analyzed to approximately 1.5 times stoichiometric. Figure A-3 presents theoretical combustion temperatures versus 2,4,5-T herbicide/air mass ratios. Figure A-4 presents equilibrium products of combustion. No phosgene or any other potential gaseous products of incomplete pyrolysis were indicated within the limits of the computer program (less than  $5 \times 10^{-6}$  mole fraction).

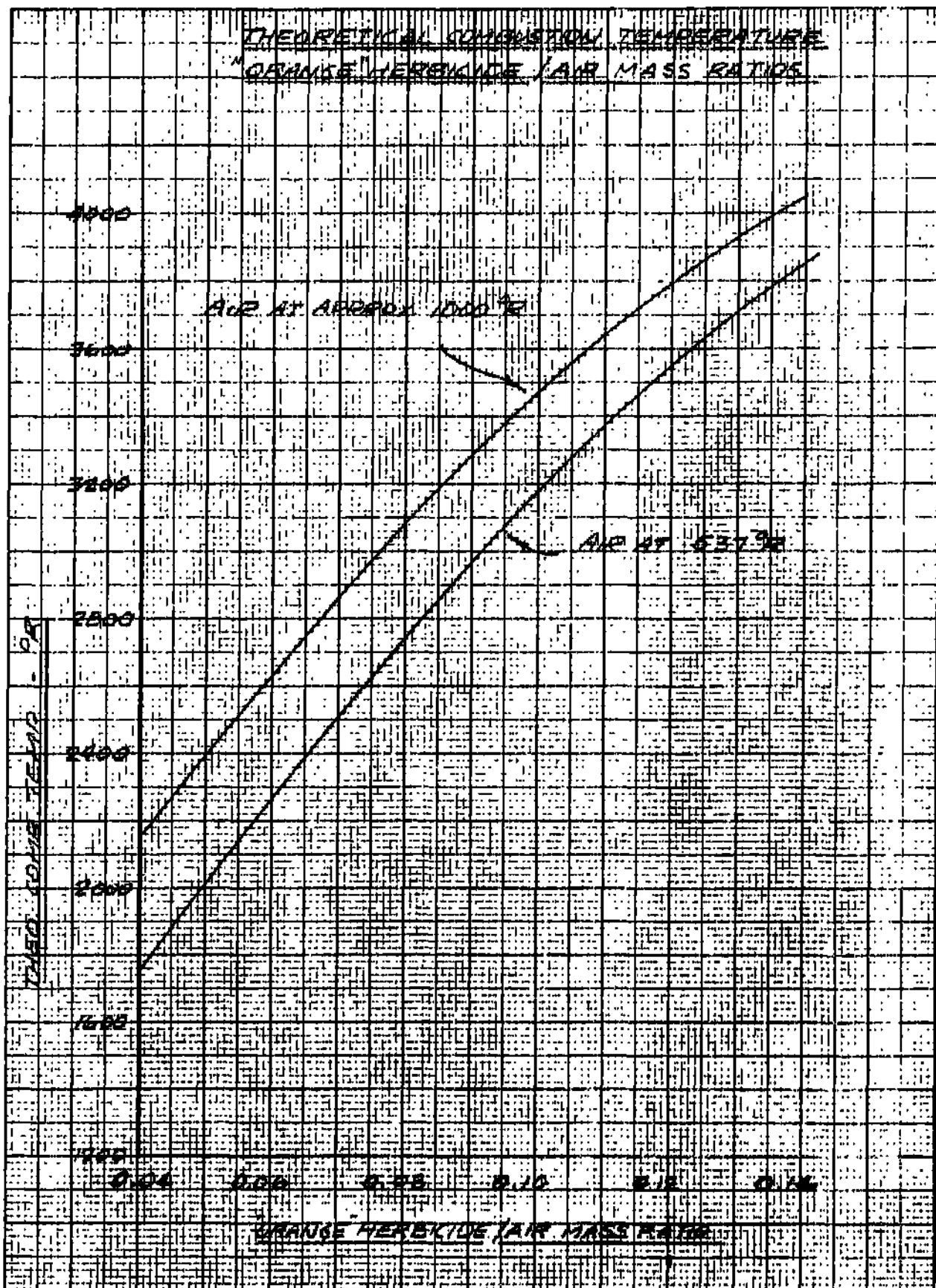
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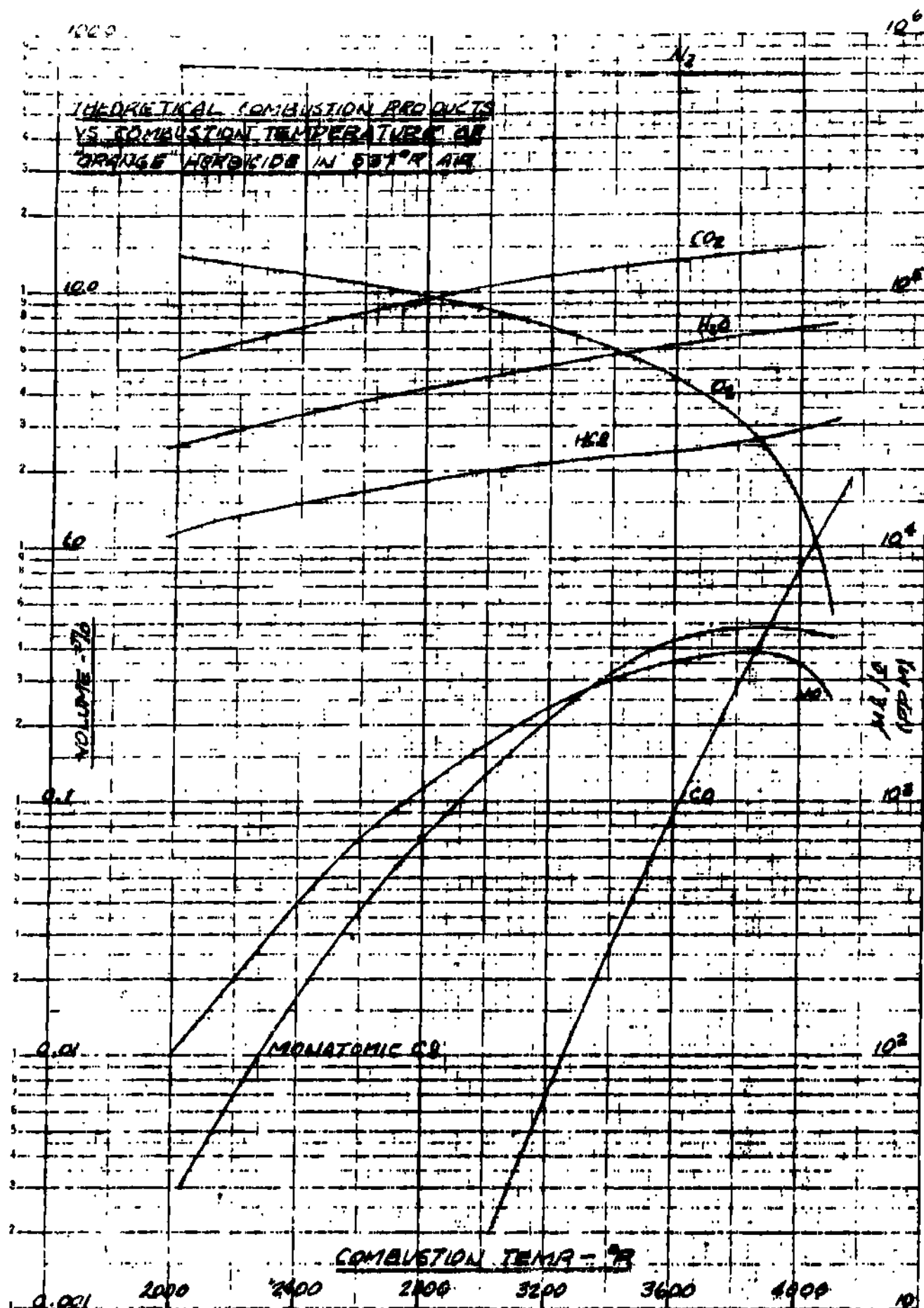
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E(A-4)

FIGURE A-2

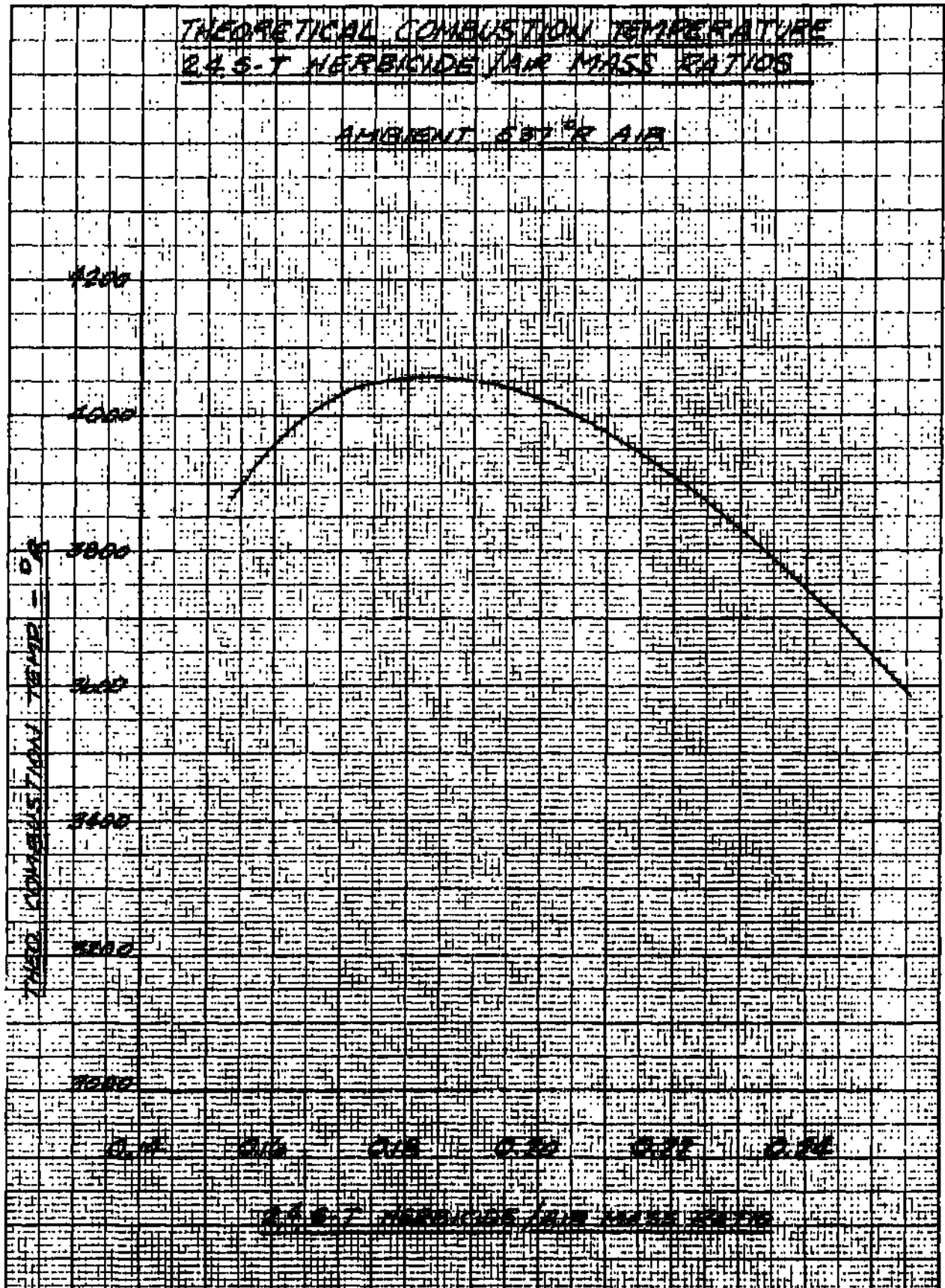


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**Marquardt**  
 CORPORATION

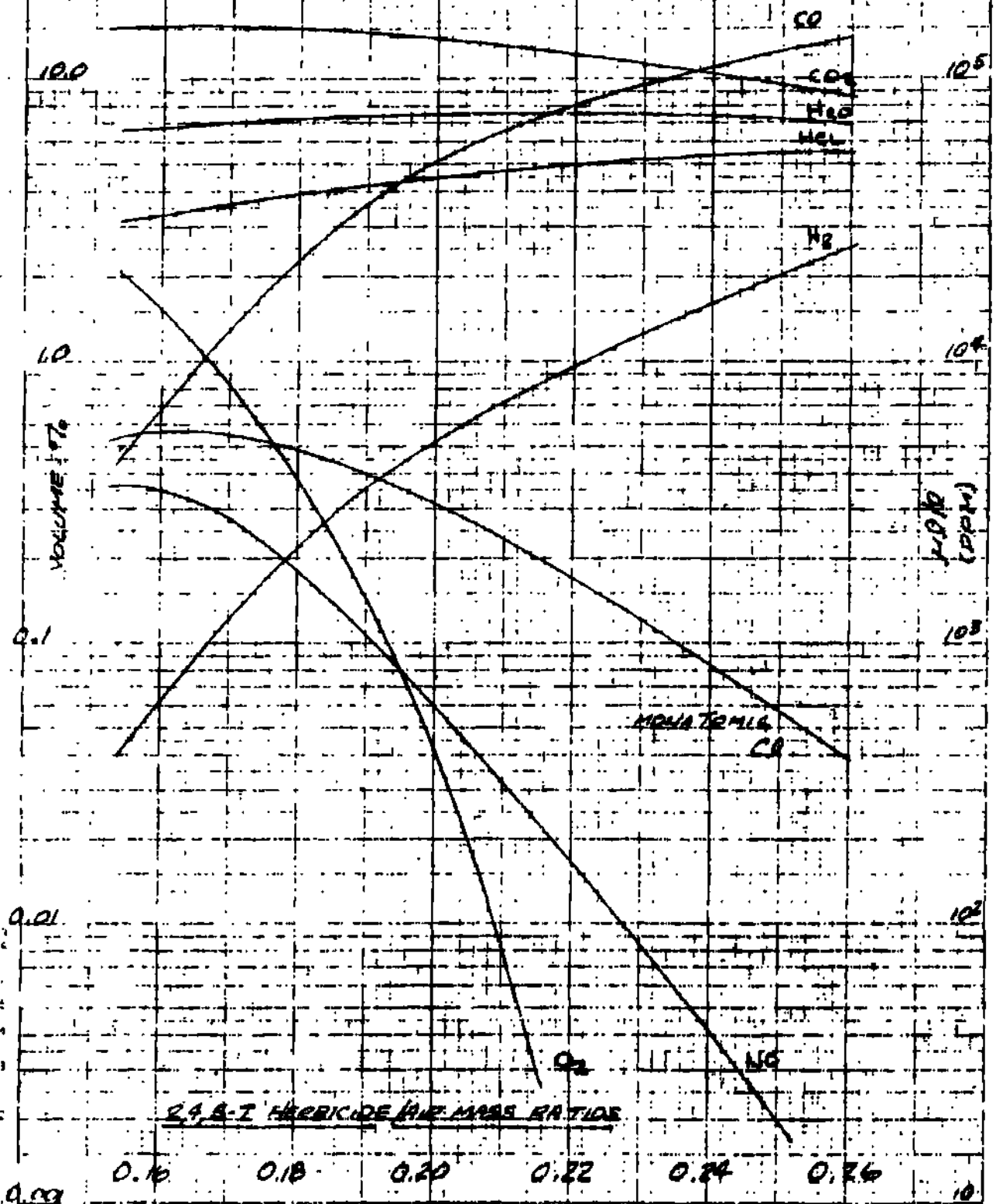
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THEORETICAL COMBUSTION PRODUCTS  
VS 2,4,5-T HERBICIDE/AIR MASS RATIOS  
FOR 532°R AMBIENT AIR



APPENDIX B.  
(TO APPENDIX E)

DETAILED DESCRIPTION OF TEST FACILITY FOR "ORANGE" HERBICIDE  
INCINERATION

A schematic of the complete test facility is shown in Figure B-1. The following discussion will describe the components and systems used during this program.

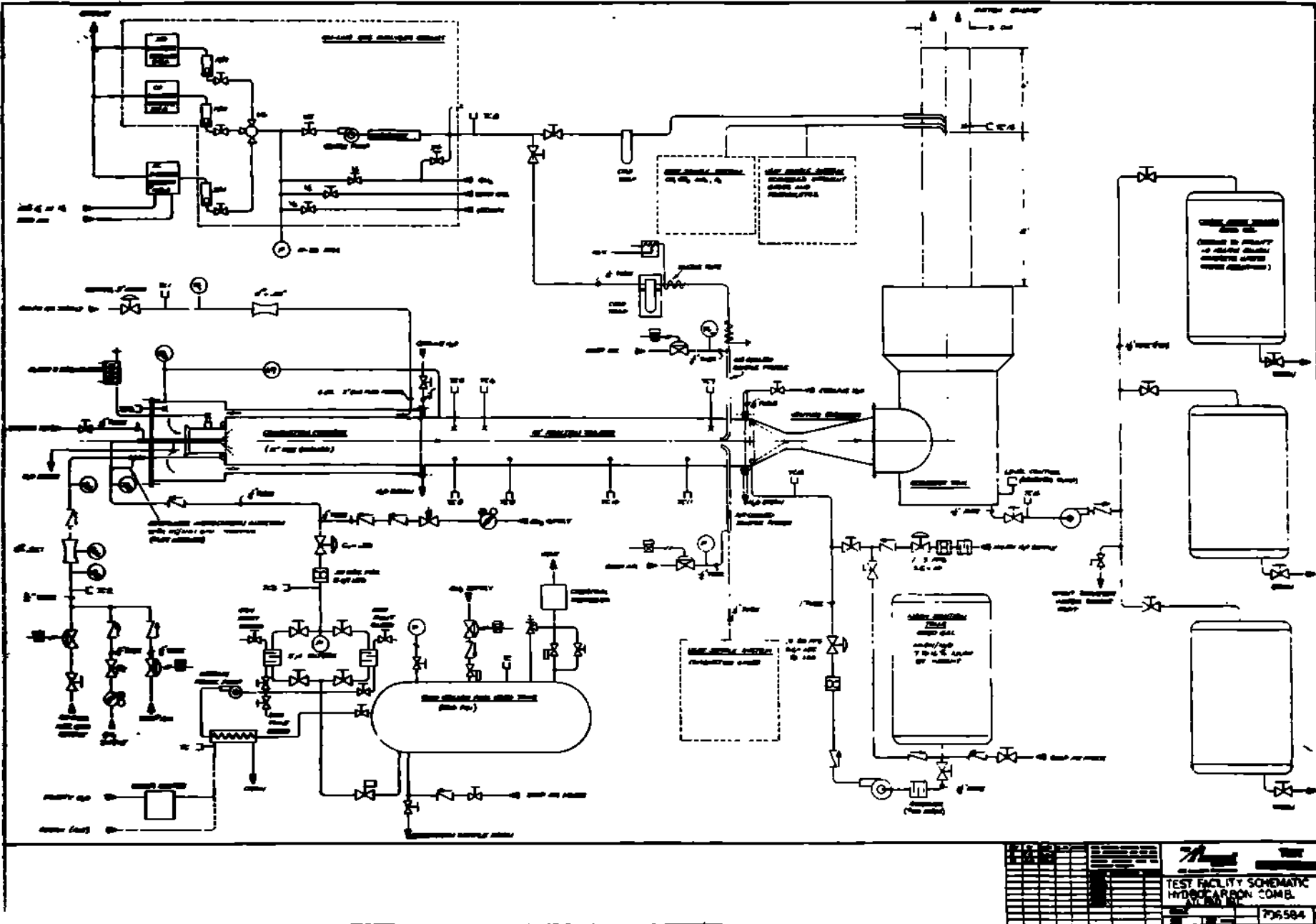
SUE® Burner Incinerator and Reaction Tailpipe

The incinerator consisted of a 12-inch diameter SUE® Burner with a 48-inch long air cooled combustion chamber and 180-inch long uncooled reaction tailpipe. The SUE® Burner insert and cooling jacket shown in Figure B-2 was identical to other standard commercial SUE® Burner units used except that the test unit had not been acoustically treated and longitudinal air vanes had been added to aid combustion chamber cooling.

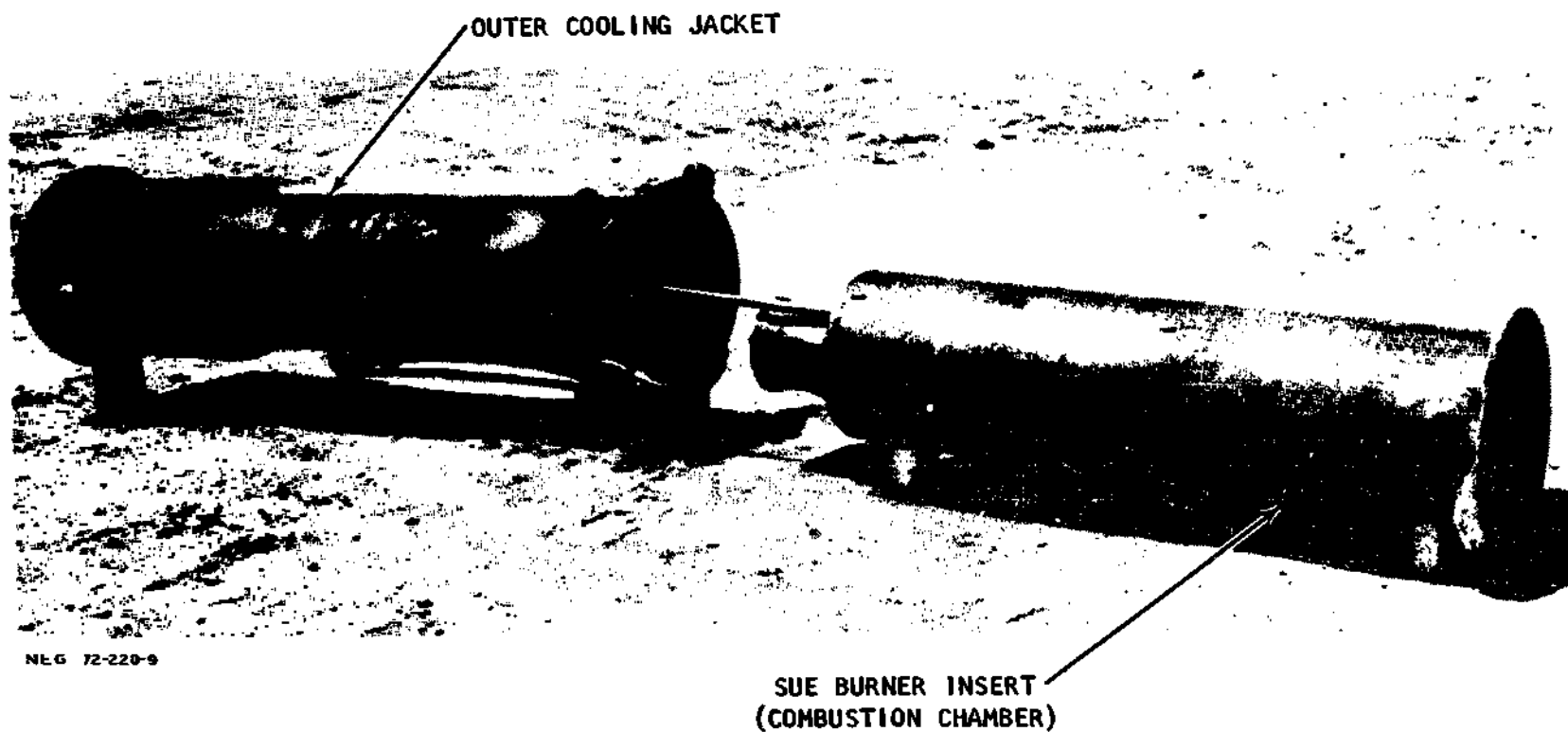
The SUE® consisted of an inlet pipe joined to a larger combustion chamber by a flat expansion plate (see Figure B-3). Fuel was injected through the plate at the "step." Because of this unique injection method, combustible fuel-air ratios were maintained in the recirculation zone, regardless of the overall fuel-air mass ratio. With this method of flame stabilization the burner was capable of operating at average combustion temperatures from 1800°F to the maximum allowable of 2800°F by varying the "Orange" Herbicide/air mass ratio. The maximum allowable temperature was determined by this program's restraint of providing a 30% minimum of excess air.

This SUE® incinerator was equipped with three separate fuel injection arrangements. One set of fuel injectors or nozzles, located in the burner expansion plate, was used to inject the pilot fuel (natural gas). The burner was started with the pilot fuel and a spark type igniter. Two different injection nozzle systems were employed for injecting "Orange" Herbicide. For tests up through Number 9 (Record Burn IV) a central poppet type nozzle was used to inject the herbicide in a finely atomized spray. This nozzle was attached to the inlet plate as shown in Figure B-4 and extended into the burner inlet pipe. Water flowing through the poppet nozzle (Figure B-4) shows its atomization characteristics. For subsequent testing (Test Numbers 10 through 13, Record Burns V through VIII) herbicide was injected with slot type nozzles located inside the natural gas nozzles in the step plate. The slot nozzle manifold and nozzles were located entirely within the natural gas manifold and sprayed into the combustion chamber through the much larger slots in the natural gas nozzles. Refer to Figure B-3. This arrangement kept the fuel nozzles cool at all times due to a small flow of air (0.04 pps) in the outer manifold.

**E(B-2)**

**FIGURE B-1**

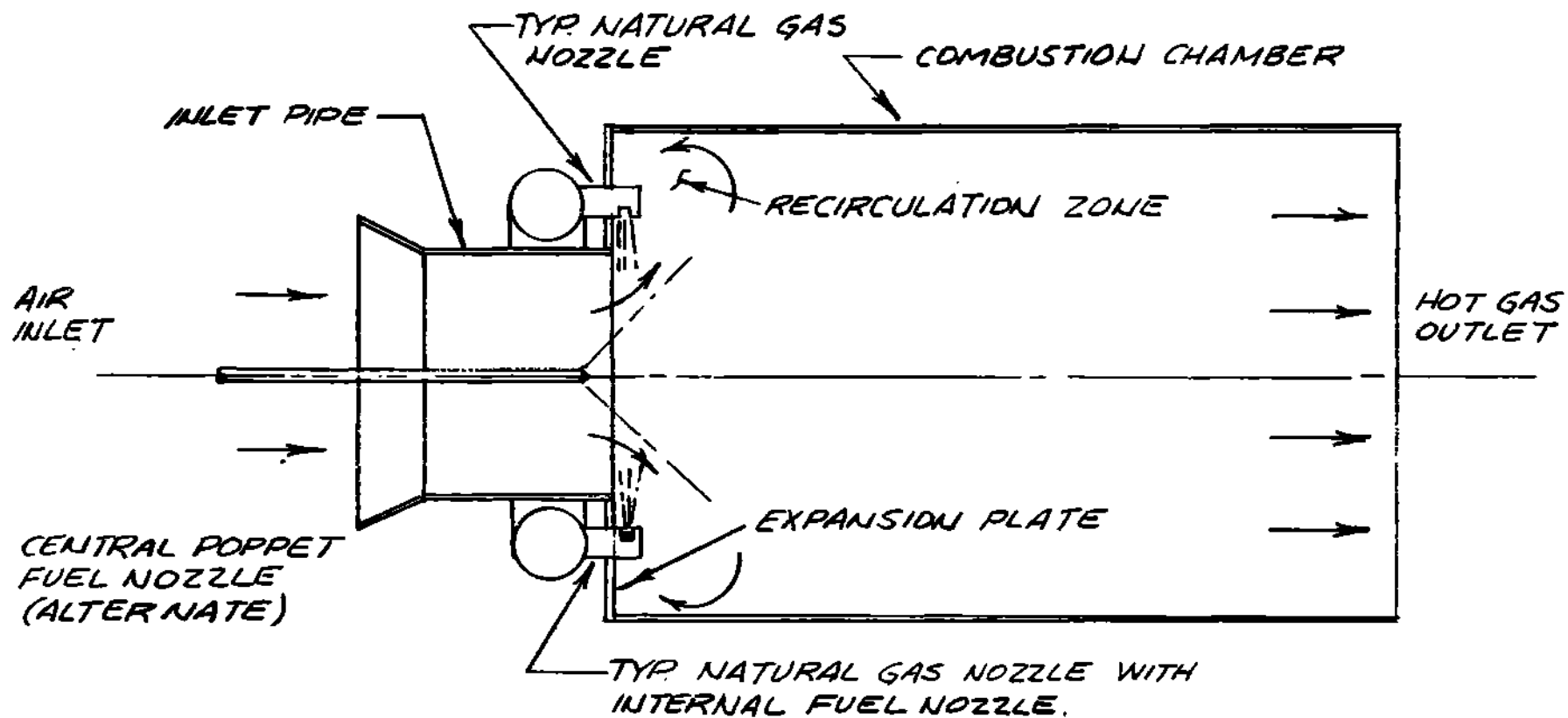
# COOLING JACKET AND SUE BURNER INSERT



E-(B-3)

FIGURE B-2

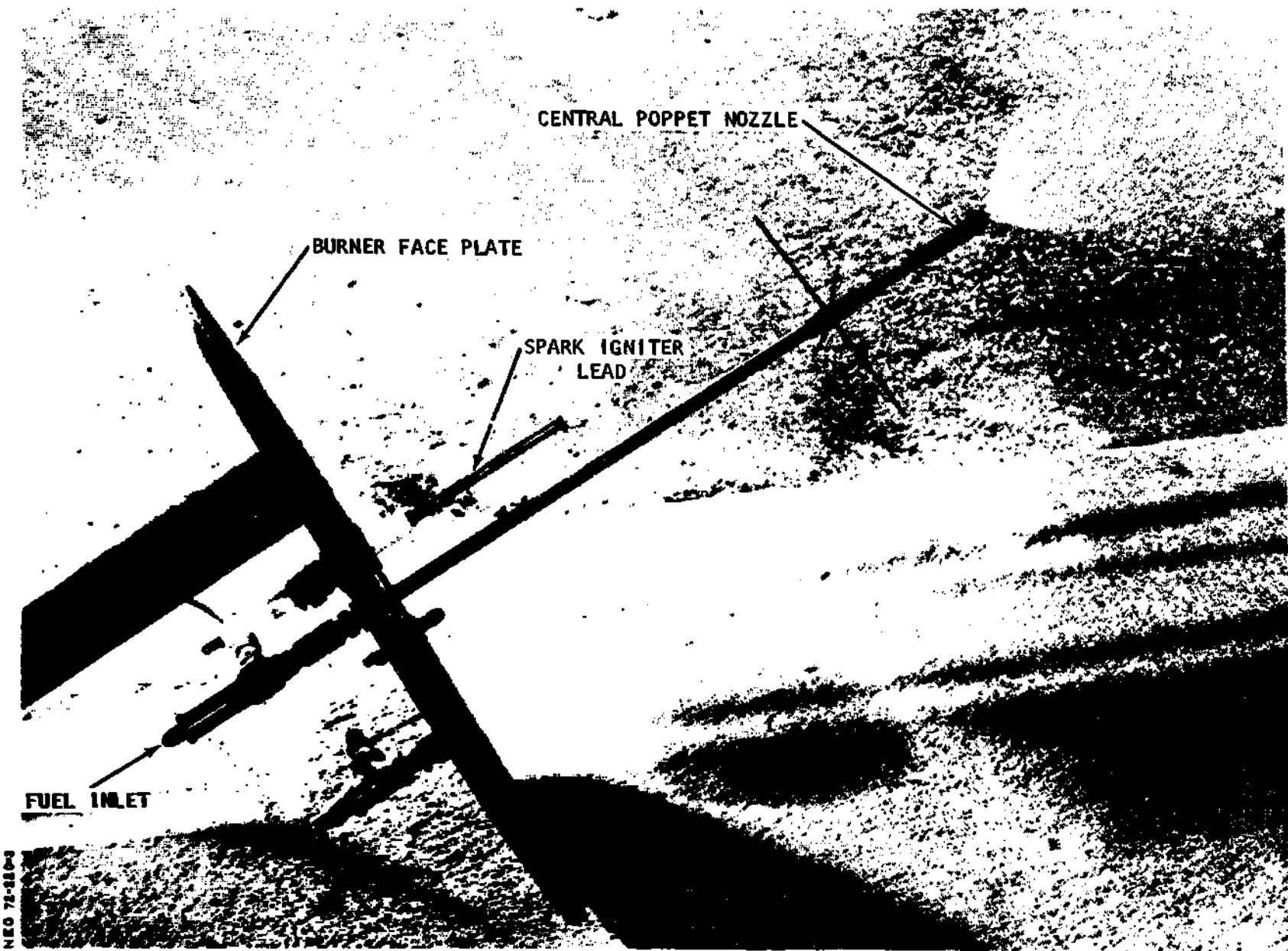
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U.S. PATENT  
NO. 3,074,469

TYPICAL SUE<sup>®</sup> BURNER CROSS-SECTION

# CENTRAL POPPET TYPE FUEL INJECTION NOZZLE



1-(B-5)

FIGURE B-4

A73-12-505-19

The combustion chamber and reaction tailpipe were fabricated from 310 stainless steel. The combustion chamber was actively cooled by passing the process air over the outside of the chamber prior to its entry into the combustion zone. Thus, the incoming air was preheated 400 to 800°F before entering the combustion zone. The 180-inch long reaction tailpipe was uncooled except by radiation to the surrounding environment. This arrangement simplified construction of the test unit and provided a hot wall for completion of the incineration process in the event combustion was not complete within the 48-inch long combustion chamber. The mating flanges of the reaction tailpipe incorporate internal water cooling which prevented warping and leakage. Flange sealing was accomplished with high temperature asbestos fiber material. Ports were provided in the reaction tailpipe for combustion gas sampling probes and instrumentation.

### Venturi Scrubber System

A venturi scrubber was located at the end of the reaction tailpipe, connecting the tailpipe to a scrubber tank. The scrubber tank was approximately eight feet in diameter, 15 feet high and was equipped with an internal water deluge system and a metex screen demistor. The spent scrubber water collected in the tank during a burn was transferred by a cyclic pumping system to holding tanks.

The venturi scrubber shown in Figure B-5 was made according to conventional design from 1/8-inch thick 310 stainless steel. The inside diameter of the inlet and exit sections were 12 inches and the convergent and divergent angles were 40° and 20°, respectively. The throat was 4.4 inches in diameter and 5 inches long. Fresh caustic scrubbing solution mixed with tap water was introduced through a manifold located at the inlet section of the venturi. The mixture was injected through twenty-four 0.094-inch diameter jets directed toward the venturi throat. See Figure B-5. The pressure in the manifold was maintained at approximately 40 psig.

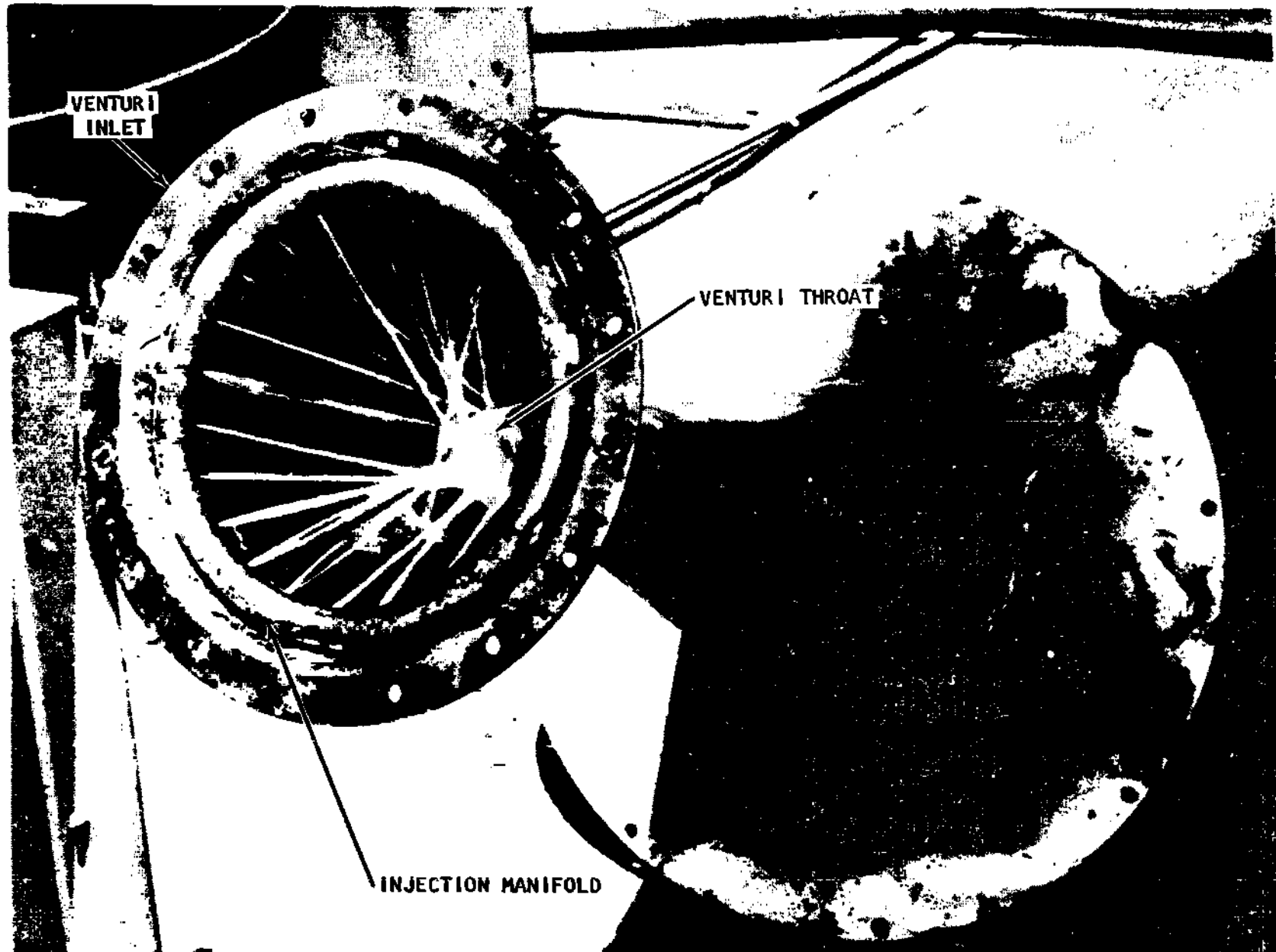
The caustic scrubbing solution cooled and scrubbed the combustion gases as well as neutralized any HCl and Cl<sub>2</sub> that may have been present. Varying amounts of cooling tap water and caustic solution could be applied to the scrubber depending on the requirements for a given burn condition.

### Caustic Solution Supply System

Caustic solution was supplied to the venturi scrubber from a 4500 gallon tank with a 2 HP pump. The flow was regulated by a remotely controlled valve and metered by a turbine flowmeter. Sodium hydroxide was loaded into the tank and diluted to a solution of desired strength. The tanks contents were mixed by shop air bubbling and the concentration of NaOH determined from the specific gravity of the mixed solution.



# VENTURI SCRUBBER



VENTURI  
INLET

VENTURI THROAT

INJECTION MANIFOLD

E-(B-7)

FIGURE B-5

NEG 72-220-5

A73-12-505-10

### Scrubber Water Collection System

The spent scrubber water collected in the bottom of the scrubber tank was transferred by a 2 HP pump to one of three holding tanks. The pump was actuated by a float switch in the scrubber tank when the liquid level had reached about eight inches. Lights in the control room indicated when the pump was on so that the pumping cycle could be monitored and scrubber water samples collected. All the scrubber solution from a burn was pumped into a holding tank and held until released by the Air Force, at which time it was drained to the main facility 1.4 million gallon concrete waste water reservoir.

### Air Supply System

For flexibility in varying and measuring the air flow rate, the 600 psig facility air supply system was used. The incinerator could also be operated with a blower if required. As shown on the schematic in Figure B-1, the air mass flow was regulated remotely with a 3-inch Annin valve and was metered by a 0.80-inch throat diameter sonic venturi. Air mass flow could thus be calculated by knowing only air pressure and temperature upstream of the venturi. The air was introduced at the downstream end of the cooling jacket at four locations through 2-inch diameter hoses (see Figure 3). The air cooled the combustion chamber and was thus preheated to 400 - 800°F before entering the combustion zone.

### Herbicide Fuel Supply System

"Orange" Herbicide or JP-4 was stored and supplied from a 500 psig, 300 gallon fuel feed tank. The tank was pressurized with nitrogen at a pressure required to force the fuel through the supply system and fuel injection nozzles. Fuel was delivered through either of two parallel 5-micron filters and controlled by a 1/2" Annin valve. Fuel mass flow was measured by a turbine flow-meter. A recirculating heater system was used to preheat the "Orange" Herbicide to 90° - 180°F prior to injection into the combustion chamber. A GN<sub>2</sub> purge system was incorporated to allow purging of the fuel supply line downstream of the controls during shutdowns.

### Natural Gas Supply System

Natural gas was supplied from the 30 psig facility system as a pilot fuel to establish temperature equilibrium in the incinerator (800°F) prior to injection and ignition of the herbicide. Natural gas flow was terminated after ignition of the herbicide and an air flow established through this system to cool the natural gas nozzles. Remotely controlled Grove regulators were used to control the natural gas or cooling air flows and metering was provided by the same 0.27-inch diameter sonic venturi.

## Instrumentation and Controls

All the parameters required for determining process mass flow rates, pressures, and temperatures were measured and recorded during each run. The parameters measured and the location of each is shown in Figure B-1 and listed in Table B-1.

Heise gauges were used to indicate total and static pressures. Barton gauges were used to measure pressure differentials. Model CF501R Anadex counters were used to indicate herbicide fuel and scrubber waters mass flow rates in pounds per second. Fluid and gas temperatures were recorded on both an 8 point 0 to 600°F and a 16 point 0 to 2400°F Honeywell Brown recorder. Iron constantan thermocouples were used to measure process temperatures below 500°F and chromel-alumel thermocouples were used to measure temperatures between 500 and 2400°F. All gauges, counters and recorders were certified by the Marquardt Instrumentation Laboratory prior to use for this program.

In measuring actual "Orange" Herbicide mass flow rates during a burn, estimated specific gravity and viscosity corrections were applied to the Anadex counters. After the burn, the herbicide mass flow rate was corrected to reflect actual herbicide specific gravity and viscosity as determined by measured herbicide temperature at the flowmeter. Figure B-6 presents "Orange" Herbicide specific gravity as a function of temperature as plotted from measurements taken during the program. Figure B-7 presents "Orange" Herbicide viscosity as a function of temperature.(4)

**TABLE B-1**  
**INSTRUMENTATION FOR "ORANGE" HERBICIDE TESTING**

SYSTEM	SYMBOL	FUNCTION	NOTE	SIZE OR RANGE
Air	d*	Air Flow Venturi	N/A	0.80"
	PT <sub>1</sub>	Upstream Total Pressure	2	0 - 200 psig
	TC-1	Inlet Total Temperature	1	0 - 100°F
Natural Gas or Nozzle	d*	Gas Flow Venturi	N/A	0.27"
	PT <sub>2</sub>	Upstream Total Pressure	2	0 - 50 psig
	PS <sub>2</sub>	Throat Static Pressure	2	0 - 50 psig
	TC-2	Inlet Total Temperature	1	0 - 100°F
	PT <sub>5</sub>	Manifold Pressure	2	0 - 10 psig
Orange Herbicide or JP-4	wf	Turbine Flowmeter	2	.05 - .20 pps
	TC-3	Inlet Fuel Temperature	1	0 - 200°F
	PT <sub>4</sub>	Manifold Pressure	2	0 - 500 psig
	P <sub>1</sub>	Supply Tank Pressure	2	0 - 500 psig
	P <sub>2</sub>	Supply Pressure D/S Filters	2	0 - 500 psig
	L <sub>1</sub>	Fuel Tank Liquid Level	3	Sight Gauge
SUE® Burner	PT <sub>3</sub>	Burner Inlet Pressure	2	0 - 10 psig
	ΔP <sub>1</sub>	Burner Pressure Drop	2	0 - 25" H <sub>2</sub> O
	TC-4	Burner Air Inlet Temperature	1	0 - 1000°F
	TC-5,6,7	Exhaust Gas Temperature	1, 2	0 - 2400°F
	TC-8,9 10,11	Exhaust Duct Skin Temperature	1, 2	0 - 2000°F

TABLE B-1 (Continued)

INSTRUMENTATION FOR "ORANGE" HERBICIDE TESTING

SYSTEM	SYMBOL	FUNCTION	NOTE	SIZE OR RANGE
Scrubber Systems	W <sub>c</sub>	Caustic Solution	2	0.5 - 2 pps
	W <sub>w</sub>	Water Flowmeter	2	0.5 - 3 pps
	TC-13	Scrubbed Effluent Gas Temperature	2	0 - 200°F
	TC-14	Scrubber Water Exit Temperature	1	0 - 200°F
	TC-15	Caustic Solution Inlet Temperature	1	0 - 100°F
Sampling Systems	PT <sub>6</sub>	Beckman Probe Cooling Air	2	0 - 100 psig
	PT <sub>7</sub>	AF Probe Purge Air	2	0 - 100 psig
	TC-12	Beckman Sample Gas Temperature	2	0 - 300°F

- NOTES: 1. Continuously measured and recorded parameter.
2. Continuously measured but manually read/recorded every 30 minutes or whenever deemed necessary by operational changes.
3. Manually measured/checked and recorded whenever deemed necessary.

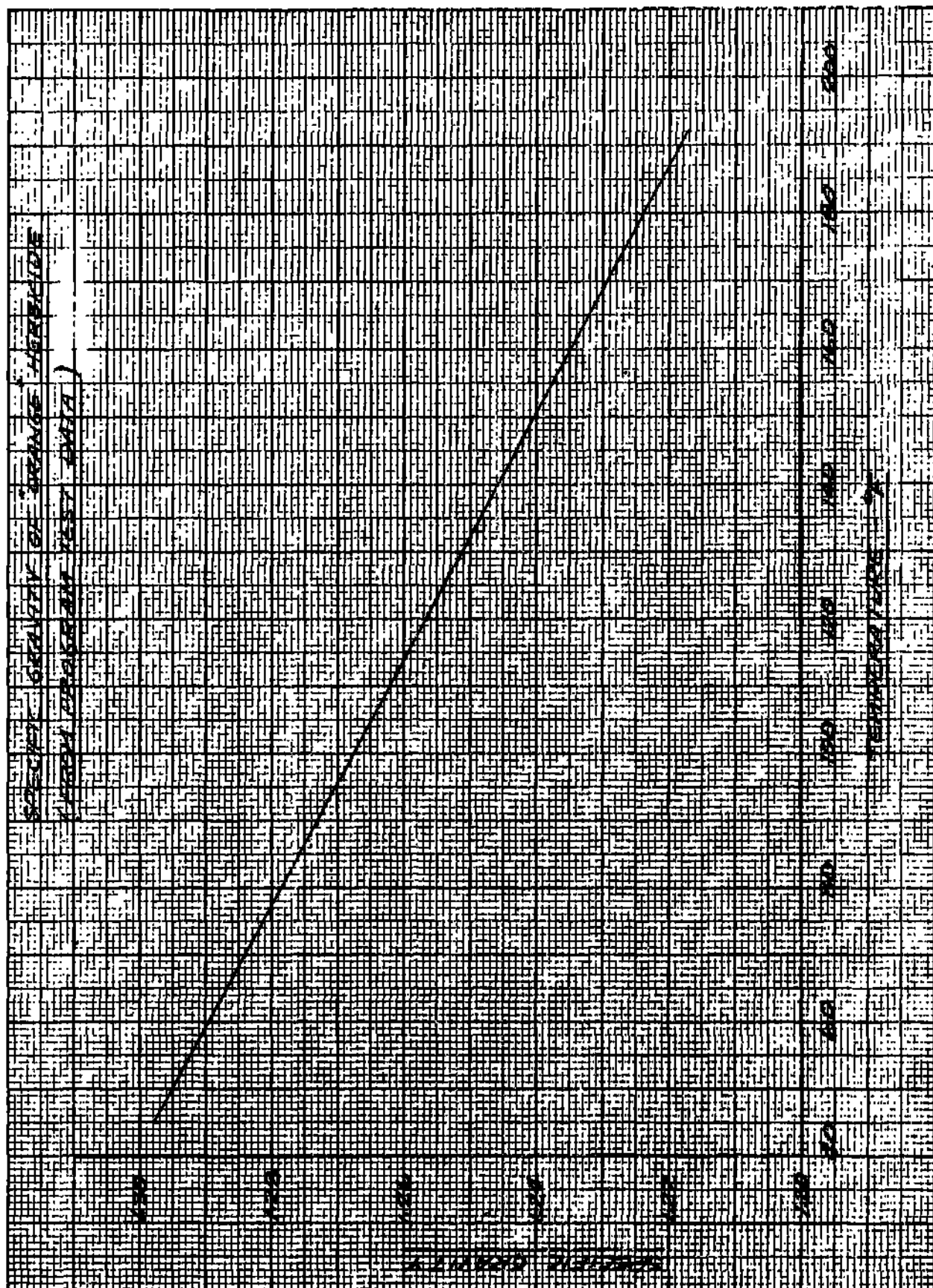
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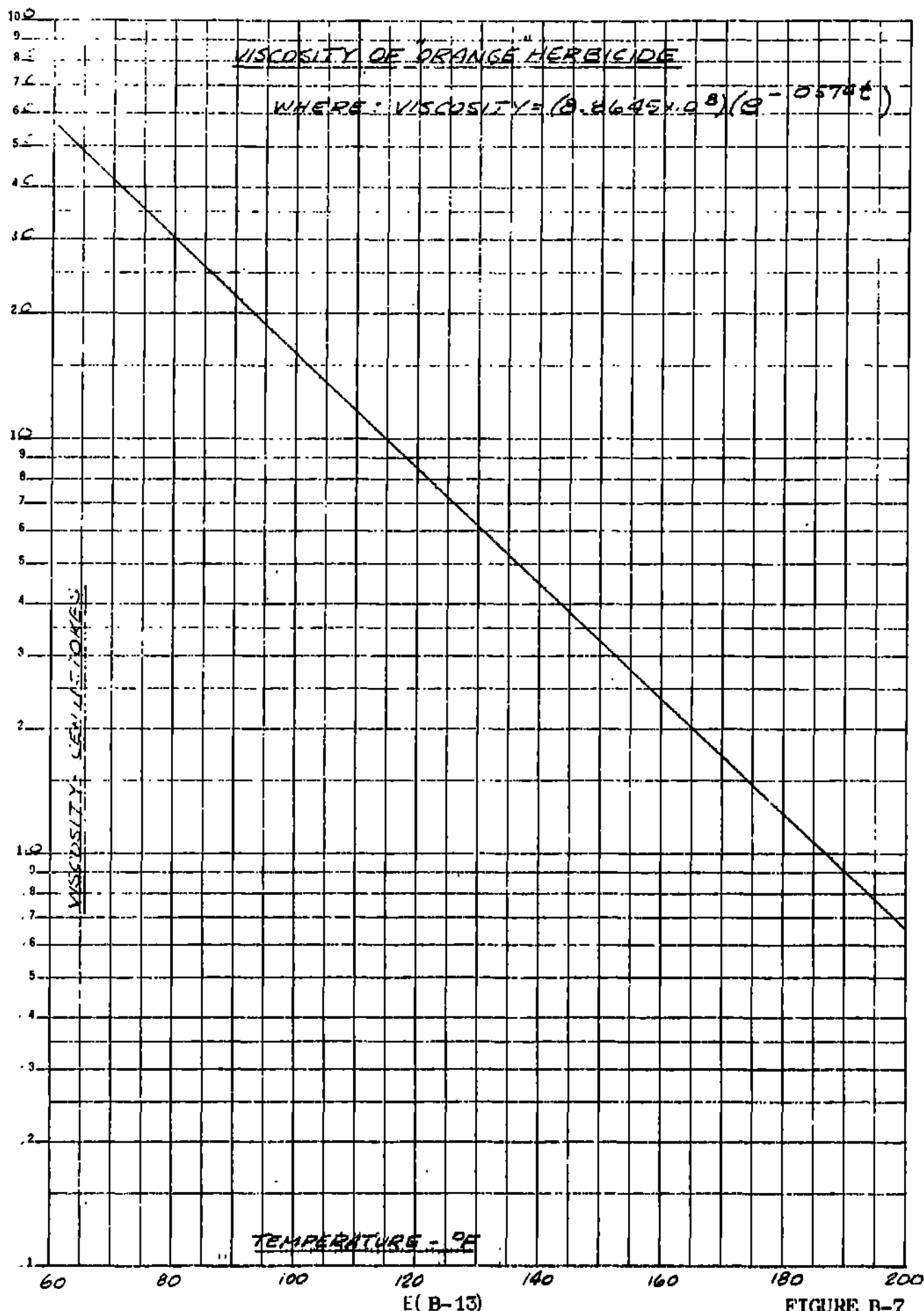
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E-34



USAF ENVIRONMENTAL HEALTH LABORATORY

Kelly AFB, TX 78241

APPENDIX C

(TO APPENDIX E)

SAMPLE CODE DESIGNATIONS

A set of sampling codes was developed and is presented in Table C-1. Each sample collected by either EHL was assigned a code for laboratory control and reporting analytical results. Samples are referenced to these codes throughout this report.

TABLE C-1: SAMPLING CODES FOR SAMPLES COLLECTED BY EHL'S

Type/Source of Sample	Code Letters	Interpretation
	I - (Roman numeral)	Test Burn numbers, I through VIII
Blended Herbicide Feed	-BH-  -number/number/etc.  (Date of Collection)	Blended herbicide feed sample.  EHL(K) red drum-head-number for drums placed into feed tank for the test burn.
Scrubber Water	-FSW-  -A. -B. -SSW- -A- -B- -C- -D- -TBC-  -ARL.  (Table C-1 cont'd next 2 pages)	Fresh scrubber water feed sample.  FSW sample sent to WCTS for analyses.  FSW sample for EHL(K) analyses.  Spent scrubber water into holding tank(s).  20-minute grabs for compositing (1500 ml).  20-minute grabs for reserve samples (1500 ml).  Composite hourly sample (~4500 ml).  Hourly grabs for EHL(K) analyses (1500 ml).  Total burn period composite (4500 to 6000 ml for WCTS and EHL(K) analyses).  Total burn period composite, ~1200 ml, for ARL analyses.

E-(C-2)

TABLE C-1: (cont'd)

Type/Source of Sample	Code Letters	Interpretation
Scrubber water (cont'd)	-number.  -HT-  -1.  -2.  (Time and Date of Collection)	Sequential number from 1 to 3 for each type of grab or hourly composite sample.  SSW collected from holding tank.  HT sample collected from port on side of HT after tank contents had settled for >24 hours.  HT sample of settled solids collected from bottom of HT after tank contents had settled for >24 hours.
Gases	-CG-  -SG-  -number.  -ACP. -WCP. -P-  -CT.  -number(s).  -ARL.  (Time Period and Date of Collection)	Combustion gases collected via sampling train at end of reaction tailpipe.  Scrubbed effluent gases collected via grabs or sampling train in discharge stack.  Impinger number (1 through 4) in sampling train from which sample was taken.  Sample rinsing of air cooled probe.  Sample rinsing of water cooled probe.  Particulate sample collected isokinetically from SG.  Cold trap sample.  Impinger number (1, 2 and/or 3) in particulate sampling train from which impinger contents were mixed for sample.  Samples collected for ARL analyses.

TABLE C-1: (cont'd)

Type/Source of Sample	Code Letters	Interpretation
Residue from within incinerator	-R-  -A-  -B-  -CC-  -1.  -2.  (Date of Collection)	Chucks/particles of residue collected from within the incinerator.  Residue sample sent to WCTS for analyses.  Residue samples kept by EHL(K) for any future analyses.  Location of sample from within the incinerator-combustion chamber.  Orange flakes of residue.  Carbon/black flakes of residue.
Holding Pond	HP-  -number.  (Time and Date of Collection)	Holding Pond  Sequential number from 1 to 4 for each composited sample collected from holding pond.
Drum Rinsing Samples	Letter-  -number-  -number-  -number.	Alphabetical letter (A,B,C or D) to indicate the set of drums receiving a particular rinse procedure.  (EHL(K)'s red number on head of drum.  Sequential number from 1 to 3 to indicate the rinse number for that drum.  Rinse volume in gallons.

USAF ENVIRONMENTAL HEALTH LABORATORY

McClellan AFB, CA 95652

APPENDIX D

(TO APPENDIX E)

COMBUSTION AND SCRUBBED EFFLUENT GAS MONITORING

E(C-5)

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F. (c-6)

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## APPENDIX D

### COMBUSTION AND SCRUBBED EFFLUENT GAS MONITORING

#### 1. Introduction

Monitoring the combustion and scrubbed effluent gases from the incineration of "Orange" Herbicide presented several unusual sampling situations. The combined sampling and analytical techniques had to be sensitive at the parts per billion level for several compounds. The sampling environment was hostile regarding temperature, moisture and potential interfering compounds. Finally the contaminants to be monitored in the scrubbed effluent gas could exist as a vapor, an aerosol or both.

A literature review did not reveal a proven source sampling technique for this work. Consequently, it was necessary to develop one. A technique used in "Orange" Herbicide pyrolysis studies at the Environmental Health Laboratory, Kelly AFB, provided a basis for this development.(D-1)

Several sampling techniques were tested. The one finally chosen was absorption in benzene using a modified EPA source sampling train. The following sections describe the sampling requirements, the sampling technique and methodology, the laboratory validation of the sampling technique, and the results of field sampling and inorganic analysis of gases. (See Appendix I for hydrocarbon results.)

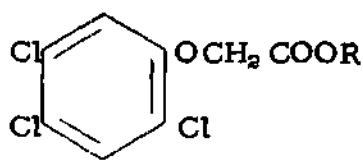
#### 2. Sampling Requirements

##### a. Potential Contaminants.

TCDD was considered the potential contaminant of primary importance. It is a trace contaminant in many lots of "Orange" Herbicide, requires greater heat energy for pyrolysis than the basic compounds of "Orange" Herbicide, and is a hypothetical partial degradation product from the incomplete pyrolysis of nb 2,4,5-T and 2,4-D ester. (See Figure D-1.)

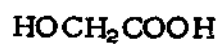
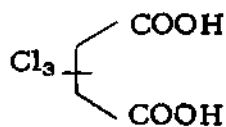
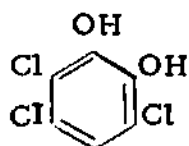
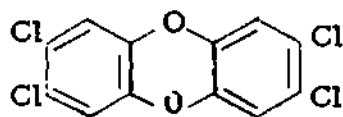
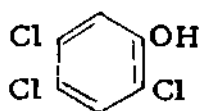
The nb esters of 2,4-D and 2,4,5-T, the principal compounds in "Orange" Herbicide, were potential contaminants and had to be monitored.

The acids of 2,4-D and 2,4,5-T could be formed from the butyl esters through two mechanisms: cleavage of the ester to the acid and butanol in the presence of heat and moisture; and hydrolysis of the ester in the caustic scrubber. Due to the possible formation of these acids they had to be monitored.



2, 4, 5-T

Oxygen Sufficient



Oxygen Deficient

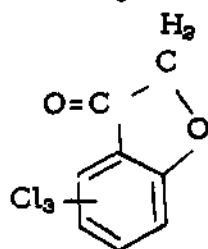
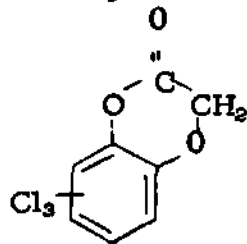
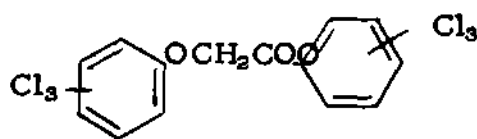
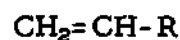
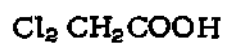


FIGURE D-1: HYPOTHETICAL PARTIAL DEGRADATION PRODUCTS OF 2,4,5-T N-BUTYL ESTER(D-2)

Consideration was given to hypothetical partial pyrolysis products. Figure D-1 is a list of hypothetical products from the incomplete pyrolysis of 2,4,5-T ester.(D-2) It would be impossible to design a practical system for each specific hypothetical pyrolysis product. As the final sampling system was developed, it was found that a majority of the hypothetical products would be trapped in the system by condensation or by absorption in the solvent. While the products might not be collected at a 100% efficiency level, they would be detected. If the products were considered significant, later laboratory studies could simulate the field conditions that existed during sampling and the efficiency of collection could be estimated.

Total particulate loading was considered important for two reasons. An environmental statement would require this information and the particulate matter could be qualitatively and quantitatively analyzed for additional information.

Finally, to evaluate the overall performance of the incinerator, it was necessary to measure the emissions of the common combustion products, CO, CO<sub>2</sub>, NO<sub>x</sub>, O<sub>2</sub>, H<sub>2</sub>O and total hydrocarbons.

#### b. Sampling Locations.

To evaluate the capability of the incinerator to incinerate "Orange" Herbicide, it was necessary to sample at two locations: in the reaction tailpipe just prior to the caustic scrubber and in the scrubbed effluent gas stack. These locations presented different sampling conditions and necessitated the use of slightly different sampling techniques.

(1) Reaction Tailpipe: In the reaction tailpipe, combustion gas temperatures averaged 1900°F. TCDD and the butyl esters and acids of 2,4-D and 2,4,5-T existed only in the vapor phase. Isokinetic sampling was not necessary to obtain a representative sample.

Samples of combustion gases had to be cooled quickly to depress chemical reactions as the gas traversed the sampling probe to the absorbent. However, the gas sample temperature had to be maintained slightly above the boiling point of TCDD and the butyl esters and acids (>350°F) to prevent condensation of these compounds in the sampling train upstream of the impingers.

Finally, measurements of combustion gas velocity were not attempted in this area because of the high temperature and unavailability of specialized equipment. The gas velocity was obtained from Marquardt theoretical data and the temperature was measured by a thermocouple installed by Marquardt. The sampling train did not need a temperature sensor or a pitot tube.

(2) Scrubbed Effluent Gas: The scrubbed effluent gas temperatures were expected to average 170°F. Any TCDD or butyl esters and acids would therefore have existed in the vapor and aerosol phases simultaneously. Isokinetic sampling was required to obtain a representative sample.

The scrubbed effluent gas, after passing the caustic scrubber, would be saturated with water vapor and contain water droplets. To prevent moisture saturation of the particulate filter it was necessary to heat the sample gas above 212°F in the probe to vaporize the water droplets.

### 3. Sampling Techniques.

To accomplish the sampling requirements of Section 2, it was necessary to operate three sampling systems simultaneously. One system was used at the reaction tailpipe section to monitor the potential vapors of TCDD and butyl esters and acids of 2,4-D and 2,4,5-T. The other two systems were used on the scrubbed effluent gas stack, one to monitor the potential vapors and aerosols of TCDD and the butyl esters and acids and the other to monitor particulate matter, hydrochloric acid, free chlorine, and total moisture in the stack.

#### a. TCDD, Ester and Acid Sampling Trains.

The trains used to sample for TCDD and the butyl esters and acids are shown in Figure D-2. The first four Greenburg-Smith impingers were modified with coarse frits and each contained 250ml pesticide quality benzene. Two modified Greenburg-Smith impingers, one containing silica gel and one containing activated carbon, were placed downstream of the four benzene impingers. The main difference between the two sampling trains was the type of probe used. At the reaction tailpipe section, the train box was connected to a stainless steel sampling probe (air cooled in burns I-V and water cooled in burns VI-VIII) via a ground glass joint. The sampling probe was cooled to prevent damage to it in the high temperature of the reaction tailpipe (1900°F). This cooling of the probe also provided the required cooling of the combustion gases (to 300-400°F) in order to suppress any continued combustion reaction within the sampling probe. The sampling train on the scrubbed effluent gas stack was attached to a heated 3-foot glass probe wrapped in asbestos and foil. Since it was necessary to sample isokinetically in the event of aerosol formation, the glass probe had a glass sampling tip of 0.25 inch inside diameter.

#### b. Particulate Sampling.

The train used for particulate matter, hydrochloric acid, free chlorine, and moisture is shown in Figure D-3. The water

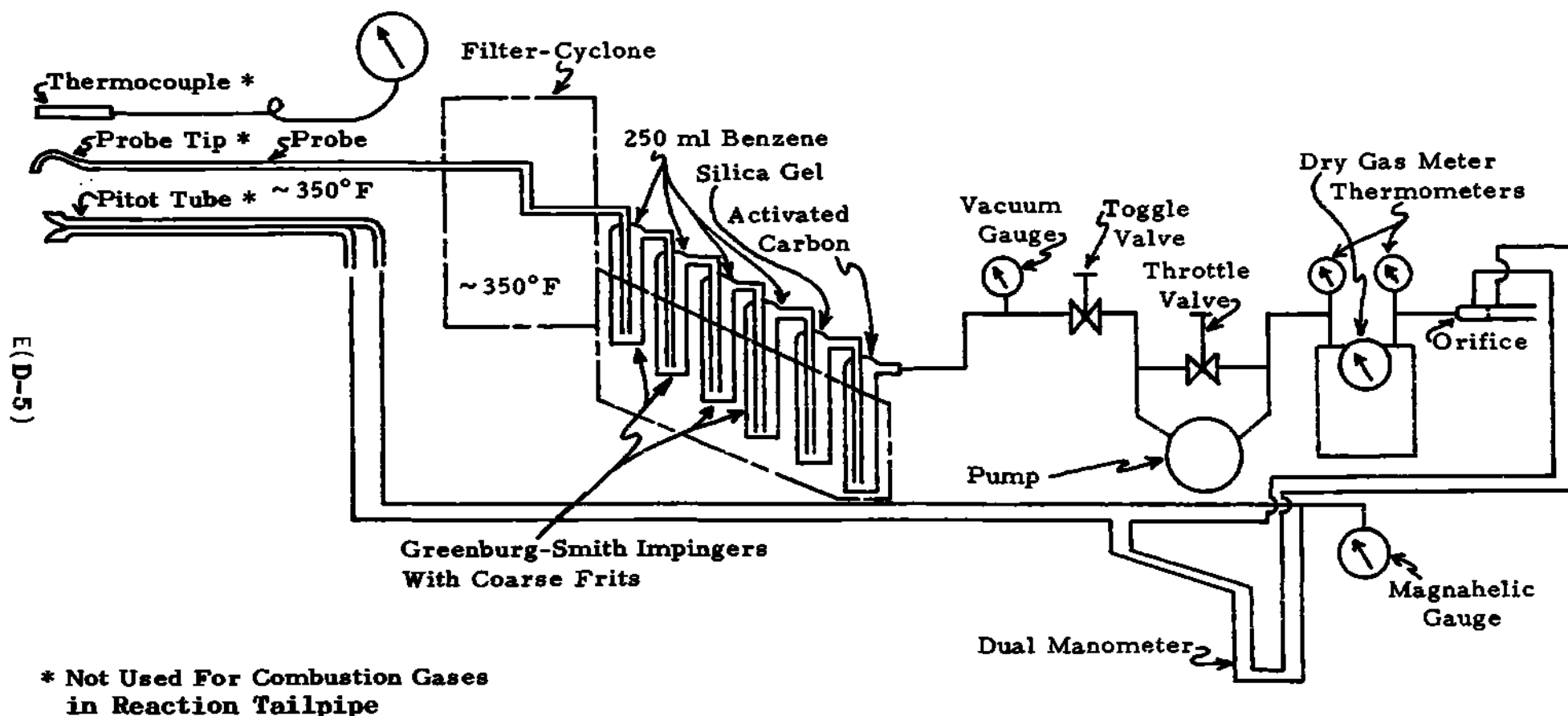


FIGURE D-2: SCHEMATIC OF SAMPLING EQUIPMENT FOR TCDD, BUTYL ESTERS AND ACIDS OF 2,4-D AND 2,4,5-T

"ORANGE" HERBICIDE PROGRAM  
NOV 73

Drawn By:  
Sgt. Frank Lessing  
USAF EHL(M)

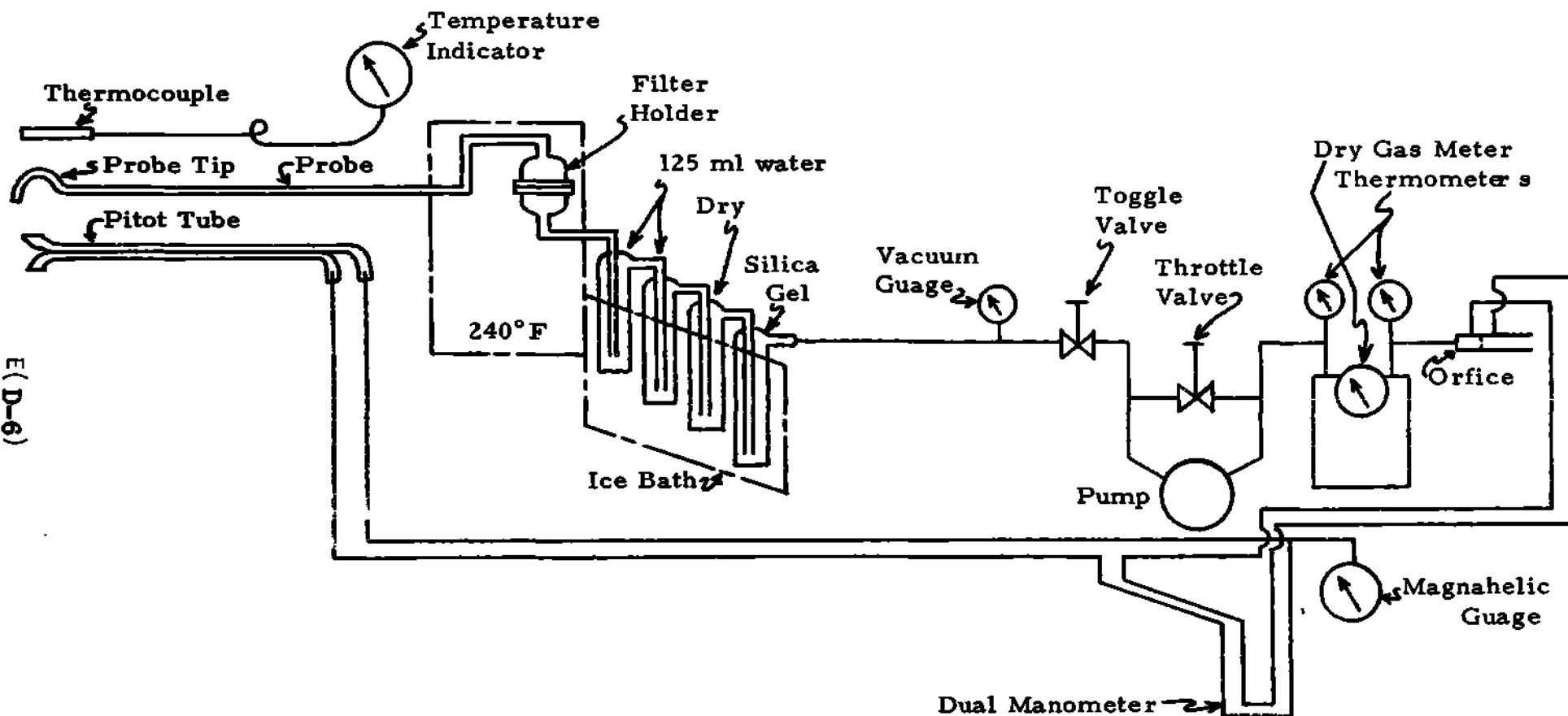


FIGURE D-3: SCHEMATIC OF EQUIPMENT FOR PARTICULATE SOURCE SAMPLING  
 "ORANGE" HERBICIDE PROGRAM  
 NOV 73

Drawn By:  
 Sgt. Frank Lessing  
 USAF EHL(M)

collected in the first two impingers was used to determine hydrochloric acid and free chlorine concentrations in the stack gas.

c. Other Contaminants.

EPA procedures given in 40 CFR 60 were used to sample and analyze the stack gas for CO, CO<sub>2</sub>, O<sub>2</sub>, and NO<sub>x</sub>. Hydrocarbons were continuously monitored by The Marquardt Company using a Beckman 109 Hydrocarbon Analyzer. (See paragraph 4.1.)

4. Validation of Sampling Technique.

Prior to use in the field, the technique of absorption of the butyl esters and acids (of 2,4-D and 2,4,5-T) in benzene was tested in the laboratory. Other sorbents were also evaluated in an effort to avoid using the very toxic and flammable benzene. See Table D-1. These included adsorption on Chromosorb 102, absorption in acetone, and collection in a cold trap.

A brief explanation of events is given below to explain the order of testing and validating the candidate sampling techniques. The original scope of the combustion gas monitoring project was the detection and quantization of TCDD and the butyl esters (2,4-D and 2,4,5-T) that might escape pyrolysis in the incineration process. The first nine experiments concentrated on the butyl esters and three candidate techniques were evaluated for collecting these esters. Then, it was speculated that acids might be formed by either hydrolysis of the butyl esters in the caustic scrubber or by cleavage of the butyl esters in the presence of heat and moisture in the combustion chamber and reaction tailpipe. The scope was expanded to include the detection and quantization of the acids (2,4-D and 2,4,5-T). Since absorption in benzene and adsorption on Chromosorb appeared equally effective for the butyl esters, both sorbents were tested for collection of the acids.

a. Testing Procedure.

The validation procedure was based upon mass balance. A known mass of the butyl esters and/or acids was vaporized and drawn through the sampling system. The collection efficiency was determined by comparing the total mass collected in the collection media with the mass vaporized.

The sampling train was operated in the laboratory exactly as it was planned to be used in the field. This procedure insured that the collection efficiency in the field would not be changed due to different operating conditions.

b. Sample Gas Generation.

Two small glass containers were used to hold individual samples of the butyl esters and acids. The containers were

TABLE D-1

## DESCRIPTION OF SAMPLING TECHNIQUES TESTED IN THE LABORATORY

Experiment #	Description
1.	Series of 4 fritted Greenburg-Smith impingers, each charged with 250ml pesticide quality benzene. Butyl esters collected.
2.	Repeat of Experiment 1.
3.	Series of 4 Greenburg-Smith impingers, 1 and 2 were standard, 3 and 4 were modified,* each charged with 250ml benzene. Butyl esters collected.
4.	Series of 4 Greenburg-Smith impingers, 1 was standard,** 2, 3 and 4 were fritted. 1 was charged with 250ml of 10% NaOH solution, 2, 3 and 4 with 250ml benzene. Butyl esters collected.
5.	Same as 4 except all impingers were fritted and 1 was charged with 250ml of a 2.5% CaOH solution. Butyl esters collected.
6.	Repeat of Experiment 1.
7.	A fiberglass filter, 6" in diameter, followed by the series of impingers described in 1. The filter had 31 gms of 40/80 mesh activated carbon spread evenly on it. Butyl esters collected.
8.	Repeat of Experiment 1.
9.	Chromosorb 102, 12 gms packed in the filter section glassware, followed by the impinger series described in 1. Butyl esters collected.
10.	Same as 1. Acids of 2,4-D and 2,4,5-T collected.
11.	Same as 1. Butyl esters and acids collected.
12-16.	Same as 9 except butyl esters and acids collected.
17.	Cold trap, acetone in an alcohol-dry ice bath followed by the series of impingers described in 1.
18.	Same as 9 except only 2,4-D acid collected.



TABLE D-1 (Continued)

<u>Experiment #</u>	<u>Description</u>
19.	Series of 4 impingers, 1 was standard charged with 250ml acetone, 2, 3 and 4 were fritted and charged with 250ml benzene. Acids and esters collected.
20.	Same as 19 except impinger 1 was charged with benzene.
21.	Repeat of Experiment 18.
22.	Same as 1 except frits on the impingers were changed from fine to coarse frits. Butyl esters and acids collected.
23.	Repeat of Experiment 22.

\*The modified impingers had a glass insert that was not tapered at the end.

\*\*The standard impinger had a glass insert that was tapered at the end and had an impaction plate attached.

attached to the end of the sampling probe by means of a glass tee and ground glass joints. The containers were designed to have identical flow resistance and to require a small vacuum to obtain a flow rate of 1 liter per minute through each. The vacuum prevented the loss of sample vapor through the container air inlet. The rate of sample vaporization was controlled by placing the containers in a portable gas chromatograph oven. The probe from the sampling train was inserted through an asbestos grommet into the oven and the sample containers were connected to it. The butyl esters were vaporized between 80 and 100°C and the acids at 160 to 180°C.

In initial experiments, excess ester was placed in the glass container. The time required to vaporize a given mass was determined and a contaminant concentration calculated from the mass and air flow rates. The results indicated that collection efficiency was independent of contaminant concentration.

#### c. Sampling System Operation.

Prior to each test, the sample was placed in the glass container and the entire unit was dessicated for two hours. The entire unit was then weighed to the nearest tenth of a milligram.

The probe on the sampling train was maintained at approximately 180 to 190°C. This temperature prevented condensation of the butyl esters or acids on the glassware. When the oven and sampling train components were at the correct temperature, the sampling train was turned on. The sample flow rate was maintained at 2 to 6 liters/minute (STP), and the samples were vaporized to provide contaminant concentrations of 0.1 to 50 ppm in the air being drawn into the sampling probe. At the end of the sampling period, the remaining fraction of the sample was weighed to the nearest tenth of a milligram after dessication for two hours. The net difference in sample weight was used to determine the mass of sample vaporized.

#### d. Analytical Procedures.

Electron capture gas chromatography was used for quantitative analysis. Two different units were used at different times. One was equipped with a  $\text{Ni}^{63}$  detector and an 8-foot column packed with 3% OV17. The other unit was equipped with a  $\text{T}^3$  detector and a 6-foot column packed with 3% SE 30. Both columns were 1/4 inch outside diameter. The column and detector temperatures of the units were maintained isothermally at about 165°C and 195°C, respectively.

Peak height comparison was used for quantitative analysis. Area measurement is usually preferred; however, peak height

comparison can be more accurate when the peaks are sharp and narrow.(D-3) The samples in this work were essentially as pure as standards and the resulting peaks were sharp and narrow and not degraded by interfering peaks (see Figure D-5). To obtain maximum accuracy each sample peak height was compared with a standard peak that was within 90 to 110% of the sample peak height. Each sample and standard was injected twice and if the injections differed by greater than 5% of their average, new injections were made until each peak height in a series of three was within 5% of the average. Linearity in the working range was verified before and after each series of samples was analyzed.

### c. Analytical Accuracy.

Weighing of samples before and after vaporization, weighing and dilution of standards, dilution of samples for analysis, and peak height variation were all sources of analytical error. However, peak height variation was considered the major source of error.

Figures D-4 through D-6 were used to illustrate this potential error. These figures depict the chromatographs of impingers 1, 2 and 3 from experiment 2. Assume the standard 2,4-D N-butyl ester peak height of 18 divisions in Figure D-4 represented 96 picograms/2  $\mu$ l, i.e., the true value. The impinger 2-1-2 sample peak height of 19 divisions in Figure D-5 represented  $(19/18)$  times 96/2 or 51 picograms/ $\mu$ l. Let the standard peak height be 5% greater than true and the sample peak height be 5% less than before. Then the impinger 2-1-2 sample peak height of 18 divisions represented  $(18/19)$  times 96/2 or 45 picograms/ $\mu$ l. The 45 picograms was 11% less than the true value. This potential error applied to the total mass in the sample. The total mass in impinger 2-1-2 was in the milligram range while the mass in impinger 2-2 was in the microgram range. Since the overall efficiency was calculated from milligrams to the nearest tenth, the error in impinger 2-1-2 was significant while the error in impinger 2-2 did not affect the calculation of overall efficiency.

The total mass vaporized during a given test was measured to the nearest tenth of a milligram. This mass always exceeded 4 milligrams; therefore, the maximum error in determining the total mass evaporated was 2.5%.

The mass used in standards was weighed to the nearest microgram on a Cahn balance. Class A volumetrics were used for dilution and dilutions were conducted with hexane and volumetrics at  $20^{\circ} \pm 1$ . The error in this procedure was considered less than 1%. Samples were diluted in Class A volumetrics at  $21^{\circ}\text{C} \pm 1$ . After dilution the samples were placed next to the standards and given time to equalize in temperature with the standards.

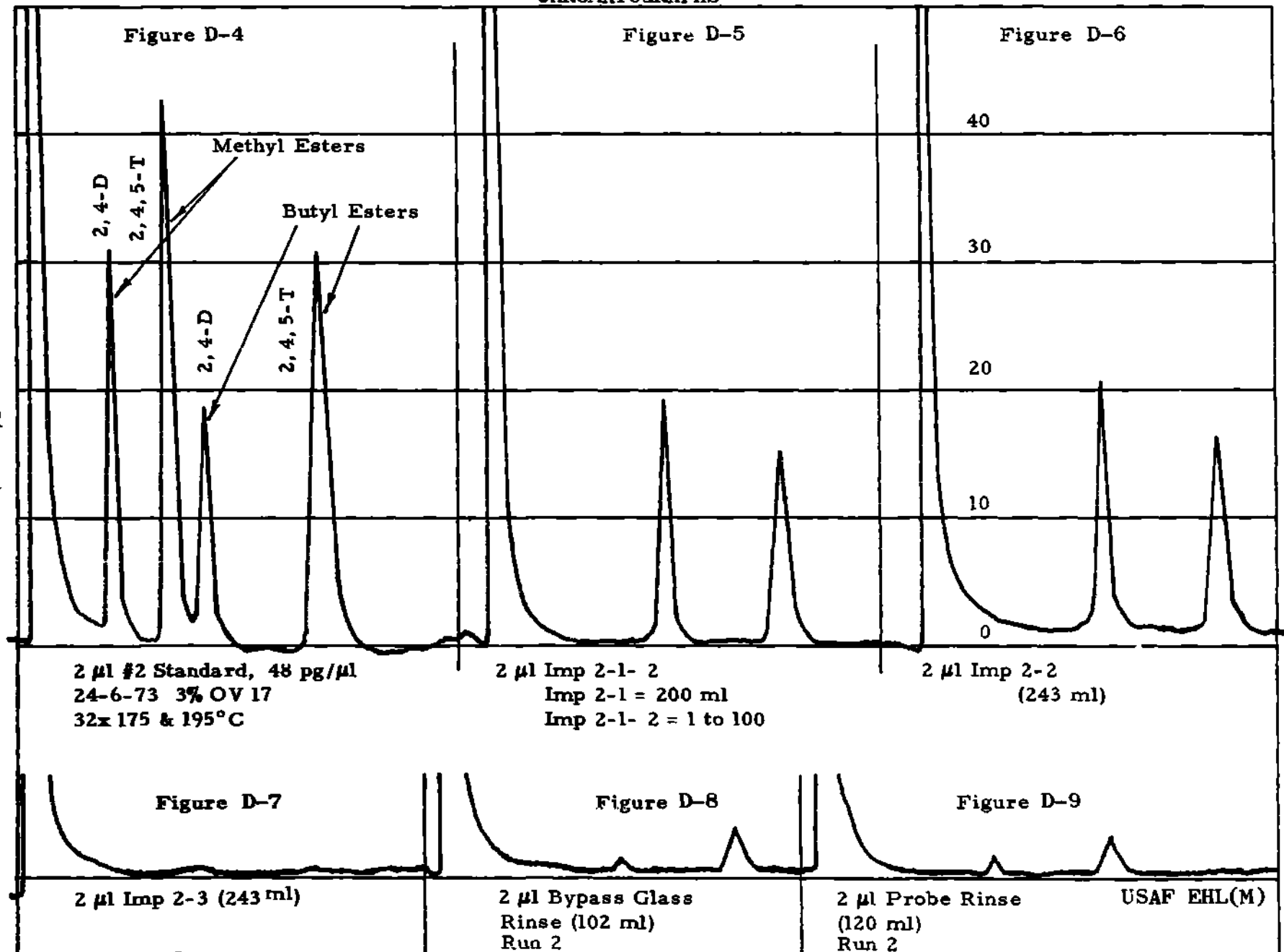
# CHROMATOGRAPHS

Figure D-4

Figure D-5

Figure D-6

E(D-12)



In view of this brief error analysis, the mass determinations were not considered more accurate than  $\pm 15\%$ . Mass recovery was considered complete if it fell between 85 and 115% of the mass vaporized, and the unconcentrated absorbent volume in the last impinger in the series showed no more than a trace amount of contaminant.

#### f. Sample Analysis.

A series of four impingers charged with benzene was used in all experiments either as the primary absorption system or as a backup system when Chromosorb 102 or activated carbon was used as the primary collection medium. To determine the quantity of esters collected in each individual impinger, the benzene volume was carefully measured and each impinger rinsed a minimum of 5 times with pesticide grade acetone. For most experiments the rinsings were added to the benzene remaining in the impinger. This sample was diluted, if necessary, and a two microliter portion injected into the chromatograph and analyzed.

For several runs, the acetone rinse was analyzed separately from the benzene in the impinger. This was done to obtain some insight into the collection mechanism. It was believed that the compounds principally absorbed in the benzene, but condensation on the frit was also an important mechanism.

The benzene and acetone rinse from the third and fourth impingers often contained masses of each ester below the detection limit of the chromatograph. These solutions were never concentrated. The volume of benzene and acetone rinse from these impingers averaged 300 milliliters. Based on the detection limit of the gas chromatograph ( $\sim 5$  picograms/ $\mu$ l), the mass contained in these impingers could not have exceeded microgram quantity unless dilution was required. Since dilution was never required, the mass contained in these impingers never exceeded 0.1% of the total vaporized.

The standard  $\text{BF}_3$  methylation procedure was used to determine concentrations of the acids in the benzene. The benzene and acetone rinses from each impinger were concentrated by rotary vaporization and transferred to a 15 milliliter conical centrifuge tube. The evaporation flask was rinsed with acetone and the rinse added to the tube. The tube content was dried with anhydrous  $\text{Na}_2\text{SO}_4$ , and then concentrated to 0.5 milliliters in a hot water bath. After the concentrate cooled, 0.5 milliliters of 14%  $\text{BF}_3$  in methanol was added and the mixture heated at  $50^\circ\text{C}$  for 30 minutes in a water or sand bath. After the mixture cooled, 0.5 milliliter benzene and 4.5 milliliter of 5% aqueous  $\text{Na}_2\text{SO}_4$  solution was added. After phase separation, the organic layer

was removed and the surface washed with 1 milliliter benzene. The organic layers were passed through a micro cleanup column of florisisil. Benzene was added to the column effluent to bring the processed sample volume to 5 milliliters. This prepared sample volume was then analyzed with an electron capture gas chromatograph.

When Chromosorb 102 or activated carbon was used as the primary collection medium, the contaminants were extracted from the medium with acetone in a Soxhlet extractor at 30 cycles per hour. Again, samples were taken directly from the volume of acetone in the extractor, usually 200 milliliters, and analyzed for butyl esters. The solution was then concentrated, and, if acids had been collected, put through the methylation procedure. In two experiments where esters and acids were collected simultaneously, the samples were evaluated for butyl esters before and after the methylation procedure. This was done to determine the possibility of transesterification of the butyl esters to methyl esters in the methylation procedure. Significant (<3%) transesterification was not detected in this work or in similar studies at the Air Force Academy.(D-4)

#### g. Findings and Discussion.

Absorption of the butyl esters (2,4-D and 2,4,5-T) in benzene was evaluated in experiments 1, 2, 6, 8, 20, 22 and 23 (see Table D-2). The collection of the esters was complete in all experiments except 20 where the first impinger in the fritted series had been replaced with a standard impinger. The collection efficiency in this first impinger dropped from an average 93% with the fritted impinger to 14% with the standard impinger. Also, the last impinger in experiment 20 had a 10% recovery while the last impinger in the other experiments never had more than a trace. Coarse frits were used in experiments 22 and 23 while fine frits were used in experiments 1, 2, 6 and 8. No trace of esters was found in the last impinger of experiments 1, 2, 6 and 8 while a trace was found in the last impinger of experiments 22 and 23. These results indicated a slight but insignificant loss of recovery efficiency with the coarse frits. Consequently, the field sampling unit was designed to use coarse frits because they operated under much less vacuum requirements than the fine frits (3"Hg vs 9"Hg) and significantly decreased the possibility of leaks in the system.

Absorption of the acids in benzene was evaluated in experiments 10, 11, 20, 22 and 23. Results of 10 and 11 were discarded due to errors in analytical procedures. The less than complete recovery in 20 was due to the replacement of the #1 fritted impinger with a standard impinger. In 22 and 23 all impingers were fritted and recovery was complete.

TABLE D-2

LABORATORY TESTING RESULTS  
 "ORANGE" HERBICIDE PROGRAM  
 NOV 1973

Exp #	Overall Efficiency %		Efficiency, Specific Components, %													
			Impinger #								Other *		Glassware Washings			
			1		2		3		4		Esters	Acids	Probe		Bypass	
	Esters	Acids	Esters	Acids	Esters	Acids	Esters	Acids	Esters	Acids			Esters	Acids	Esters	Acids
1	96		76		T		ND		ND				ND		20	
2	105		104		<1		ND		ND				T		T	
3	89		48		36		5		T				T		ND	
4	99		46	<1	52	ND	T	ND	ND	ND			<2			
5	98		97	<1	T	ND	ND		ND							
6	106		90		3		<1		ND						12	
7	103		1		1		T	ND			99		<2		<1	
8	115		113		2		T		ND				ND		<1	
9	98		ND		ND		NE		NE		98		ND		ND	
10+		5		4		>1		ND		ND				ND		ND
11+		ND		ND		ND		ND		ND				ND		ND
12		~1		ND		ND		ND		ND	NE	~1		ND		ND
13		~1	ND	ND	ND	ND	ND	ND	ND	ND	NE	~1				
14		~1	ND	ND					ND	ND	NE	~1				
15			SAMPLE LOST DUE TO CONTAMINATION													
16	87		ND		ND		ND		ND		87		ND		ND	
17	NE	NE	12	12	NE	NE	NE	NE	6	4			ND	ND	ND	ND
18	NE	22	NE	ND	NE	ND	NE	ND	NE	ND	NE	22		ND		ND
19	62	97	13	39	21	37	13	13	15	8			ND	ND	ND	ND
20	80	89	14	32	38	32	18	15	10	10						
21		35		ND		ND						35		<1		<1
22	90	90	86	83	4	7	<1	<1	T	T			ND	ND	ND	ND
23	89	91	87	75	2	13	<1	3	T	T						

T - Trace, None Quantitable Mass

ND - None Detected

NE - Not Evaluated

$$\text{Efficiency} = \frac{\text{Mass Recovered}}{\text{Mass Vaporized}} \times 100$$

Mass Measured to 0.1 Milligram

\* Other Collection Medium

+ Experiment results were discarded due to errors in analytical procedures.

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E-(D-15)

In experiment 19, the first impinger was a modified one charged with acetone. Recovery of acids was 95% while ester recovery was only 62%. Experiment 20 was a duplicate of 19 except the first impinger was charged with benzene. Recovery of esters improved while recovery of acids appeared to decline with the change to benzene. In both experiments, less than 85% of the esters and acids was recovered in the last impinger and recovery was therefore not considered complete.

Adsorption of the butyl esters on 40/60 mesh activated carbon was evaluated in experiment 7. Carbon was spread evenly on a fiberglass filter and the assembly was maintained at 350°F in the filter section. The carbon effectively adsorbed the esters with less than 3% of the esters breaking through to the benzene impingers. The esters were not easily extracted from the carbon and twenty-four hours of Soxhlet extraction was necessary to achieve total ester recovery. This medium was not further evaluated for acid adsorption because of the later experience with adsorption on Chromosorb.

A cold trap of acetone in an alcohol-dry ice bath was evaluated in experiment 17. The acetone was contained in a modified impinger. The impinger insert was a ½ inch inside diameter glass tube that extended to within ¼ inch of the impinger bottom. After a sample volume of only 85 liters had been collected, the impinger insert became totally blocked with ice. Also, the collection efficiency in the trap was only 12%. This sampling technique was discarded due to the icing problem which would be severe in scrubbed effluent gas sampling and the low collection efficiency in the trap.

Adsorption of butyl esters on Chromosorb 102 was evaluated in experiment 9 and for the esters and/or acids in experiments 12, 13, 14, 15, 16, 18, and 21. The Chromosorb was packed in the bypass glassware in the filter section and maintained at 370°F during sampling. Even at this elevated temperature, the Chromosorb effectively adsorbed the butyl esters in experiments 9 and 16. Due to the negative recovery of the acids in experiments 12, 13 and 14, recovery of the butyl esters was not evaluated. In experiments 9 and 16, problematic extraction of the esters from the Chromosorb required sixteen hours of Soxhlet extraction at 30 cycles per hour to effect >85% recovery.

Experiments 18 and 21 were conducted in an attempt to determine the reason for negative acid recovery in experiments 12, 13 and 14. Apparently chemical alteration of the acids was occurring on the Chromosorb due to the significantly elevated adsorption temperature. As a simple test, the Chromosorb was carefully weighed before and after adsorption of the acids. The weight gain indicated



complete mass recovery and no acids were detected in the backup benzene train; however, the Chromosorb was discolored at the upstream interface and only 22 and 35% of the acids were recovered in experiments 18 and 21, respectively. The temperature in experiment 21 was 320°F compared to 370°F in experiment 18. A relationship between temperature and recovery of the acids was indicated during these Chromosorb experiments.

In experiments 2, 6, 7 and 8 the acetone impinger rinse was evaluated separately from the benzene in the #1 impinger. The percent of esters collected in the acetone rinse relative to the total collected in the impinger benzene was 12, 6, 30 and 44% respectively. In experiments 2 and 6 the impinger insert remained in the benzene for several minutes before the benzene was removed. This allowed the esters condensed on the frit to become dissolved in the benzene. In experiments 7 and 8 the benzene was removed immediately after sampling ceased. These data indicated that condensation on the frit was an important collection mechanism. This procedure was not used in the acid experiments; however, condensation on the frit was indicated. The resistance in the sampling system increased or the sample flow rate decreased as sampling progressed. Also, the first acetone rinse percolated through the frit slowly. By the fifth rinse, the acetone passed through the frit freely. The only obvious cause of these anomalies was condensation of the acids on the frit. Since the acids had a much higher boiling temperature than the butyl esters, the condensation mechanism was important in acid collection and accounted for the excellent collection efficiency of acids in benzene even though the solubility of the acids was less than 1% in benzene.

A caustic scrubber was simulated in experiments 4 and 5 by replacing the benzene in the first impinger with caustic solution. A standard impinger and a 10% NaOH solution was used in experiment 4 and a fritted impinger and a 2.5% Ca(OH)<sub>2</sub> solution was used in experiment 5. The purpose of these two experiments was to evaluate the possible hydrolysis of the butyl esters in a caustic scrubber. In both experiments the hydrolysis, if it occurred, was less than 1%. The methyl esters that were detected could have been formed from transesterification of the butyl esters remaining in the solution after extraction. No conclusions could be drawn from these experiments.

Experiments 8 and 22 evaluated the presence of water vapor on sampling efficiency. Fifty milliliters of water were placed in the first impinger. The oven air used to generate samples was also saturated with water vapor by allowing a beaker of water to boil in the oven throughout the sampling period. The sampling efficiency was not degraded by this water.

In the pyrolysis of the butyl esters large amounts of HCl would be produced. To test the effect that HCl might have on the collection efficiency of the butyl esters, five milliliters of concentrated HCl were poured through the first impinger frit just before sampling in experiment 6. As the data indicated, no effect was noticed. There was no reason to suspect that HCl would have any effect upon absorption of the 2,4-D and 2,4,5-T acids.

#### h. Conclusions.

Complete absorption (>85%) of the butyl esters and acids of 2,4-D and 2,4,5-T in benzene, using a series of four fritted Greenburg-Smith impingers, was documented. Test data were conclusive for contaminant concentrations between 0.1 and 50 ppm (by volume) and flow rates between 2 and 6 liters per minute (STP). Collection efficiency was not a function of contaminate concentration or flow rate.

Substitution of a standard impinger for the first fritted impinger in the impinger series decreased absorption efficiency to <85%. Test data were not sufficient to document the precise decrease in efficiency.

TCDD, in view of its chemical similarities to the butyl esters, should be as effectively absorbed in the benzene-fritted impinger system as were the esters. Due to its extreme toxicity, impinger collection of TCDD was not tested in the laboratory.

Water in the impingers and/or the sample gas did not degrade sampling efficiency. Test data verified this at benzene to water ratios of greater than 5 by volume.

The presence of HCl in the benzene did not affect the absorption of butyl esters and there was no reason to suspect that HCl would affect the absorption of the acids. In a very strong acid solution the esters could be hydrolyzed to their respective acids. If only the acids of 2,4-D and 2,4,5-T are detected in the field sampling impingers where HCl will be high, the sampling condition will be duplicated and further evaluated in the laboratory.

#### 5. Sampling Procedure.

Sampling was designed to monitor TCDD and the butyl esters and acids of 2,4,-D and 2,4,5-T simultaneously in the reaction tailpipe section upstream of the scrubber and in the scrubbed effluent gas stack downstream of the scrubber. This sampling scheme in combination with simultaneous scrubber water sampling provided data required to perform certain material balances of the incineration process.

a. Prior to Run:

Minimizing potential contaminants that would interfere with gas chromatographic analyses was essential. All glassware in the TCDD systems was soaked in hot, soapy water, rinsed 5 times with distilled water, and rinsed 5 times with pesticide quality acetone. The first four impingers were charged with 250ml pesticide quality benzene. The last two impingers were charged respectively with silica gel and activated charcoal and weighed. The entire train was then sealed with aluminum foil until sampling commenced. The particulate sampling train was prepared in accordance with procedures established in 40 CFR 60.

Prior to sampling, all three sampling trains were leak tested in accordance with procedures recommended in 40 CFR 60. To verify that no leak occurred in the TCDD sampling train on the stack, the water collected during sampling was compared with the quantity of water collected in the particulate train during the same burn. The water collected in the reaction tailpipe TCDD sampling train was compared to the theoretical amount predicted by the contractor's calculations.

b. During Run:

Sampling was begun after herbicide combustion parameters in the incinerator had stabilized and remained so for a period of time, usually 45 to 60 minutes into the burn.

All three sampling systems were activated as near the same time as possible. The two TCDD sampling systems were always activated within five minutes of each other to provide simultaneous samples pre- and post scrubber.

The sampling system used at the reaction tailpipe section was operated at a sampling rate of 8 to 20 liters per minute and was constant for each burn. Loss of benzene due to evaporation necessitated the low sampling rate and also controlled the duration of sampling. The total sample volume for each burn usually exceeded 500 liters at conditions in the reaction tailpipe section.

The particulate and TCDD sampling systems used on the scrubbed effluent gas stack were operated isokinetically. The system used to sample for TCDD and the butyl esters and acids (of 2,4-D and 2,4,5-T) was not traversed across the stack. Movement of this system would have broken the unprotected glass probe, so it was necessary to conduct single point sampling. This was acceptable because temperature and velocity traverses across the stack showed uniform velocity and temperature profiles. The glass probe tip was sized to keep the sample flow rate between 4 and 6 liters per minute to prevent benzene loss. Sample volume for each burn was between 200 and 400 liters at stack conditions.

The particulate sampling train was traversed across one diameter of the stack. Eight points were sampled with a sampling time of 10 minutes at each point. Because of the presence of the other sampling train in the stack, it was impossible to sample along the other diameter. The average sample volume was 500 liters at standard temperature and pressure, and dry. This train was operated in accordance with procedures recommended in 40 CFR 60 for isokinetic stack sampling.

c. After Run:

Upon completion of the sampling run, the trains used to sample for TCDD and the butyl esters and acids (of 2,4-D and 2,4,5-T) were cleaned according to the following procedures. The final volume of benzene and water in each impinger was measured. Each impinger was then rinsed five times with pesticide quality acetone followed by a deionized water rinse. The volume of this rinse was recorded and added to the benzene and water for that particular impinger. All glassware from the probe tip to the first impinger was rinsed with about 200ml of acetone and the rinsings added to the liquid from the first impinger. This volume was also recorded. All glass connectors between impingers were rinsed into the preceding impinger. Both impingers containing silica gel and activated carbon were weighed. This weight was used to determine the amount of benzene vapors that were adsorbed on the silica gel and carbon. If more benzene was lost from the impingers than was recovered, a sample volume adjustment was necessary. However, the data indicated that all benzene vapors were recovered in the adsorption media.

The particulate train samples were handled in accordance with recommended EPA procedures. Additionally, a small sample of water from the first two impingers in this train was analyzed for hydrochloric acid and free chlorine by the Environmental Health Laboratory, Kelly AFB, Texas. After the particulate sample filter was dessicated and weighed the particulate matter was qualitatively and quantitatively analyzed by WCTS.

6. Field Sampling Results and Discussion

a. Results.

(1) Particulates. These data are presented in Table D-3. The Federal particulate emission standard for incinerators used in Federal government activities is 0.2 grains per standard cubic foot of dry flue gas corrected to 12% carbon dioxide (40 CFR 76). The particulate emissions in the incinerator's scrubbed effluent gases during these tests averaged 0.076 gr/scf (standard deviation = 0.035), and were thus well below the Federal standard. Also, these particulates, by visual observation, appeared to be mostly sodium salts that had been entrained in the scrubbed effluent gas during the scrubbing process in the caustic scrubber (see second paragraph, page G-7, Appendix G).

TABLE D-3  
 SCRUBBED EFFLUENT GAS PARTICULATE SAMPLING DATA  
 "ORANGE" HERBICIDE INCINERATION TESTS  
 12 - 30 NOV 73

Burn#	STACK				Sample Volume Dry @ Stp Ft <sup>3</sup>	lbs/hr	PARTICULATES		
	Temp °F	Dry Gas Fraction	Pressure Inches Hg	Flow Dry @ Stp ft <sup>3</sup> /min			Gr/SCF		
							@12%CO <sub>2</sub>	%Isokinetic*	
I	161	0.66	30.07	1551.2/1211.8	22.58	0.72	0.054	+	72.7/ 93.1
II	166	0.62	30.04	1465.0/1256.2	13.66	0.64	0.051	+	93.1/109.0
III	163	0.65	30.09	1415.4/1290.1	24.49	0.39	0.032	+	86.4/ 95.0
IV	163	0.65	29.96	1515.9/1417.9	26.05	0.71	0.055	0.055	85.8/ 91.7
V	156	0.71	30.28	1719.1/1269.1	27.26	1.39	0.095	0.095	79.2/107.0
VI	175	0.53	30.20	1222.5/1306.9	15.69	0.91	0.087	0.087	85.1/ 79.6
VII	170	0.59	30.12	1447.0/1252.5	20.85	1.05	0.085	0.082	71.9/ 83.1
VIII	151	0.74	30.09	1589.9/ 896.5	20.28	1.98	0.145	+	63.7/116.5

Stack Area: 1003.8 Square Inches.

Velocity is at stack conditions.

\*1st number is based on actual velocity pressure measurements/2nd number is based on velocities calculated from theoretical data (see Appendix I for discussion).

+Not calculated due to erroneous CO<sub>2</sub> measurements during Burns I, II, III, and VIII.

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E-(D-21)

(2) Butyl Esters and Acids (of 2,4-D and 2,4,5-T) and TCDD. Sample volume data are presented in Table D-4. Neither TCDD, the butyl esters nor the acids (of 2,4-D and 2,4,5-T) were detected in any of the combustion or scrubbed effluent gas samples. Detection limits for these compounds during the different burns are presented in Tables G-2 and G-3 in Appendix G. Also see further discussion in Appendix I.

(3) Hydrocarbons. Results and discussion of these data are presented in Appendix I.

(4) CO, CO<sub>2</sub> and O<sub>2</sub>. These data are presented in Tables D-5 and D-6. Concentrations of CO, CO<sub>2</sub> and O<sub>2</sub> in the scrubbed effluent gas for burns IV, V, VI and VII were indicative of efficient combustion. A sampling probe leak invalidated CO, CO<sub>2</sub> and O<sub>2</sub> results for burns I, II, III and VIII.

(5) NO<sub>x</sub>. These data are presented in Table D-5. NO<sub>x</sub> emissions from incinerators are normally low due to the low combustion temperature (<2900°F). NO<sub>x</sub> emissions from the incinerator during "Orange" Herbicide incineration were low (<100 ppm) and in agreement with combustion temperatures and the excess air.

#### b. Discussion.

(1) Particulates. Isokinetic sampling was difficult due to the low velocity pressure (0.008 to 0.01 inch of water pressure) which could not be read more accurately than  $\pm 10\%$  in the scrubbed effluent gas stack. A greater than 100% carbon recovery (Table D-6) as calculated from measured gas velocity pressures and mole fractions of CO<sub>2</sub> and CO in the scrubbed effluent gas indicated that gas velocity pressures were read consistently high and that the scrubbed effluent gas velocities were greater than the actual velocities. To evaluate this possibility revised, scrubbed effluent gas velocities for each burn (see Table D-3) were calculated based on theoretical combustion data (Marquardt) and a chlorine mass balance. The ratio of measured/calculated scrubbed effluent gas velocities averaged 1.15 with a standard deviation of 0.14. Thus it was concluded that measured velocity pressures were read high. A thorough discussion of the revised, calculated scrubbed effluent gas velocities is given in Appendix I.

The EHL(M) thermocouple used to obtain the scrubbed effluent gas temperature was reading 20°F too high (discovered during recalibration after this program). The dry gas fraction used to establish isokinetic sampling parameters had to be calculated from the water vapor saturation value of the scrubbed effluent gas at the sampling temperature. With the incorrect temperature, the indicated dry gas fraction was smaller than the actual. Calculations based on these data indicated that scrubbed effluent gas sampling had been performed at less than isokinetic flow. Fortunately, with the aforementioned revised scrubbed effluent gas

TABLE D-4

TCDD, BUTYL ESTER &amp; ACID (OF 2,4-D &amp; 2,4,5-T) SAMPLING VOLUMES, RATES, AND TIMES

"ORANGE" HERBICIDE INCINERATION TESTS

12 - 30 NOV 73

Burn #	Sample	SAMPLE VOLUME, Liters			Date Nov	Start Time Duration	RATE, Liters/Min	
		Meter Con'd	Stack Con'd	Dry @ STP			Dry @ STP	Stack Con'd
I	CG	184.4	512.6	137.4	13	1445/61	2.25	8.40
	SG	139.3	188.3	106.6		1455/59	1.81	3.19
II	CG	45.0	131.1	34.0	16	1550/17	2.00	7.71
	SG	158.3	228.5	120.4		1622/55	2.19	4.15
III	CG	294.2	790.9	223.2	19	1432/64	3.49	12.36
	SG	126.9	174.8	97.2		1428/57	1.70	3.07
IV	CG	334.0	956.9	250.3	20	1357/60	4.17	15.95
	SG	176.2	242.7	134.4		1345/60	2.24	4.05
V	CG	7.9	24.6	6.0	27	1350/10	0.60	2.41
	SG	145.3	179.7	111.1		1356/60	1.85	3.00
VI	CG	220.9	582.1	165.9	28	1158/31	5.35	18.77
	SG	50.7	81.3	36.3		1207/36	1.01	2.26
VII	CG	150.7	437.2	112.15	29	1007/23	4.89	19.00
	SG	115.5	165.3	82.6		1030/56	1.48	2.95
VIII	CG	169.4	615.0	128.2	30	0952/33	3.88	18.64
	SG	124.0	142.3	90.4		0957/58	1.56	2.45

CG: Combustion Gas, Prescrubber (Reaction Tailpipe)

SG: Scrubber Gas, Postscrubber (Scrubbed Effluent)

Duration, in minutes

USAF EHL(M)

TABLE D-5

CO, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O AND NO<sub>x</sub> SAMPLING RESULTS

## "ORANGE" HERBICIDE INCINERATION TESTS

12 - 30 NOV 73

Burn #	Sample	CONCENTRATION % BY VOLUME				NO <sub>x</sub> ppm	Temp °F	Inches Hg Pressure
		CO	CO <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> O			
I	CG	<0.01	9.1	9.7	4.3	---	1875	36.9
	SG	-----	---	---	34	44.2	161	30.07
II	CG	<0.01	9.6	9.1	4.5	---	1850	35.4
	SG	-----	---	---	38	43.3	166	30.04
III	CG	<0.06	11.5	6.6	5.4	---	1975	41.0
	SG	-----	---	---	35	50.6	163	30.09
IV	CG	0.07	11.5	NA	5.4	---	1840	35.9
	SG	0.90	12.0	4.8	35	48.7	163	29.96
V	CG	0.16	12.9	4.7	6.1	---	2140	38.1
	SG	0.90	12.0	4.8	29	44.8	156	30.28
VI	CG	0.03	11.5	NA	5.4	---	1780	38.1
	SG	0.90	12.0	4.8	47	46.3	175	30.20
VII	CG	0.14	12.7	4.9	6.0	---	2200	41.0
	SG	0.90	12.4	4.8	41	95.9	170	30.12
VIII	CG	0.19	12.7	4.8	6.0	---	2160	32.8
	SG	-----	---	---	26	100.5	151	30.09

SG - Values are average of 4 measurements

CG - Values are theoretical (see main report paragraph 2.6)

## NOTES:

NA - Not available

CG - Combustion gas pre-scrubber

SG - Stack gas post-scrubber



TABLE D-6

## CARBON MASS BALANCE ON SCRUBBED EFFLUENT GASES

## "ORANGE" HERBICIDE INCINERATION TEST

12 - 30 NOV 73

Burn #	Flow*	CO <sub>2</sub> Volume	CO %	CO <sub>2</sub>	CO	Feed Rate		Recovery** %
	Dry @ STP ft <sup>3</sup> /min			Mass as C lbs/min		Fuel lbs/min	Air lbs/min	
IV	1515.9/1417.9	12.0	0.9	5.65/5.28	0.42	4.80	0.01	126/119
V	1719.1/1269.1	12.0	0.9	6.41/4.73	0.48	5.45	0.01	126/ 96
VI	1222.5/1306.9	12.0	0.9	4.56/4.87	0.34	4.80	0.01	102/108
VII	1447.9/1252.5	12.4	0.8	5.57/4.82	0.40	5.48	0.01	109/ 95

\*First number based on measured velocity pressures/second number based on Marquardt theoretical data, see discussion, Appendix I.

\*\*Does not include carbon mass as CO<sub>2</sub> removed by the caustic scrubber or the carbon mass as particulate matter and as hydrocarbon gases escaping in the scrubbed effluent gas.

E-(D-25)

velocities, recalculated isokinetic sampling flows were 96.9% (s=12.9%) and no adjustments of particulate data were necessary.

(2) Butyl Esters and Acids (of 2,4-D and 2,4,5-T) and TCDD. All sample volumes were sufficient to detect  $\pm 5$  ppb of these compounds, except for the six liters of combustion gas sampled from burn V when the air cooled sampling probe clogged part way through the desired sampling period. Although the air cooled sampling probe clogged during burn II, a sufficient sample volume was obtained.

A set of three identical sampling probes was used in burns I through V. The same probe was used in burns II and V. Since the clogging problem was isolated to one probe used in burns II and V, it seemed probable that the sampling conduit was crimped or the 90° bend was too sharp allowing particulate matter to build up. A new water cooled probe was used in burns VI, VII and VIII. This new probe had a 3/16" ID conduit versus the 1/8" ID conduit in the air cooled probe. The larger conduit allowed the high pressure in the reaction tailpipe section to be transmitted to the sampling train. The sample flow rate had to be increased to neutralize the positive pressure in the sampling train.

(3) Hydrocarbons. See Appendix I.

(4) CO, CO<sub>2</sub>, O<sub>2</sub>. A sampling probe leak developed in burns I, II, III and VIII. The CO, CO<sub>2</sub> and O<sub>2</sub> data for these burns were considered invalid.

CO<sub>2</sub> and O<sub>2</sub> concentrations in the scrubbed effluent gas of burns IV, V, VI and VII were in excellent agreement (even though CO<sub>2</sub> was absorbed in the scrubber) with the theoretical values calculated by The Marquardt Company. However, CO values were not in agreement. The measured concentrations of CO were significantly greater than the theoretical values (Marquardt). These data indicated that actual combustion efficiency was slightly less than theoretical efficiency.

(5) NO<sub>x</sub>. These data were taken in anticipation of higher combustion temperatures than were actually attained. NO<sub>x</sub> emissions from the incinerator were low (<100 ppm) and would not be expected to pose any environmental impact.

## 7. Definitions and Formulas

Butyl Esters: Includes N-Butyl 2,4,5 Trichlorophenoxy-acetate and N-Butyl 2,4 Dichlorophenoxy-acetate.

TCDD: 2,3,7,8 - tetrachlorodibenzo-p-dioxin.

**Acids:** Free acids of 2,4,5 Trichlorophenoxy-acetate and 2,4 Dichlorophenoxy-acetate.

**STP:** 70°F and 29.92 inches of Hg.

**Isokinetic Sampling:** Extracting a gas sample from a flowing gas stream at the same velocity of the gas flow.

**Meter Conditions:** Temperature and pressure of gas being measured by the dry gas meter.

**Stack Conditions:** Temperature, pressure, and moisture content of the gas at the sampling point.

**DGF:** Dry gas fraction, the mole fraction of dry gas in the sample volume.

**Gr/scf:** Grains per standard cubic feet dry.

**40 CFR 60:** Code of Federal Regulations, Protection of the Environment, Part 60, Standards of Performance for New Stationary Sources.

Conversion From Volume at Standard Conditions To Volume at Stack Conditions:

$$V_{stk} = V_{stp} \times \frac{T_{stk}^{OR}}{530} \times \frac{29.92}{P_{stk, \text{ in Hg}}} \times \frac{1}{DGF}$$

Conversion From Volume at Meter Conditions To Volume at Standard Conditions:

$$V_{stp} = V_m \times \frac{530^{OR}}{T_m} \times \frac{P_m}{29.92}$$

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APPENDIX E

(TO APPENDIX E)

SCRUBBER WATER MONITORING

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## APPENDIX E

### SCRUBBER WATER MONITORING

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## APPENDIX E

### SCRUBBER WATER MONITORING

1. **INTRODUCTION:** This appendix describes the equipment, procedures, and techniques used to collect scrubber water samples for chemical analyses and bioassay studies. Methods and results of chemical analyses performed by EHL(K) are also described, presented, and related to the combustion system operating parameters.

#### 2. **CLEANING OF SAMPLE CONTAINERS**

a. Containers for Chemical Samples: Upon receipt of the bottles from the manufacturer, EHL(K) washed all bottles and caps once with detergent and rinsed them thoroughly several times with hot tap water. Bottles and caps were then dried for about an hour in a 110°C drying oven. Dried bottles and caps were finally rinsed twice with pesticide grade quality hexane. New aluminum foil was likewise rinsed with pesticide grade hexane and then used to line all bottle caps before the caps were placed on the bottles.

b. Containers for Bioassay Samples: The contractor provided reconditioned 55-gallon drums which had been steamed cleaned. EHL(K) then rinsed these drums with a 25% by weight NaOH solution and then thoroughly flushed them with copious amounts of tap water.

3. **DESCRIPTION OF SAMPLE BOTTLES FOR CHEMICAL SAMPLES:** All water and residue samples collected for chemical analyses were composited and stored for analyses in new, especially cleaned glass bottles. Dark amber, wide mouth glass bottles of 250, 1250, 1500, and 2000 ml capacity were used with molded black plastic caps lined with plastic ringlite. Clear, wide mouth glass bottles of three gallon capacity were also used and had metal screw caps lined with plastic ringlite. The clear bottles were always stored at room temperature in their cardboard shipping containers to keep light away from the collected samples. Bottle caps lined with new aluminum foil were used if the bottle contents were to be analyzed for herbicide and its associated products. Aluminum foil was discarded and not used on the caps of other sample bottles because the alkaline samples would dissolve the aluminum and thus cause analytical interferences with the inorganic analyses.

#### 4. **SAMPLE COLLECTION AND COMPOSITING**

a. Fresh Scrubber Water: A 1500 ml sample of fresh scrubber water was collected prior to commencing record burn tests I, II, III and IV. The supply tank had just been well mixed via agitation with shop air and the samples were taken from the tank's side port.

#### b. Scrubber Water Discharge to Holding Tanks

(1) Spent scrubber water samples were collected from a sample port downstream of the scrubber discharge pump, see paragraph 3.7 and Figure 6 of the report. Sampling was begun after a period in which incinerator operation had stabilized to equilibrium conditions and a cycle of accumulated spent

scrubber water had been pumped from the bottom of the scrubber tank. This period was usually thirty minutes after the caustic scrubber water flow and herbicide ignition had begun. The rate of spent scrubber water accumulation in the bottom of the scrubber tank was such that the float actuated discharge pump cycle was approximately seven minutes in the "ON" mode followed by about thirteen minutes in the "OFF" mode. This twenty minute pumping cycle varied  $\pm 2$  minutes for all record test burns. The discharge pump was allowed to run about one minute and the sample port line was purged before a "pump cycle grab sample" was collected.

(2) Grab sample volumes collected during each pump cycle were: 1500 ml for compositing into a hourly composite, about 1300 ml for a reserve sample, and three to five gallons for compositing a drum of total burn period sample to be used for bioassay studies. A 1200 ml volume (or a proportional fraction) of each hourly composite was used to prepare a total burn period composite (TBC).

c. Scrubber Water Collected From Holding Tanks: After at least 24 hours of quiescent settling, a 1500 ml sample was collected from the side port on a holding tank. This sample was for EHL(K) chemical analyses. At the same time, the bottom valve on the holding tank was opened slowly and a 1500 ml sample of settled particulates was collected. A fraction of this particulate sample was analyzed by WCTS for hydrocarbons and the remaining fraction of this sample was kept by EHL(K) for any future analyses.

d. Holding Pond Waters: Six two-quart grab samples were collected one foot below the surface and at equal distant points around the holding pond. These six grabs were blended to form a composited holding pond sample. The holding pond was so sampled once before any spent scrubber water had been discharged into it. Spent scrubber water from the following groups of record test burns were then discharged into the holding pond and a holding pond composite sample collected 24 hours after the last record burn's water had been discharged: I and II; III and IV; V, VI and VII.

5. EHL/K METHODS AND EQUIPMENT FOR INORGANIC ANALYSES OF SCRUBBER AND HOLDING POND WATER SAMPLES: Tables E-1 and E-2 list the techniques and equipment used by EHL/K to measure physical and analyze inorganic chemical parameters of collected water samples. Additional comments are:

a. The analyses of diluted samples for specific conductance were multiplied by two different factors to relate the two different dilutions back to the original sample strength. These factors were different because specific conductance readings are nonlinear with dilutions (see Table 154 of reference cited in Table E-1). Analyses of 1/99 dilutions were multiplied by 80.44 while 10/90 dilutions were multiplied by 8.73.

b. Solids analyses that required filtration were filtered through 0.6 $\mu$  glass fiber filter disks. Since the volatile solids fractions from burns I and II were such an insignificant fraction of their respective total solids, the volatile solids were not analyzed in subsequent samples.

c. Total dissolved solids were measured per Standard Methods (TDS-Ms) and with a meter (TDS-Mt) in order to compare the meter's results to the conven-

TABLE E-1: EHL/K TECHNIQUES OF ANALYSES OF WATER SAMPLES

Inorganic or Physical Parameter	Volume of Sample Analyzed (ml) /Dilution Volume (ml)					Reference to Procedures Followed** (pages/method)
	FSW*	SSW*	HT*	HP*	SG-P* 1 & 2	
Temperature	N/A	N/A	N/A	N/A	NT	N/A
pH	100/0	100/0	100/0	100/0	"	500
Specific Gravity	250/00	250/0	250/0	250/0	"	550
Specific Conductance	1/99	10/90	10/90	100/0	"	323-327
Total Solids (TS)	10/0	10/0	10/0	10/0	"	535-541
Volatile Total Solids (VTS)	NT	10/0	10/0	NT	"	"
Total Dissolved Solids (TDS) - Meas.	10/0	10/0	10/0	10/0	"	"
Total Dissolved Solids (TDS) Meter	1/199	1/199	1/199	NT	"	NA
Volatile Total Dissolved Solids (VTDS)	NT	10/0	10/0	NT	"	535-541
Suspended Solids (SS)	NT	100/0	100/0	NT	"	"
Volatile Suspended Solids (SS)	NT	100/0	100/0	NT	"	"
Chlorides	1/99	1/99	1/99	100/0	100/0	377/203B
Total Chlorine Residual	2/0	1/249	1/249	2/0	2/0	385/204B
Free Available Chlorine	2/0	1/249	1/249	2/0	2/0	"
Sodium	1/2499	1/999	1/999	1/9	NT	317/153A
Iron, Total	20/0	20/0, 1/249	20/0	20/0	"	211/129A
Total Alkalinity	2/98	2/98	2/98	100/0	"	370/pH meter
Hydroxyl Alkalinity	2/98	2/98	2/98	100/0	"	"
Bicarbonate Alkalinity	2/98	2/98	2/98	100/0	"	"
Carbonate Alkalinity	2/98	2/98	2/98	100/0	"	"

\*See Appendix C for definition of these sample codes.

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NT - Not Tested

\*\*Standard Methods for the Examination of Water and Wastewater, 13th Ed, American Public Health Association, 1015 18th St NW, Washington DC 20036 (1971).

TABLE E-2: EQUIPMENT USED BY EHL/K TO ANALYZE WATER SAMPLES

Measured Parameter	Equipment Description
Temperature	Immersion mercury thermometer
pH	Beckman Century SS pH Meter with combination 0-14 pH electrode. Meter Model 76. Standardized with pH buffers 4.0, 7.0, 10.0, and 12.45.
Sp. Gravity	Hydrometers: For liquids 1.000-1.200, and for liquids 1.200-1.400
Sp. Conductance	Delta Scientific Conductivity Monitor/Recorder, Model 3314-01, Serial No. 2277.
TDS-Mt	Total Dissolved Solids Meter, Model 512T5, Serial No. 062137, Myron L. Company.
Chlorine Residuals	Hellige Chlorine Comparator
Sodium	Atomic Absorption, Perkin Elmer, Model 403.
Iron, Total	" " " " " "
Weights	Mettler Balance, Model H-10Tw, accurate to 0.1 mg.

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tional standard method. This was done because the standard method was very time consuming and subject to larger errors because of weighing and calculations based on a 10 ml sample. Figure E-1 presents these different TDS values. Although the values differed by an order of magnitude, the meter values were acceptably correlated to the measured values. The error in correlation was acceptable considering the overall error ( $\pm 15\%$ ) in measuring such high concentrations of hygroscopic solids, i.e. sodium hydroxide and sodium salts.

d. EHL/K chlorine residuals of burn I were verified by WCTS analyses using the iodometric method. Since acceptable agreement of these analyses was within  $\pm 20$  mg/l, subsequent chlorine residual analyses were done using the Hellige chlorine comparator.

e. Alkalinities were analyzed per the potentiometric method using pH titration endpoints of 10.0, 8.3, 4.5, and 4.2. All results were expressed as mg/l as calcium carbonate.

## 6. ANALYTICAL RESULTS AND DISCUSSION OF SCRUBBER WATERS INORGANIC QUALITY

a. Fresh scrubber water analyses in Table E-3 showed the quality of this highly caustic solution which was prepared to range from 8.7 to 15.5% by weight NaOH. From data in Tables E-4 through E-11, spent scrubber water (SSW) quality was essentially constant between hourly composites, the TBC, and the holding tank sample for a given burn. The only inconsistency was in burn VI when the applied caustic flow rate was increased from 1.73 pps to 2.32 pps. This change in scrubber water quality in burn VI SSW-CI's indicated the very strong effect that applied caustic had on the SSW quality. Chemical constituents in each burn's SSW holding tank were converted to total mass produced (pounds) and pounds per drum of herbicide burned. This last value was calculated so that the chemical constituents could be compared directly between burns and independent of the volume of scrubber/cooling water produced or the durations of the burns.

b. Although the concentrations of SSW inorganic constituents changed between burns because of different applied caustic and herbicide fuel feed rates, the following concentrations were consistently within the following ranges and worth noting:

(1) pH: 10.5 to 11.8.

(2) Specific Gravity: 1.040 to 1.075

(3) Specific Conductance ( $\times 10^4 \mu\text{mho/cm}$ ): 11.3 to 15.8

(4) Total Solids or Total Dissolved Solids - both being about equal ( $\times 10^3$  mg/l): 61.0 to 87.0

(5) Suspended Solids (mg/l): 56 to 97. As discussed in Appendix I, these solids contained no hydrocarbons and were essentially carbon containing less than 10% by weight iron. The volatile fraction of the suspended and total solids was considered insignificant. The concentration of suspended solids increased significantly to 500-800 mg/l because of iron content when applied caustic was decreased below two times theoretical requirements.

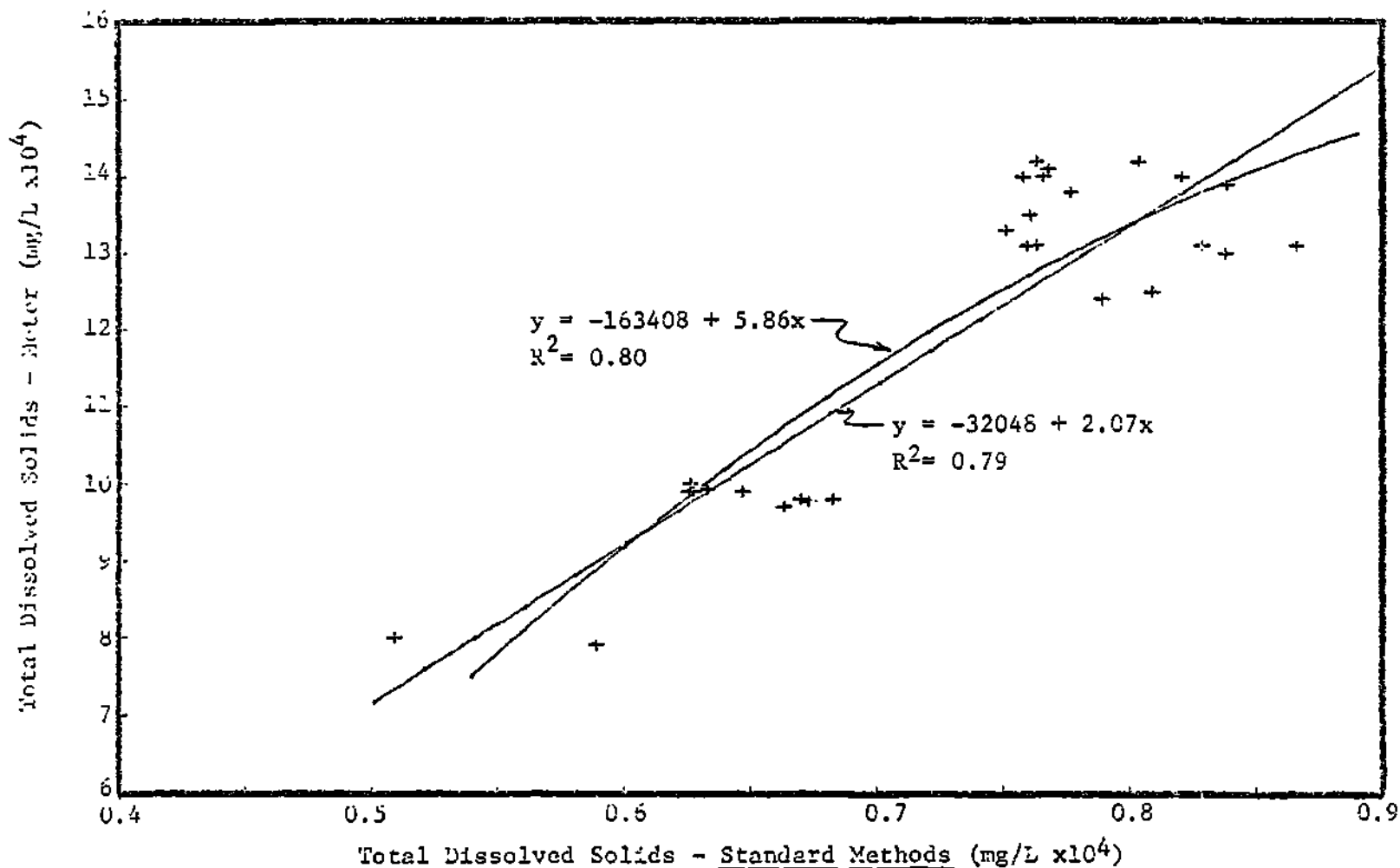


FIGURE E-1: RELATIONSHIP OF TOTAL DISSOLVED SOLIDS MEASUREMENTS  
ON SPENT SCRUBBER WATER - STANDARD METHODS vs METER

TABLE E-3: SUMMARY OF EHL/K FRESH SCRUBBER  
WATER ANALYSES

SAMPLE NUMBER		III-FSW B	IV-FSW B	AVERAGE VALUES
Time Collected (hrs)		1000	1450	
Date Collected (Nov 73)		Mon 19	Tue 20	
Date Analyzed (Nov 73)		Sat 24	Sat 24	
GENERAL	Parameter (mg/l unless noted)			
	Temp (°F) at time:			
	Collected	66.	63.	-
	Analyzed	72.	72.	-
	pH	13+	13+	13+
	Sp. Gravity	1.149	1.154	1.151
SOLIDS	Sp. Cond. ( $\times 10^4$ $\mu$ mho/cm)	65.9	68.3	67.1
	TS ( $\times 10^3$ )	174.77	189.37	182.07
	VTs ( $\times 10^3$ )	-	-	-
	TDS, Mt ( $\times 10^4$ )	50.0	50.0	50.0
	TDS, Ms ( $\times 10^3$ )	-	-	-
	VTDS ( $\times 10^3$ )	-	-	-
	SS	-	-	-
	VSS	-	-	-
	Chlorides ( $\times 10^3$ )	0.014	0.014	0.014
	Total Chl. Resid.	0.0	0.0	0.0
IONS/RADICALS	Free Avail. Chl.	0.0	0.0	0.0
	Sodium ( $\times 10^3$ )	97.5	97.5	97.5
	Iron, Total	1.45	1.61	1.53
ALKALINITY	Total Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	195.8	198.0	196.9
	OH-Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	193.3	196.3	194.8
	$\text{HCO}_3$ -Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	0.0	0.0	0.0
	$\text{CO}_3$ -Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	2.5	1.7	2.1

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TABLE E-4: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN I

SAMPLE NUMBER	I - SSW-						HT-1	
	C-1	C-2	C-3	Ave. C-1/C-3	TBC	HT-1		
Time Collected (Hrs)	1430- 1503	1520- 1555	1613- 1647	1430- 1647	1430- 1706	1045	lbs	lb/Drum of Herbicide Burned
Date Collected (Nov 73)	Tue 13	Tue 13	Tue 13	Tue 13	Tue 13	Sat 17		
Date Analyzed (Nov 73)	Wed 14	Wed 14	Wed 14	Wed 14	Wed 14	Sat 17		
GENERAL	Parameter (mg/l unless noted)							
	Temp ( <sup>o</sup> F) at time:							
	Collected	164.	164.	164.	164.	-	-	-
	Analyzed	72.	73.	73.	73.	72.	75.	-
	pH	11.65	11.75	11.60	11.70	11.85	11.50	-
	Sp. Gravity	1.060	1.060	1.060	1.060	1.060	1.055	-
SOLIDS	Sp. Cond. ( $\times 10^4$ $\mu$ mho/cm)	14.9	15.1	14.8	14.9	14.8	14.0	-
	TS ( $\times 10^3$ )	78.77	74.28	75.77	74.94	75.61	71.23	2462.14
	VTS ( $\times 10^3$ )	4.10	4.11	6.05	4.75	5.82	-	-
	TDS, Mt ( $\times 10^4$ )	13.1	13.3	14.1	13.5	13.1	11.8	4078.80
	TDS, Ms ( $\times 10^3$ )	76.35	75.13	76.82	76.10	75.97	-	2626.02*
	VTDS ( $\times 10^3$ )	6.78	5.02	7.23	6.341	5.86	-	-
	SS	74.	73.	70.	72.	-	-	2.49
	VSS	<10.	<10.	<10.	<10.	<10.0	-	-
	Chlorides ( $\times 10^3$ )	17.5	18.3	17.9	17.9	18.0	14.5	501.21
	Total Chl. Resid.	281.	281.	281.	281.	280.	225.	7.78
IONS/RADICALS	Free Avail. Chl.	281.	281.	281.	281.	280.	225.	7.78
	Sodium ( $\times 10^3$ )	35.0	35.0	35.0	35.0	35.0	32.0	1106.11
	Iron, Total	5.00	4.89	4.01	4.63	4.88	0.99	0.17
ALKALINITY	Total Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	45.5	46.3	46.8	46.2	45.6	44.3	1531.28
	OH-Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	18.9	18.5	17.6	18.3	18.2	17.1	591.08
	$\text{HCO}_3$ -Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	0.0	0.0	0.0	0.0	0.0	0.0	0.00
	$\text{CO}_3$ -Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	26.7	27.8	29.3	27.9	27.4	27.2	940.20

\*Based upon concentration in TBC sample.

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TABLE E-5: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN II

SAMPLE NUMBER		II -SSW-						HT-1	
		C-1	C-2	C-3	Ave. C-1/C-3	TBC	HT-1		
Time Collected (Hrs)		1552- 1633	1651- 1731	1751- 1831	1552- 1831	1552- 1831	0900	lbs	lb/Drum of Herbicide Burned
Date Collected (Nov 73)		Fri 16	Fri 16	Fri 16	Fri 16	Fri 16	Tue 20		
Date Analyzed (Nov 73)		Sat 17	Sat 17	Sat 17	Sat 17	Sat 17	Wed 21		
GENERAL	Parameter (mg/l unless noted)								
	Temp ( <sup>0</sup> F) at time:								
	Collected	164.	163.	163.	163.	-	-	-	-
	Analyzed	72.	72.	72.	72.	72.	72.	-	-
	pH	11.40	11.45	11.55	11.50	11.50	11.50	-	-
	Sp. Gravity	1.062	1.063	1.062	1.062	1.062	1.064	-	-
SOLIDS	Sp. Cond. (x10 <sup>4</sup> μmho/cm)	15.7	15.7	15.7	15.7	15.5	15.8		
	TS (x10 <sup>3</sup> )	75.97	75.62	75.10	75.56	75.74	78.32	2586.98	862.08
	VTS (x 10 <sup>3</sup> )	1.41	1.55	2.88	1.95	0.00	-	-	-
	TDS, Mt (x10 <sup>4</sup> )	14.0	14.2	13.8	14.0	14.2	14.3	4723.41	1574.02
	TDS, Ms (x10 <sup>3</sup> )	75.82	76.36	77.72	76.63	80.40	-	2655.68	884.98*
	VTDS (x10 <sup>3</sup> )	1.52	2.21	5.22	2.98	8.73	-	-	-
	SS	69.**	60.**	58.**	62.	65.**	-	2.15	0.72*
	VSS	<10.	<10.	<10.	<10.	<10.	-	-	-
	Chlorides (x10 <sup>3</sup> )	18.5	18.1	18.4	18.3	18.3	16.0	528.49	176.11
	Total Chl. Resid.	250.	260.	280.	263.	250.	225.	7.43	2.48
IONS/RADICALS	Free Avail. Chl.	250.	260.	280.	263.	250.	225.	7.43	2.48
	Sodium (x10 <sup>3</sup> )	37.0	36.0	37.0	36.7	37.0	36.0	1189.11	396.26
	Iron, Total	3.36	2.71	3.79	3.29	3.29	0.73	0.11	0.04*
	Total Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	52.5	52.0	52.0	52.2	52.5	51.6	1704.39	567.97
ALKALINITY	OH-Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	20.8	20.3	20.3	20.5	20.8	21.7	716.77	238.86
	HCO <sub>3</sub> -Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00
	CO <sub>3</sub> -Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	31.7	31.7	31.7	31.7	31.7	29.9	987.62	329.11

\* Based upon concentration in TBC sample.

\*\* Average of replicate samples.

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TABLE E-6: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN III

SAMPLE NUMBER	III -SSW-						HT-1	
	C-1	C-2	C-3	Ave. C-1/C-3	TBC	HT-1		
Time Collected (Hrs)	1435- 1519	1535- 1616	1638- 1718	1435- 1718	1435- 1718	1000		lb/Drum of Herbicide Burned
Date Collected (Nov 73)	Mon 19	Mon 19	Mon 19	Mon 19	Mon 19	Tues 20		
Date Analyzed (Nov 73)	Wed 21	Wed 21	Wed 21	Wed 21	Wed 21	Wed 21	lbs	
GENERAL	Parameter (mg/l unless noted)							
	Temp ( <sup>0</sup> F) at time:							
	Collected	164.	164.	163.	164.	-	-	-
	Analyzed	72.	72.	72.	72.	72.	-	-
	pH	11.60	11.55	11.60	11.60	11.60	11.65	-
	Sp. Gravity	1.050	1.050	1.048	1.049	1.050	1.053	-
SOLIDS	Sp. Cond. (x10 <sup>4</sup> μmho/cm)	11.9	11.9	11.5	11.8	11.6	11.3	-
	TS (x10 <sup>3</sup> )	61.64	81.06	65.21	69.30	66.02	72.58	2414.00
	VTS (x 10 <sup>3</sup> )	-	-	-	-	-	-	-
	TDS, Mt (x10 <sup>4</sup> )	9.80	9.80	9.70	9.77	9.80	9.90	3292.73
	TDS, Ms (x10 <sup>3</sup> )	-	68.29	66.36	67.32	67.01	-	2228.75
	VTDS (x10 <sup>3</sup> )	-	-	-	-	-	-	-
IONS/RADICALS	SS	76.	81.	81.	79.	78.	-	2.55
	VSS	<10.	<10.	<10.	<10.	<10.	-	-
	Chlorides (x10 <sup>3</sup> )	20.1	20.1	20.0	20.1	20.1	19.6	651.89
	Total Chl. Resid.	280.	280.	280.	280.	280.	225.	7.48
	Free Avail. Chl.	280.	280.	280.	280.	280.	225.	7.48
	Sodium (x10 <sup>3</sup> )	28.0	27.0	28.0	27.7	24.0	30.0	997.80
ALKALINITY	Iron, Total	3.49	2.86	3.21	3.19	3.37	0.85	0.11
	Total Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	33.5	32.7	32.4	32.9	32.9	32.9	1094.25
	OH-Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	6.6	5.9	6.0	6.2	6.2	5.5	182.93
	HCO <sub>3</sub> -Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	0.0	0.0	0.0	0.0	0.0	0.0	0.00
	CO <sub>3</sub> -Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	26.9	26.8	26.4	26.7	26.7	27.4	911.32

\*Based upon concentration in TBC sample.

USAF EHL(K)

TABLE E-7: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN IV

SAMPLE NUMBER		IV -SSW-						HT-1	
		C-1	C-2	C-3	Ave. C-1/C-3	TBC	HT-1		
Time Collected (Hrs)		1355- 1445	1505- 1553	1609 1659	1355- 1659	1355- 1659	1000	lbs	lb/Drum of Herbicide Burned
Date Collected (Nov 73)		Tue 20	Tue 20	Tue 20	Tue 20	Tue 20	Wed 21		
Date Analyzed (Nov 73)		Fri 23	Fri 23	Fri 23	Fri 23	Fri 23	Fri 23		
GENERAL	Parameter (mg/l unless noted)								
	Temp ( <sup>0</sup> F) at time:								
	Collected	161.	160.	161.	161.	-	-	-	-
	Analyzed	72.	72.	72.	72.	72.	72.	-	-
	pH	11.60	11.60	11.55	11.60	11.55	11.60	-	-
	Sp. Gravity	1.052	1.052	1.052	1.052	1.052	1.051	-	-
Sp. Cond. (x10 <sup>4</sup> μmho/cm)		11.6	11.8	11.8	11.7	11.8	11.4	-	-
SOLIDS	TS (x10 <sup>3</sup> )	60.52	62.09	63.98	62.20	62.16	61.05	2140.25	545.73
	VTS (x 10 <sup>3</sup> )	-	-	-	-	-	-	-	-
	TDS, Mt (x10 <sup>4</sup> )	10.00	9.90	9.90	9.93	9.90	10.00	3505.72	893.90
	TDS, Ms (x10 <sup>3</sup> )	62.64	64.71	62.57	63.31	62.77	-	2200.54*	561.10*
	VTDS (x10 <sup>3</sup> )	-	-	-	-	-	-	-	-
	SS	73.	62.	56.	64.	70.	-	2.45*	0.63
	VSS	<10.	<10.	<10.	<10.	<10.	-	-	-
IONS/RADICALS	Chlorides (x10 <sup>3</sup> )	16.8	16.7	16.5	16.7	16.6	16.1	564.42	143.92
	Total Chl. Resid.	280.	280.	280.	280.	280.	225.	7.89	2.01
	Free Avail. Chl.	280.	280.	280.	280.	280.	225.	7.89	2.01
	Sodium	27.0	29.0	27.0	27.7	27.0	31.0	1086.78	277.11
	Iron, Total	3.07	3.07	2.57	2.90	2.86	0.74	0.10*	0.03*
ALKALINITY	Total Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	34.7	35.1	34.8	34.9	34.7	33.9	1188.44	303.03
	OH-Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	10.1	9.5	10.0	9.9	10.3	9.9	347.07	88.50
	HCO <sub>3</sub> <sup>-</sup> Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	0.0	0.0	0.0	0.0	0.0	0.0	0.00	0.00
	CO <sub>3</sub> <sup>-</sup> Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	24.6	25.7	24.8	25.0	24.4	24.0	841.37	214.54

\*Based upon concentration in TBC sample.

USAF EHL(K)

TABLE E-8: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN V

SAMPLE NUMBER	V -SSW-						HT-1	
	C-1	C-2	C-3	Ava. C-1/C-3	TBC	HT-1		
Time Collected (Hrs)	1344- 1423	1442- 1523	1542- 1614	1344 1614	1344- 1614	1310		lb/Drum of Herbicide Burned
Date Collected (Nov 73)	Tue 27	Tue 27	Tue 27	Tue 27	Tue 27	Wed 28		
Date Analyzed (Nov 73)	Wed 28	Wed 28	Wed 28	Wed 28	Wed 28	Thur 29	lbs	
GENERAL	Parameter (mg/l unless noted)							
	Temp ( <sup>o</sup> F) at time: Collected	164.	166.	166.	165.	-	-	-
	Analyzed	72.	72.	72.	72.	72.	-	-
	pH	11.50	11.55	11.45	11.50	11.40	11.45	-
	Sp. Gravity	1.072	1.074	1.073	1.073	1.072	1.070	-
	Sp. Cond. (x10 <sup>4</sup> $\mu$ mho/cm)	13.2	13.1	13.9	13.4	13.2	13.1	-
SOLIDS	TS (x10 <sup>3</sup> )	91.06	86.99	87.14	88.40	86.33	86.94	2592.50
	VTS (x 10 <sup>3</sup> )	-	-	-	-	-	-	-
	TDS, Mt (x10 <sup>4</sup> )	12.5	13.0	13.9	13.1	13.1	12.7	3787.06
	TDS, Ms (x10 <sup>3</sup> )	80.91	83.81	83.88	82.87	86.63	-	2583.25
	VTDS (x10 <sup>3</sup> )	-	-	-	-	-	-	-
	SS	89.	97.	94.	93.	87.	-	2.39
	VSS	<10.	<10.	<10.	<10.	<10.	-	-
IONS/RADICALS	Chlorides (x10 <sup>3</sup> )	23.2	23.4	23.6	23.4	23.3	22.2	661.99
	Total Chl. Resid.	500.	500.	500.	500.	500.	438.	13.06
	Free Avail. Chl.	500.	500.	500.	500.	500.	438.	13.06
	Sodium (x10 <sup>3</sup> )	33.0	33.0	37.0	34.3	36.0	35.0	1043.68
	Iron, Total	4.36	4.30	4.59	4.42	3.78	0.93	0.11*
ALKALINITY	Total Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	44.6	46.3	46.8	45.9	45.6	44.6	329.94
	OH-Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	11.8	11.6	11.6	11.7	11.8	11.8	351.87
	HCO <sub>3</sub> -Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	0.0	0.0	0.0	0.0	0.0	0.0	0.00
	CO <sub>3</sub> -Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	32.8	34.7	35.2	34.2	33.8	32.8	978.08

\*Based upon concentration in TBC sample.

USAF EHL(K)

TABLE E-9: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN VI\*

SAMPLE NUMBER	VI -SSW-						
	C-1	C-2	D-1	D-2	D-3	D-4	HT-1
Time Collected (Hrs)	1108- 1156	1213- 1231	1111	1133	1156	1213	-
Date Collected (Nov 73)	Wed 28	Wed 28	Wed 28	Wed 28	Wed 28	Wed 28	Thur 29
Date Analyzed (Nov 73)	Thur 29	Thur 29	Thur 29	Thur 29	Thur 29	Thur 29	Thur 29
GENERAL	Parameter (mg/l unless noted)						
	Temp (°F) at time: Collected	167.	165.	-	-	-	-
	Analyzed	72.	72.	72.	72.	72.	72.
	pH	11.40	11.40	2.0	11.3	11.3	-
	Sp. Gravity	1.042	1.062	1.025	1.050	1.060	1.062
	Sp. Cond. ( $\times 10^4$ $\mu$ mho/cm)	8.4	12.3	-	-	-	-
SOLIDS	TS ( $\times 10^3$ )	70.03	85.43	-	-	-	-
	VTS ( $\times 10^3$ )	-	-	-	-	-	-
	TDS, Mt ( $\times 10^4$ )	8.0	12.4	-	-	-	-
	TDS, Ms ( $\times 10^3$ )	50.95	78.94	-	-	-	-
	VTDS ( $\times 10^3$ )	-	-	-	-	-	-
	SS	799.	89.	-	-	-	-
	VSS	<10.	<10.	-	-	-	-
IONS/ RADICALS	Chlorides ( $\times 10^3$ )	21.0	23.2	-	-	-	-
	Total Chl. Resid.	38.	350.	-	-	-	-
	Free Avail. Chl.	38.	350.	-	-	-	-
	Sodium ( $\times 10^3$ )	22.0	35.0	-	-	-	-
	Iron, Total	303.57	5.47	-	-	-	-
ALKALINITY	Total Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	19.5	42.8	-	-	-	-
	OH-Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	4.3	14.6	-	-	-	-
	$\text{HCO}_3$ -Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	0.0	0.0	-	-	-	-
	$\text{CO}_3$ -Alk ( $\text{CaCO}_3$ ) ( $\times 10^3$ )	15.2	28.2	-	-	-	-

\*A TBC was not prepared for this burn due to the distinct differences in SSW C-1 and C-2. Also, a holding tank liquid sample was not collected because the tank did not fill to the sampling port.

USAF EHL(K)

TABLE E-10: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN VII

SAMPLE NUMBER	VII -SSW-					VI/VII -SSW-		
	C-1	C-2	C-3	Ava. C-1/C-3	TBC	HT-1	HT-1	
Time Collected (Hrs)	0947- 1027	1047- 1127	1150- 1227	0947- 1227	0947- 1227	1230		lb/Drum of Herbicide Burned
Date Collected (Nov 73)	Thur 29	Thur 29	Thur 29	Thur 29	Thur 29	Sat 1 DEC		
Date Analyzed (Nov 73)	Fri 30	Fri 30	Fri 30	Fri 30	Fri 30	Sat 1 Dec	lbs	
Parameter (mg/l unless noted)								
Temp ( <sup>0</sup> F) at time:								
Collected	166.	166.	172.	168.	-	-	-	-
Analyzed	72.	73.	72.	72.	72.	72.	-	-
pH	11.30	11.30	11.35	11.32	11.35	11.35	-	-
Sp. Gravity	1.071	1.073	1.075	1.073	1.073	1.065	-	-
Sp. Cond. (x10 <sup>4</sup> $\mu$ mho/cm)	-	-	-	-	15.1	13.7	-	-
TS (x10 <sup>3</sup> )	-	-	-	-	87.31	81.67	3859.00	612.63
VTS (x 10 <sup>3</sup> )	-	-	-	-	-	-	-	-
TDS, Mt (x10 <sup>4</sup> )	13.9	14.0	14.0	14.0	14.0	12.0	5670.13	900.15
TDS, Me (x10 <sup>3</sup> )	-	-	-	-	82.08	-	3878.37	615.71*
VTDS (x10 <sup>3</sup> )	-	-	-	-	-	-	-	-
SS	-	-	-	-	83.	-	3.92	0.62*
VSS	-	-	-	-	14.	-	-	-
Chlorides (x10 <sup>3</sup> )	23.0	24.0	23.6	23.5	23.6	22.4	1058.42	168.03
Total Chl. Resid.	438.	438.	438.	438.	438.	275.	12.99	2.06
Free Avail. Chl.	438.	438.	438.	438.	438.	275.	12.99	2.06
Sodium (x10 <sup>3</sup> )	38.0	36.0	35.0	36.3	33.0	35.0	1653.79	262.55
Iron, Total	4.48	3.43	3.84	3.92	4.53	0.77	0.21*	0.03*
Total Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	-	-	-	-	45.8	39.8	1880.59	298.55
OH-Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	-	-	-	-	12.6	12.9	609.54	96.77
HCO <sub>3</sub> -Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	-	-	-	-	0.0	0.0	0.00	0.00
CO <sub>3</sub> -Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	-	-	-	-	33.2	26.9	1271.05	201.78

\*Based upon concentration in TBC sample.

USAF EHL(K)

TABLE E-11: SUMMARY OF EHL/K SPENT SCRUBBER WATER ANALYSES - BURN VIII

SAMPLE NUMBER	VIII -SSW-						HT-1	
	C-1	C-2	C-3	Ave. C-1/C-3	TBC	HT-1		
Time Collected (Hrs)	0946- 1041	1109- 1208	1232- 1300	0946- 1300	0946- 1300	1235		1b/Drum of Herbicide Burned
Date Collected (Nov 73)	Fri 30	Fri 30	Fri 30	Fri 30	Fri 30	Sat 1 Dec	1bs	
Date Analyzed (Nov 73)	Sat 1 Dec	Sat 1 Dec	Sat 1 Dec	Sat 1 Dec	Sat 1 Dec	Sat 1 Dec		
Parameter (mg/l unless noted)								
Temp ( <sup>0</sup> F) at time:								
Collected	164.	164.	165.	164.	-	-	-	-
Analyzed	72.	73.	72.	72.	72.	73.	-	-
pH	10.95	11.05	9.05	10.35	10.80	10.80	-	-
Sp. Gravity	1.044	1.046	1.041	1.044	1.044	1.041	-	-
Sp. Cond. (x10 <sup>4</sup> μmho/cm)	-	-	-	-	8.9	8.5	-	-
TS (x10 <sup>3</sup> )	-	-	-	-	82.06	68.01	1816.20	406.86
VTS (x 10 <sup>3</sup> )	-	-	-	-	-	-	-	-
TDS, Mt (x10 <sup>4</sup> )	7.9	8.0	7.4	7.8	7.9	7.5	2002.86	448.68
TDS, Ms (x10 <sup>3</sup> )	-	-	-	-	58.92	-	1573.45	352.48*
VTDS (x10 <sup>3</sup> )	-	-	-	-	-	-	-	-
SS	-	-	-	-	560.	-	14.95	3.35*
VSS	-	-	-	-	<10.	-	-	-
Chlorides (x10 <sup>3</sup> )	27.7	27.6	28.1	27.8	27.9	26.7	713.02	159.73
Total Chl. Resid.	275.	275.	275.	275.	275.	138.	3.69	0.83
Free Avail. Chl.	275.	275.	275.	275.	275.	138.	3.69	0.83
Sodium (x10 <sup>3</sup> )	24.0	25.0	24.0	24.3	25.0	24.0	640.92	143.58
Iron, Total	160.00	191.96	407.26	253.07	214.29	0.74	5.72*	1.28*
Total Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	-	-	-	-	12.7	11.3	301.76	67.60
OH-Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	-	-	-	-	0.0	0.0	0.00	0.00
HCO <sub>3</sub> -Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	-	-	-	-	0.1	0.9	24.03	5.38
CO <sub>3</sub> -Alk (CaCO <sub>3</sub> ) (x10 <sup>3</sup> )	-	-	-	-	12.6	10.4	277.73	62.22

\*Based upon concentration in TBC sample.

USAF EHL(K)

(6) Chlorides ( $10^3 \times \text{mg/l}$ ): 16.5 to 28.0. Chloride concentrations were independent of applied caustic as long as applied caustic was two times theoretical.

(7) Chlorine Residuals ( $\text{mg/l}$ ): 250 to 500. There was no combined available chlorine and thus the free available chlorine residual equalled the total chlorine residual.

(8) Sodium ( $10^3 \times \text{mg/l}$ ): 32 to 38. Sodium concentrations were directly related to the applied caustic. Burn VIII applied caustic averaged 0.054 pps (less than half the lowest rate of any other burn) to cause the SSW sodium concentration to average only  $25.0 \times 10^3 \text{ mg/l}$  even though Burn VIII applied water recovery (59.1%) was the lowest of all burns. Sodium masses were considered conservative through the scrubber system except for the minor fractions of sodium salts entrained and exhausted in the scrubbed effluent gases.

(9) Iron, Total ( $\text{mg/l}$ ): 3.0 to 5.0 except up to 400 when applied caustic fell below two times theoretical. Lack of adequate caustic allowed the  $\text{HCl}$ ,  $\text{Cl}_2$ , and any monatomic chlorine of the combustion gas to react with the metal of the scrubber tank walls.

(10) Total alkalinity as  $\text{CaCO}_3$  ( $\times 10^3 \text{ mg/l}$ ): 32.0 to 52.5 except down to 12.0 ( $\pm 0.7$ ) when applied caustic was less than two times theoretical. As long as applied caustic was twice theoretical, carbonate alkalinity averaged 70( $s=8$ )% of total alkalinity, the remaining alkalinity was hydroxyl, and no bicarbonate alkalinity was detected. At caustic less than twice theoretical, carbonate alkalinity increased to 90( $s=10$ )% of total alkalinity, the remaining alkalinity was bicarbonate, and no hydroxyl alkalinity was detected.

## 7. EFFECT OF INCINERATOR OPERATING PARAMETERS ON SPENT SCRUBBER WATER INORGANIC QUALITY

a. Table E-12 presents the quality and chemical constituent loading in each burn's total SSW as a function of drums of herbicide incinerated. Values for burns VI and VII were averaged into the VI/VII column. Comparison of data in Table E-12 indicated that all measured parameters except the relatively constant temperatures ( $\bar{x}=1640^\circ\text{F}$ ), specific gravities ( $\bar{x}=1.057$ ), and chlorides ( $\bar{x}=167$  pounds/drum burned) were directly related to applied caustic and independent of F/A or Percent Excess Air. Multiple regression statistics were applied to these data and excellent correlation coefficients were obtained to relate these chemical product loadings to the ratio of applied caustic to that required to neutralize the theoretically expected amounts of  $\text{HCl}(\text{N}_\text{H}/\text{N}_\text{T})$  - see Figures E-2 through E-4. Except as discussed in paragraph "e" below, all of these relationships were linear.

b. The following reasoning substantiated why these correlations agreed so well with expectations:

(1) Temperature was a function of combustion gas temperature, combustion gas volume, and total water volumes feed to the scrubber. Since all of these parameters were consistent in relative proportions and gas/water contact time in the scrubber tank was probably consistent, the effluent scrubber water



TABLE E-12: QUALITY AND CHEMICAL LOADINGS IN SPENT SCRUBBER WATER FOR THE TEST BURNS

BURN NUMBER	I	II	III	IV	V	VI/VII	VIII
Unit Operations -Average NaOH <sub>used</sub> /NaOH <sub>theory</sub>	3.05	3.18	2.06	2.16	2.23	2.20	1.29
Fuel to Air Mass Ratio (F/A)	0.086	0.086	0.106	0.105	0.120	0.115	0.118
% Excess Air	89.	89.	52.	53.	34.	40.	37.
Spent Scrubber Water - Holding Tank <u>Physical Parameters</u>							
Temp (°F) @ Collection*	164.	163.	164.	161.	165.	166.	164.
pH	11.50	11.50	11.65	11.60	11.45	11.35	10.80
Sp. Gravity	1.055	1.064	1.053	1.051	1.070	1.065	1.041
Sp. Conductance (x10 <sup>4</sup> μmho/cm)	14.0	15.8	11.3	11.4	13.1	13.7	8.5
<u>Chemical Mass (lbs) Per Drum of Herbicide Incinerated</u>							
Total Solids	943.34	862.08	614.46	545.73	645.38	612.63	406.86
Total Dissolved Solids-MS*	1006.13	884.98	567.31	561.10	643.08	615.71	352.48
Suspended Solids*	0.95	0.72	0.66	0.63	0.65	0.62	3.35
Chlorides	192.03	176.11	165.93	143.92	164.80	168.03	159.73
Free Available Chlorine	2.98	2.48	1.90	2.01	3.25	2.06	0.83
Sodium	423.79	396.26	253.98	277.11	259.82	262.55	143.58
Iron-Total*	0.06	0.04	0.03	0.03	0.03	0.03	1.28
Total Alkalinity as CaCO <sub>3</sub>	586.69	567.97	278.53	303.03	331.08	298.05	67.60
OH-Alkalinity as CaCO <sub>3</sub>	226.47	238.86	46.56	88.50	87.60	96.77	0.00
HCO <sub>3</sub> -Alkalinity as CaCO <sub>3</sub>	0.00	0.00	0.00	0.00	0.00	0.00	5.38
CO <sub>3</sub> -Alkalinity as CaCO <sub>3</sub>	360.23	329.11	231.97	214.54	243.48	201.78	62.22

\*Data/calculation based on analyses of total burn composite (TBC) sample.

USAF EHL(K)

F-(E-17)

E(E-18)

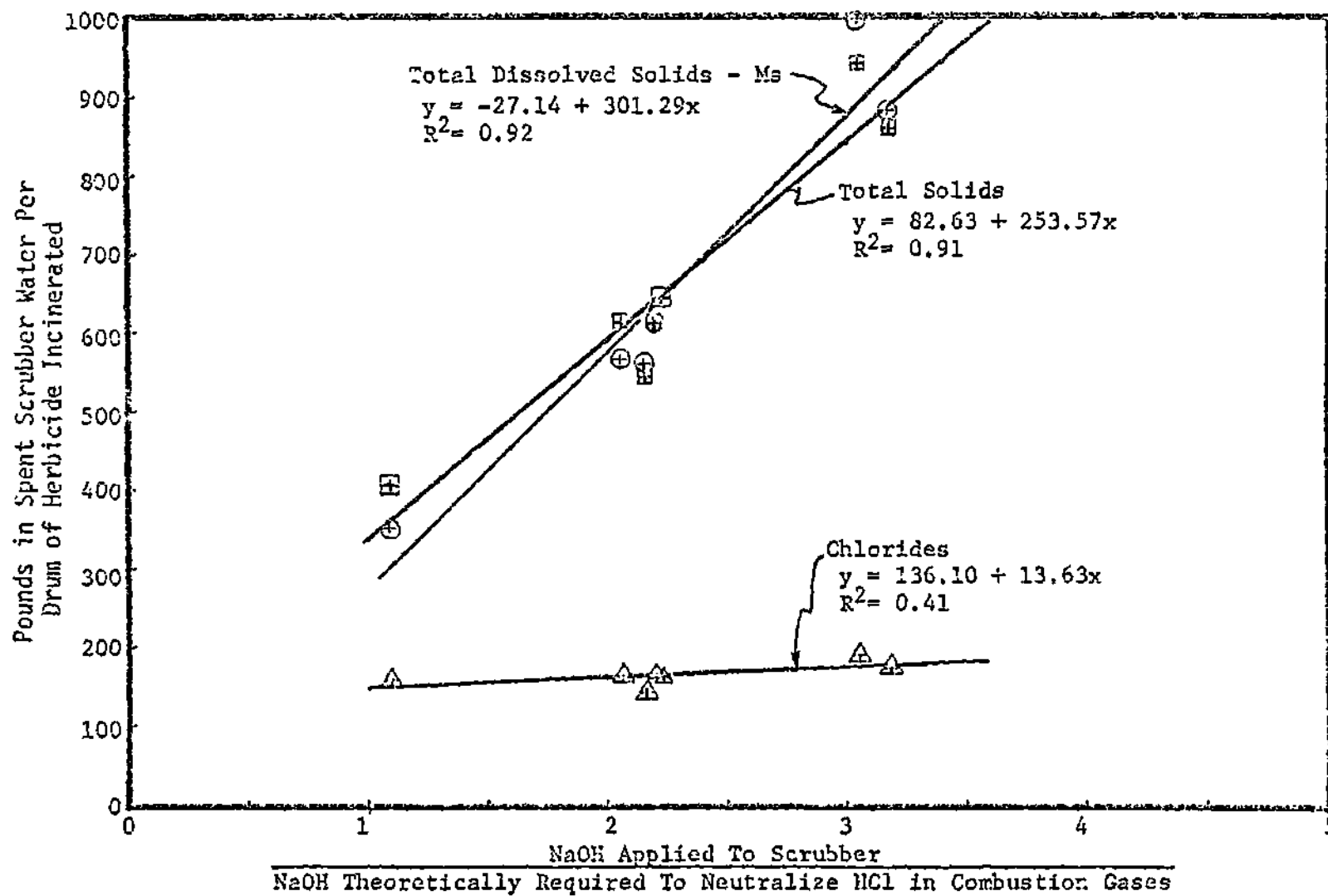


FIGURE E-2

RELATIONSHIP OF CAUSTIC USED TO TOTAL SOLIDS, DISSOLVED SOLIDS,  
AND CHLORIDES IN SPENT SCRUBBER WATER

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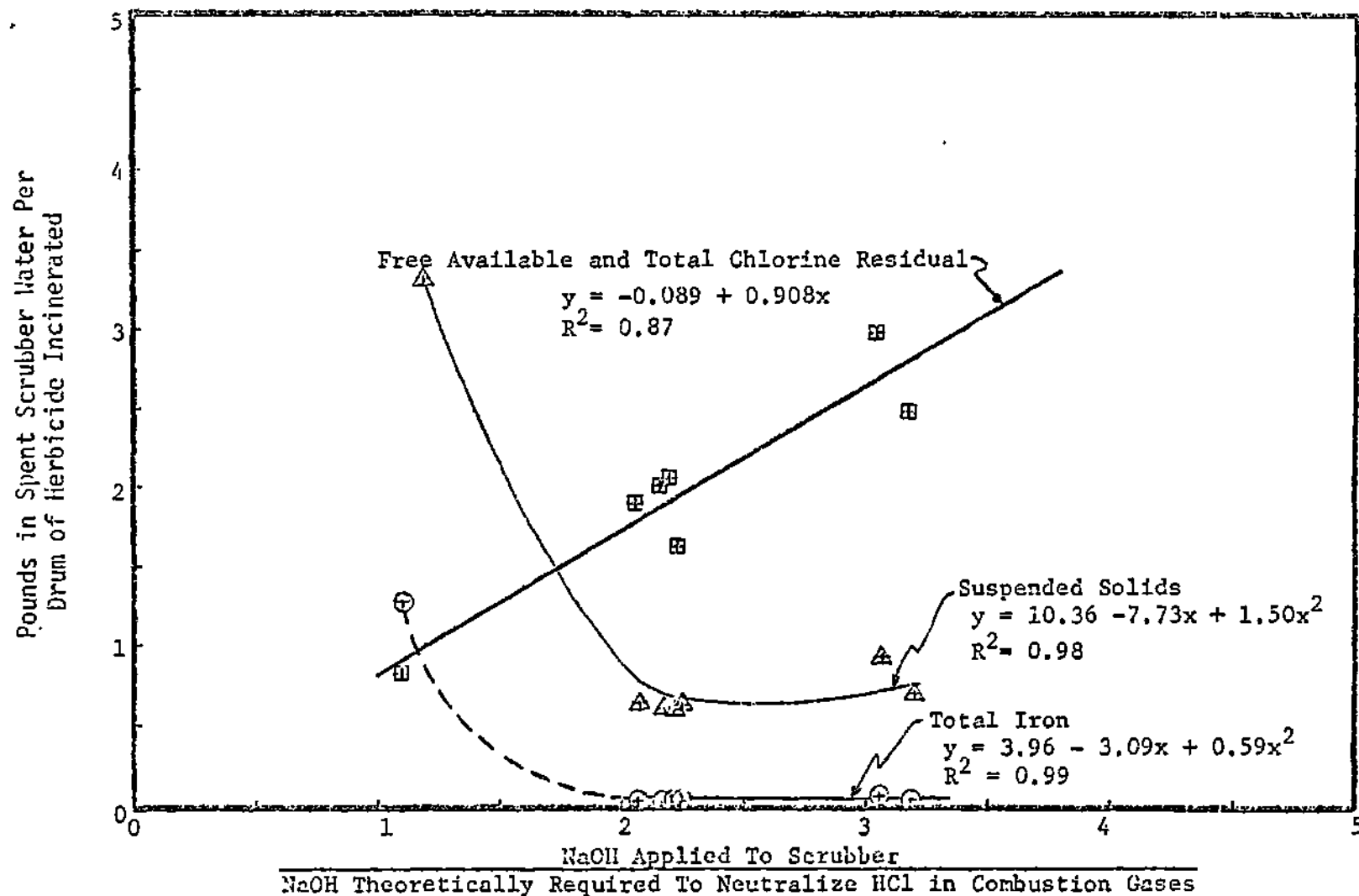


FIGURE E-3 :

RELATIONSHIP OF CAUSTIC USED TO CHLORINE RESIDUAL  
 AND TOTAL IRON IN SPENT SCRUBBER WATER

USAF EHL(K)

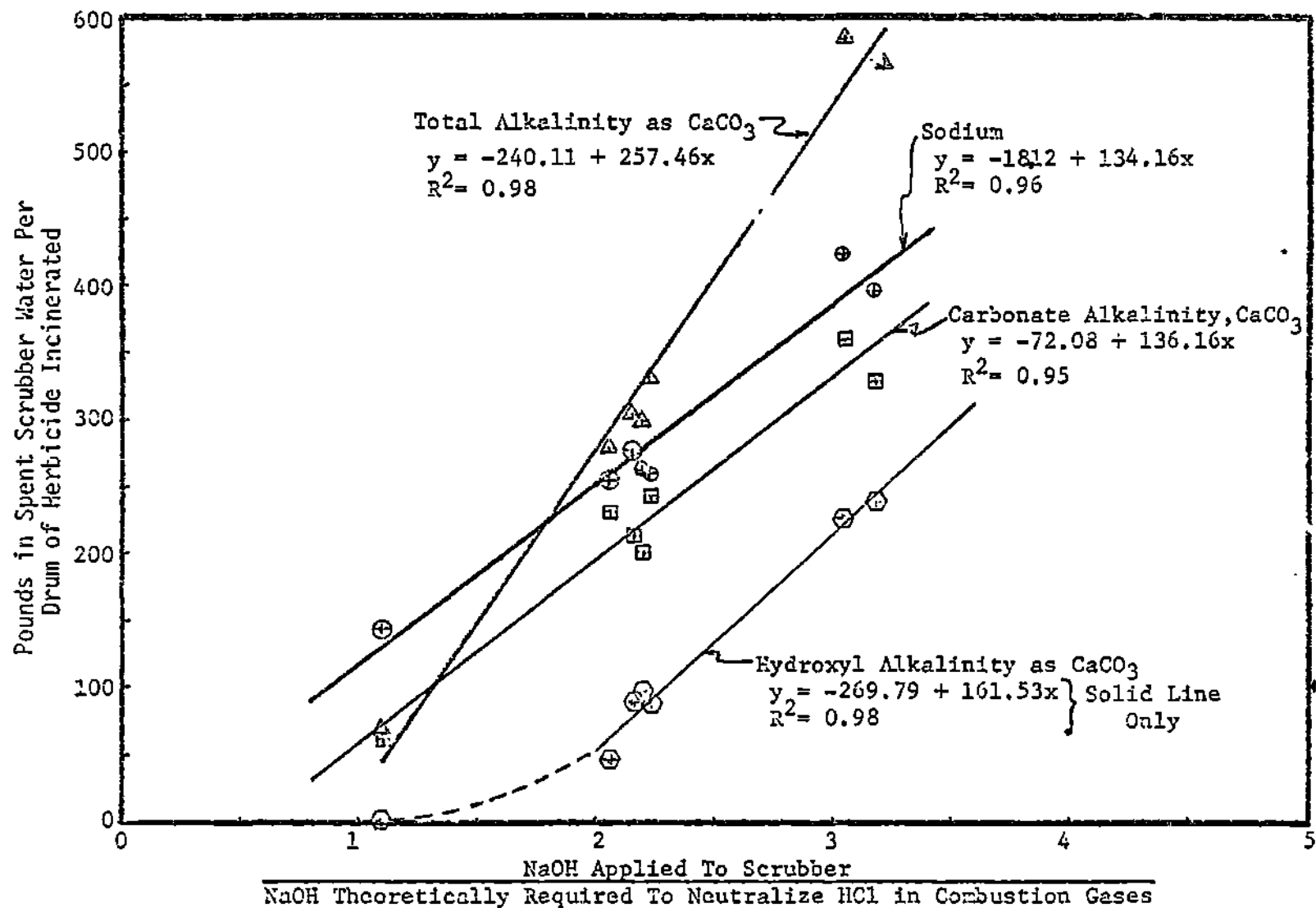


FIGURE E-4 : RELATIONSHIP OF CAUSTIC USED TO ALKALINITIES AND SODIUM IN SPENT SCRUBBER WATER

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temperature was relatively constant.

(2) Specific gravity was dependent on these same parameters plus caustic feed. However, specific gravity is a relatively insensitive measurement and would be expected to change only when the parameters on which it depended had changed more dramatically.

(3) The slightly variable chlorides in pounds per drum of herbicide burned was apparently due to its following consistencies of:

(a) Chlorine weight percent in the herbicide feed,

(b) percent production of  $\text{HCl}$ ,  $\text{Cl}_2$ , and monatomic chlorine from the incinerated chlorinated hydrocarbons, and

(c) efficiency of the caustic scrubber to collect chlorine species as long as the applied caustic was greater than twice theoretical.

Thus, these combined situations allowed collection of chlorides almost independent of any  $N_U/N_T$  ratios greater than 1.1.

(4) The inorganic loading of the fresh scrubber water into the spent scrubber water far outweighed any contributions that the herbicide combustion products ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , any hydrocarbons) may have produced. Only the chlorine species of the combustion gases exerted any significant effects on inorganic scrubber water loads, and their effects were independent of  $N_U/N_T$  greater than 1.1.

c. All but three of the correlated inorganic parameters increased directly over the range of  $N_U/N_T=1$  to  $N_U/N_T=3$ . Total iron decreased rapidly to a constant value as  $N_U/N_T$  increased from one to two. This was because at  $N_U/N_T$  greater than 1.1 enough caustic was available to neutralize the  $\text{HCl}$  which otherwise reacted with the scrubber tank walls to produce ferric precipitates. Suspended solids responded in the same manner because the ferric precipitates were a large fraction of suspended solids when  $N_U/N_T$  was less than 1.29 (Burn VIII). The last exception was hydroxyl alkalinity which was zero at (1)  $N_U/N_T$ , increased nonlinearly with  $N_U/N_T$  from one to two and then increased directly when  $N_U/N_T$  was greater than two. Hydroxyl alkalinity approached zero at (1)  $N_U/N_T$  because it was depleted via reaction with the  $\text{HCl}$  in the combustion gases. For  $N_U/N_T$  between 1.0 and 2.0, excess hydroxyl ions were present above  $\text{HCl}$  requirements but they were being reacted with  $\text{CO}_2$ . Excess of hydroxyl ion rose steadily for  $N_U/N_T$  values greater than about two because all  $\text{HCl}$  demands were met and the short water/gas contact time in the scrubber tank precluded any additional reaction with  $\text{CO}_2$ . These relationships of hydroxyl utilization for  $\text{HCl}$  and  $\text{CO}_2$  reactions were very correlatable to calculated data; see Figure E-5 which was plotted from the data in Table E-13. It was interesting to note that an average of  $10(\pm 4)\%$  of the calculated  $\text{CO}_2$  in the combustion gas was reacted with  $\text{NaOH}$  to produce carbonates.

## 8. SCRUBBER WATER REQUIREMENTS AND RECOVERY

a. Caustic solution and cooling water mass flow rate requirements to cool

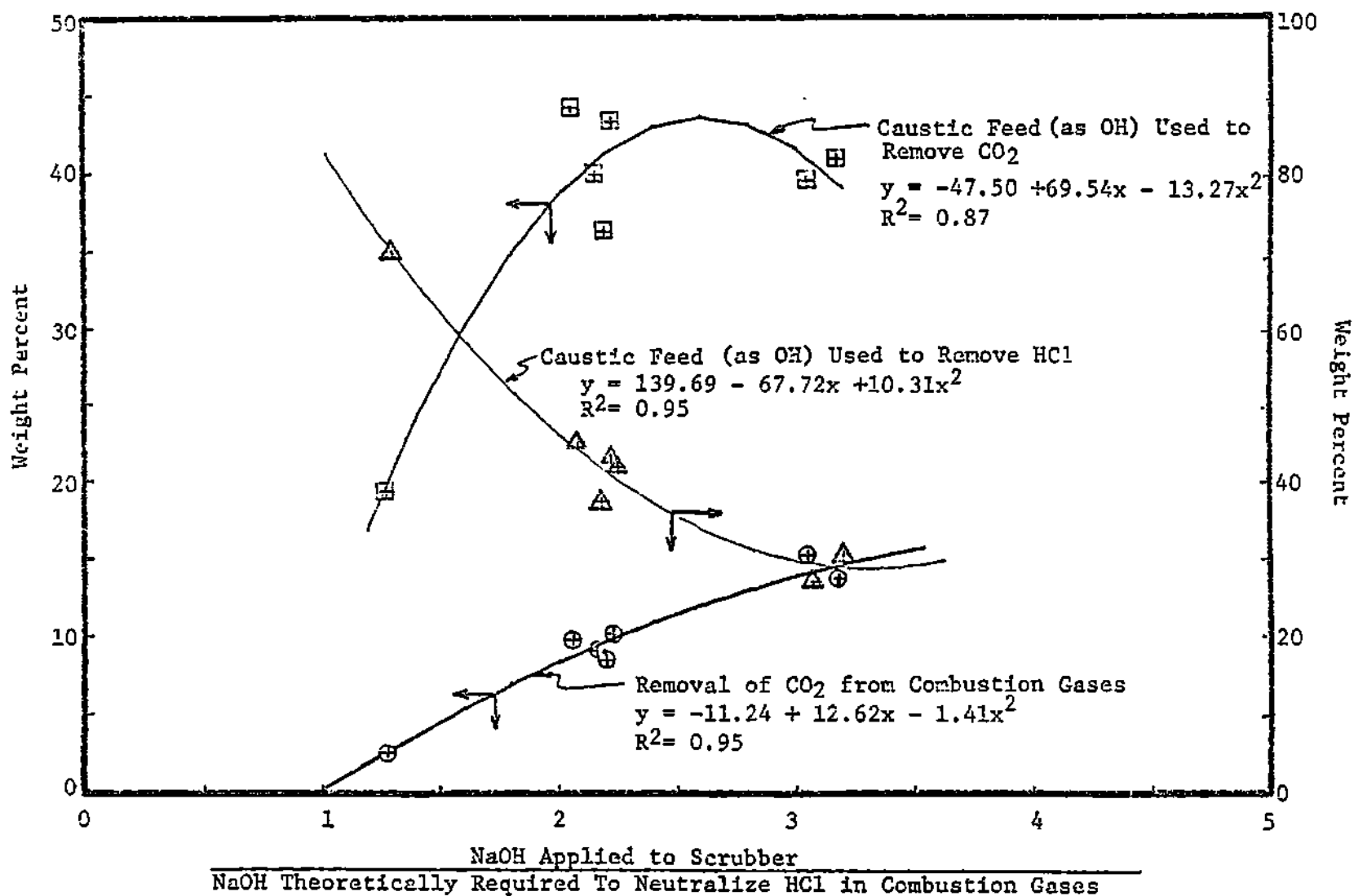


FIGURE E-5: CAUSTIC USED vs PERCENT  $\text{CO}_2$  REMOVAL AND PERCENT OF CAUSTIC USED TO REMOVE HCl AND  $\text{CO}_2$

TABLE E-13: PERCENT OF CAUSTIC FEED USED TO REMOVE CO<sub>2</sub> FROM COMBUSTION GASES

Burn No.	Scrubber Percent Removal of CO <sub>2</sub> From Combustion Gases*	Percent Of Caustic Feed Used To Remove CO <sub>2</sub> *	$\frac{NaOH_{used}}{NaOH_{Theory}}$
I	15.3	39.6	3.05
II	13.8	41.0	3.18
III	9.8	44.2	2.06
IV	9.1	39.9	2.16
V	10.2	43.3	2.23
VI/VII	8.5	36.3	2.20
VIII	2.6	19.3	1.29
Ave	9.9	37.7	2.31
Std D.	4.1	8.5	0.64

\*Weight Percent

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and neutralize the combustion gases were based on estimates of combustion gas mass flows, chlorine composition, and temperature. These three parameters were dependent on the fuel to air mass ratios (F/A), see Appendix A. Consistent selection of scrubber water flow rates in relation to F/A were thus expected to produce correlations between scrubber water feed volumes, collected spent scrubber water volumes, and F/A. Excellent correlation of these variables are shown in Figure E-6 as plotted from the data in Table E-14. Even though total water flow into the scrubber was comparable, scrubber water recovery from burns VI and VIII did not correlate to the other burns. The most likely reason for this poorer water recovery in VI and VIII was that the effective caustic strength of the scrubber water into the venturi was lower and thus had a higher vapor pressure than in other burns. This difference of physical property allowed more scrubber water volatilization in burns VI and VIII than in the other burns.

b. Evaluation of Figure E-6 showed that higher strength caustic stock solution (~15% by weight NaOH) was used to minimize total scrubber water requirements to 1200 ( $\pm 50$ ) gallons/drum of herbicide burned at F/A's of 0.115 ( $\pm 0.005$ ). Scrubber water recovery averaged about 75% or 1000 gallons/drum of herbicide burned.

9. REMOVAL OF IRON FROM SPENT SCRUBBER WATER: The color of spent scrubber water sediments indicated the presence of particulate iron; particularly burns VI and VIII. Iron concentrations in well mixed SSW-TBC samples were compared with concentrations in settled holding tank supernatant. The average percent iron removal after settling was 77.5 percent and increased as iron concentration in the SSW-TBC increased. (See Table E-15). Thus conventional settling tanks would effectively reduce the iron to acceptable concentrations for discharge.

#### 10. MASS BALANCE OF SYSTEM CHLORINE, SODIUM, AND HYDROXIDE

a. These mass balances were based upon the inorganic analyses of fresh and spent scrubber water and chlorine's theoretical average composition in the herbicide fuel. Considering the limited number of samples and the calculation errors involved in determining masses for each burn, the average accountability of sodium (104.1%), hydroxide (95.4%), and feed chlorine (96.2%) attested to the overall accuracy of scrubber water collection and analyses.

b. Data presented in Table E-16 denote the fractions of hydroxide used to react with HCl and CO<sub>2</sub>. Table E-17 shows that scrubber water analyses indicated that about 98.7% of the herbicide chlorine was converted to HCl and monatomic chlorine while 1.3% was formed into diatomic chlorine.

#### 11. EFFECTS OF SPENT SCRUBBER WATER ON INORGANIC QUALITY OF HOLDING POND WATER

a. Inorganic analyses of holding pond water were conducted on samples collected before and after incremental volumes of spent scrubber water were dumped into the 1.4 million gallon concrete wastewater reservoir. No other known industrial wastewaters of any significant detriment were discharged to this reservoir during the sampling period.



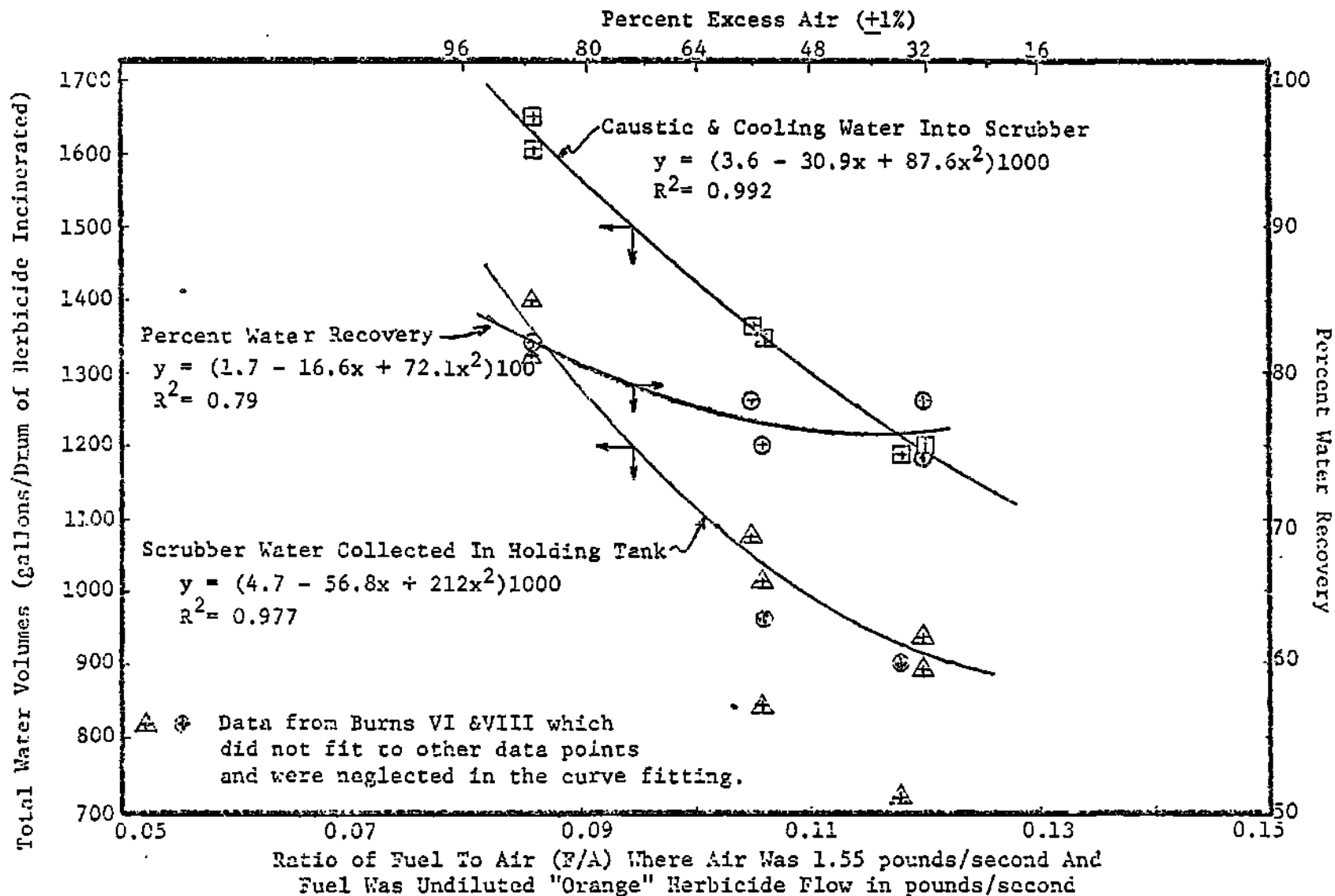


FIGURE E-6: RELATIONSHIP OF WATER USED/DISCHARGED TO FUEL/AIR RATIOS DURING INCINERATION OF ORANGE HERBICIDE

TABLE E-14: SCRUBBER WATER USED/RECOVERED FOR BURN CONDITIONS

Burn Number	F/A	Percent Excess Air	$\frac{\text{NaOH}_{\text{used}}}{\text{NaOH}_{\text{Theory}}}$	TOTAL WATER		
				Into Scrubber (Gallons per Drum of Herbicide Incinerated)	Recovered in Holding Tank (Gallons per Drum of Herbicide Incinerated)	Percent Recovery
I	0.086	89.	3.05	1650.	1397.	84.7
II	0.086	89.	3.18	1606.	1322.	82.3
III	0.106	52.	2.06	1353.	1013.	74.9
IV	0.105	53.	2.16	1364.	1073.	78.7
V	0.120	34.	2.23	1204.	892.	74.1
VI	0.106	52.	2.11	1342.	841.	62.7
VII	0.120	34.	2.26	1199.	934.	77.9
VIII	0.118	37.	1.29	1214.	717.	59.1
Average	0.106	55.	2.27	1366.	1023.	74.3
Std. Deviation	0.014	23.	0.64	176.	234.	9.0

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TABLE E-15: TOTAL IRON REMOVAL FROM SPENT SCRUBBER WATER  
VIA SETTLING

Burn No.*	Total Iron Concentration		Percent Removal (Based on Concentration)
	Into Holding Tank (TBC - mg/l)	Holding Tank Supernatant (mg/l)	
I	4.88	0.99	79.7
II	3.29	0.73	77.8
III	3.37	0.85	74.8
IV	2.86	0.74	74.1
V	3.78	0.93	75.40
VII	4.53	0.77	83.00
VIII	214.29	0.74	99.7
Average +	3.79	0.84	77.5
*Burn No. VI data were not evaluated because the holding tank did not fill enough to get a sample from the sampling port. +Based on Burns I, II, III, IV, V, and VII			

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TABLE E-16: CAUSTIC MATERIAL BALANCE FOR SODIUM AND  
HYDROXIDE FOR THE BURNS

Burn No.	Sodium Percent of FSW Feed Accounted For In Holding Tank	Hydroxide Percent of FSW					$\frac{\text{NaOH}_{\text{Used}}}{\text{NaOH}_{\text{Theory}}}$
		Used to React With		Unused and In Holding Tank	Accounted For	Unaccounted For	
		HCl	CO <sub>2</sub>				
I	101.3	26.8	39.6	24.9	91.3	8.7	3.05
II	112.7	30.3	41.0	29.7	100.0	0.0	3.18
III	105.2	44.8	44.2	8.9	97.9	2.1	2.06
IV	109.4	37.2	39.9	16.1	92.2	7.8	2.16
V	100.5	41.7	43.3	15.6	100.6	0.0	2.23
VI/VII	102.6	42.8	36.3	17.4	96.5	3.5	2.20
VIII	96.7	69.8	19.3	0.0	89.1	10.9	1.29
Ave.	104.1	41.9	37.7	16.1	95.4	4.7	2.31
Std D.	5.5	14.0	8.5	9.8	4.5	4.4	0.64

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TABLE E-17: CHLORINE MATERIAL BALANCE  
FOR THE BURNS

Burn No.	Percent of Feed Chlorine (Mass)		Accounted For **
	Converted To *		
	HCl % (Cl)	Cl <sub>2</sub>	
I	98.46	1.54	110.09
II	98.60	1.40	100.91
III	98.86	1.14	94.96
IV	98.61	1.39	83.00
V	98.05	1.95	94.98
VI†/VII	98.78	1.22	96.81
VIII †	99.48	0.52	92.77
Ave	98.69	1.31	96.22
Std D.	0.44	0.44	8.21

Based on analytical measurements of spent scrubber water and assuming:

\*100% scrubbing efficiency.

\*\* 29.78% weight chlorine in herbicide feed and all settled iron was as FeCl<sub>3</sub>.

† Stack sampling crew could smell chlorine in scrubbed exhaust gases.

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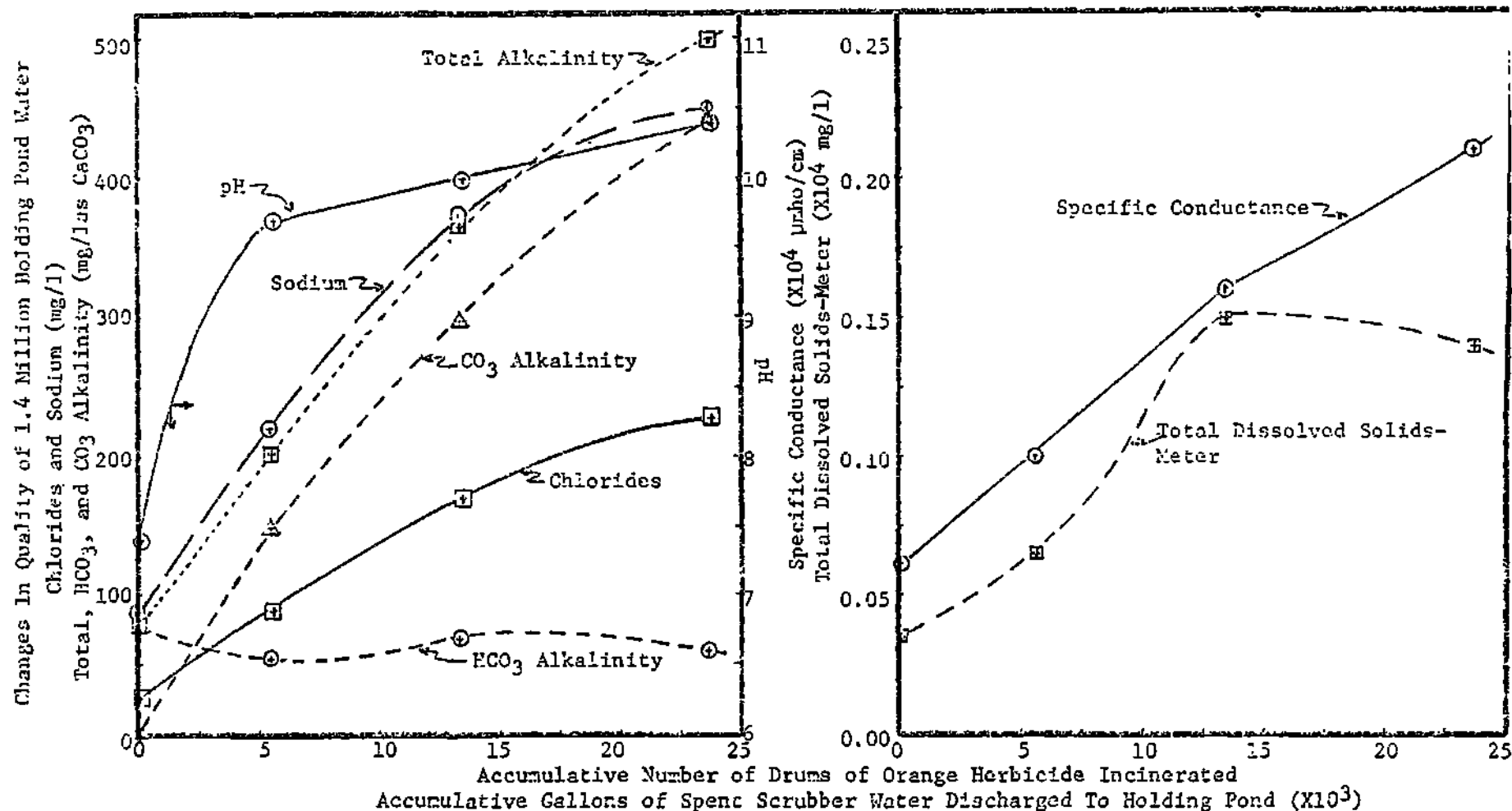
b. Analytical results are presented in Table E-18 and graphed in Figure E-7. The abscissa was double labeled and related the average gallons (1000) of spent scrubber water discharged per drum of herbicide incinerated. The "freshwater" quality of the reservoir changed significantly in rising pH, total and carbonate alkalinity, sodium, chlorides, specific conductance, and total dissolved solids. The rise in pH from 7.4 to 9.7 was the most noticeable and easily measured parameter of change. The pH then slowly increased to the equilibrium value of 10.4 for the bicarbonate-carbonate system. The fluctuating bicarbonate alkalinity indicated the water system's attempt to equilibrate the carbonate alkalinity reactions. Total dissolved solids content stabilized as the pH reached 10.0 -- indicating precipitating reactions had begun. Spent scrubber water caused no significant changes in any other measured parameters of the reservoir's water quality: specific gravity, total solids, chlorine residuals (0.0 mg/l), or hydroxyl alkalinity (0.0 mg/l as  $\text{CaCO}_3$ ).

c. The elevated chemical concentrations in the holding pond would begin to decrease as the system slowly adjusts to a more natural equilibrium, with a pH of approximately 8. Exceptions to this natural adjustment would be the conservative sodium and chloride which would increase the reservoir's salinity, but to a level much less than that of sea water.

TABLE E-18: SUMMARY OF EHL/K HOLDING POND WATER ANALYSES

Sample No: HP-		1	2	3	4
Accumulative Holding Tanks Dumped to Holding Pond		NONE	I & II	III & IV	V, VI & VII
Date Holding Tanks were dumped (Nov 73)		N/A	Mon 19 Wed 21	Tue 27 Thu 29	Tue 4 Dec
Date Collected (Nov 73)		Mon 19	Sat 24	Sat 1 Dec	Wed 5 Dec
Date Analyzed (Nov 73)		Wed 21	Mon 26	Sat 1 Dec	Wed 12 Dec
GENERAL	Parameter (mg/l unless noted)	Mid 60's			
	Temp ( <sup>0</sup> F) at time: Collected				
	Analyzed	72.	72.	73.	72.
	pH	7.40	9.70	10.00	10.40
SOLIDS	Sp. Gravity	1.0005	1.0010	1.0020	1.0010
	Sp. Cond. ( $\times 10^4$ $\mu$ mho/cm)	0.06	0.10	0.16	0.21
	TS ( $\times 10^3$ )	0.40	1.48	0.85	1.24
	VTS ( $\times 10^3$ )	-	-	-	-
	TDS, Mt ( $\times 10^4$ )	0.035	0.065	0.150	0.140
	TDS, Ms ( $\times 10^3$ )	-	-	-	-
	VTDS ( $\times 10^3$ )	-	-	-	-
	SS	-	-	-	-
	VSS	-	-	-	-
IONS/RADICALS	Chlorides	26.0	88.0	170.	228.
	Total Chl. Resid.	0.0	0.0	0.0	0.0
	Free Avail. Chl.	0.0	0.0	0.0	0.0
	Sodium	85.0	220.0	370.0	450.0
	Iron, Total	0.48	0.68	0.58	0.55
ALKALINITY	Total Alk ( $\text{CaCO}_3$ )	77.	202.	365.	515.
	OH-Alk ( $\text{CaCO}_3$ )	0.0	0.0	0.0	0.0
	$\text{HCO}_3$ -Alk ( $\text{CaCO}_3$ )	77.	53.5	68.0	59.
	$\text{CO}_3$ -Alk ( $\text{CaCO}_3$ )	0.0	148.5	297.0	456.

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NOTE: No significant changes occurred in other measured parameters; specific gravity, total solids, chlorine residuals (0.0 mg/l), or hydroxyl alkalinity (0.0 mg/l as CaCO<sub>3</sub>).

FIGURE E-7: EFFECTS OF SPENT SCRUBBER WATER DISCHARGE AND ORANGE HERBICIDE INCINERATED ON HOLDING POND WATER QUALITY.



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APPENDIX F

(TO APPENDIX E)

DRUM CLEANING, DISPOSAL, AND ANALYSES OF DRUM RINSE SAMPLES

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## APPENDIX F

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## APPENDIX F

### DRUM CLEANING, DISPOSAL, AND ANALYSES OF DRUM RINSE SAMPLES

#### 1. Introduction

This task was investigative in nature and was not designed necessarily for future use in any drum cleaning requirements. The objective of this study was to assess the maximal removal of normal butyl esters of 2,4-D and 2,4,5-T from the drums. TCDD removal was not measured but estimates of its removal were made. This appendix describes the equipment and procedures used to clean and dispose of the drums. Methods and results of USAF Environmental Health Laboratory-Kelly AFB (EHL/K) drum rinse analyses are also presented and discussed.

#### 2. Drum Cleaning Procedures

a. Drum cleaning operations were performed in the partially enclosed area north of Building 57. This area was curbed and had a sloped concrete floor with a catchment type drain (see Figure 9).

b. Less than two quarts of "Orange" Herbicide were usually left in each drum after the drum's contents had been transferred to the fuel feed tank. Before each drum was rinsed, the contractor upended it and its contents were allowed to "free board" drain until steady dripping stopped. This drain time depended on the herbicide's drip rate, and the drain time ranged from six to nine minutes with an average of 7.3 minutes ( $s = 0.90$ ). See Table F-1. Herbicide color and drip rate were subjectively observed and no consistent relationship was obtained between herbicide color and drip rate/total drain time.

c. As specified by EHL/K, the contractor used the following procedure to clean the twenty-eight drums that had been drained per paragraph "b" above:

(1) To a first set of seven random drums:

(a) Five gallons of unused JP-4 were poured into a drum and the drum was recapped.

(b) The drum was placed in a barrel rolling device for five minutes.

(c) Drum contents were poured into a "rinse collection" drum as EHL/K personnel collected a 250ml sample of the rinse solution midway through this draining step. The 250ml sample container had been specially cleaned and the cap lined with aluminum foil per the procedure described in paragraph 2a, Appendix E.

TABLE F-1: DRUM DRAINING/DRIPPING DATA

3 Dec 73 (1230-1625 hrs)				4 Dec 73 (0615-0845 hrs)			
EHL (K) DRUM NO.	DRAIN TIME (MIN)	REMARKS		EHL (K) DRUM NO.	DRAIN TIME (MIN)	REMARKS	
		HERBICIDE COLOR	DRIP RATE			HERBICIDE COLOR	DRIP RATE
83	8	Dark	Slow	73	8	Light	Slow
88	6	Honey	Fast	74	8	Light	Slow
90	8	Dark	Slow	68	7	Light	Slow
82	6	Honey	Fast	75	7	Light	Slow
71	6	Honey	Fast	62	9	Dark	Slow
81	7	Dark	Slow	91	8	Light	Slow
92	7	Honey	Fast	65	8	Light	Slow
66	8	Dark	Slow	76	8	Dark	Slow
80	6	Honey	Slow	63	9	Dark	Slow
84	7	Dark	Slow	64	7	Light	Slow
70	6	Honey	Fast	77**	8	Light	Slow
86	7	Honey	Fast				
69	7	Honey	Fast				
78	6	Honey	Fast				
87	8	Dark	Slow				
89*	8	Dark	Slow				
85	7	Dark	Slow				
* Drum 89 was a damaged Drum and was manually shaken.				** Drum 77 Was suspected of having H <sub>2</sub> O in it. However none was observed.			
NOTES: (1) Average drain time for all drums was 7.32 minutes, s = 0.90 (2) Average ambient air temperature was 60°F during drainings.							

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(d) Steps (a) through (c) above were repeated twice.

(e) Drum was then recapped and stored for disposal.

(2) To a second set of seven random drums, (1) above was accomplished except three gallons of unused JP-4 were used for each of the three rinses per drum.

(3) To a third set of seven random drums, (1) above was accomplished except two gallons of unused JP-4 were used for each of the three rinses per drum.

(4) To a fourth set of the seven remaining drums, (1) above was accomplished except that the following volumes of unused JP-4 were used for each rinse: five gallons for the first rinse, three gallons for the second rinse, and two gallons for the third rinse.

### 3. Drum Disposal

a. EHL/K inquired locally about public landfills which were approved by regulatory agencies for burial of hazardous materials. The Los Angeles County "Class 1" Landfill Number 5 at Calabasas, CA was so approved and selected by EHL/K for the drum disposal. Mr. Robert Van Huet, Los Angeles County Sanitation Office (213-484-1370) and Mr. Jack Johnson, Site Foreman of the Calabasas Landfill (213-889-1430), approved the drum burial after they had been briefed by EHL/K on the following characteristics of the drums:

(1) Quantity and quality of the drums.

(2) Herbicidal content of the drums and the method of drum cleaning that had been accomplished.

(3) Requirement that the drums be crushed and buried to preclude any chance of them being salvaged and recycled for anyone's use.

b. The cleaned drums were loaded onto a flatbed truck, uncapped, and loaded with several cups of laundry detergent and about twenty gallons of tap water. This detergent solution sloshed around in the drums as the truck was driven to the landfill. This action of detergent rinsing was taken to stop any JP-4 vaporization and emulsify any residual JP-4/herbicide that may have been in the drums.

c. The uncapped drums were rolled from the truck bed into a pit freshly dug by the landfill operators. The drums were then immediately crushed, mixed, and compacted with other refuse, and buried while EHL/K personnel observed.

#### 4. EHL/K Procedures/Methods of Analyses of Drum Rinse Samples

##### a. Equipment and Materials.

(1) Gas Chromatograph - Tracor 220 equipped with flame ionization detector (FID).

(2) Chromatographic column: 4 feet glass "U" tube packed with 3% ov-1 on Chromosorb W, 80/100 mesh.

(3) Chromatographic operating conditions:

(a) Injector temperature - 225°C.

(b) Detector temperature - 175°C.

(c) Column temperature:

1 Programmed initial temperature at 150°C for six minutes rising at 10°C per minute to a final temperature of 200°C.

2 Isothermal condition of 160°C.

(d) Carrier gas - nitrogen.

(e) Gas flow - 70 cc/minute.

b. Standards. Standard solutions of nb 2,4-D and nb 2,4,5-T esters were prepared in JP-4. Standard curves were prepared for the nb 2,4-D and nb 2,4,5-T esters at three different concentrations: 6 µg/µl, 2 µg/µl, and 0.2 µg/µl. Linearity was obtained from 0.2 µg to 24 µg but was lost above 24 µg for both the 2,4-D and 2,4,5-T nb esters. Standard curves were prepared by plotting peak height (cm) vs concentration of ester in micrograms (µg).

##### c. Procedure.

(1) Samples were injected into the gas chromatograph at an adjusted injection volume so that the concentration would be within the concentration of the prepared standard curves. Sample dilution was therefore unnecessary.

(2) Samples from the first and second rinses were analyzed using the column temperature program. Samples from the third rinse were analyzed using the isothermal column temperature. This was done because samples from the third rinse had the lowest ester concentrations and the solvent interfered with the 2,4-D n-Butyl ester peak when using the temperature program.



(3) Concentration of the samples was calculated using the standard curves. The value obtained was in micrograms per microliter which was then converted to milligrams per liter of sample.

## 5. Analytical Results and Discussion of Drum Rinse Samples

### a. Presentation of Analytical Results.

(1) Analytical results were obtained for each individual nb 2,4-D and nb 2,4,5-T ester in each rinse sample (mg/L). These data were reduced to determine the:

(a) Mass (gm) of each ester and the sum of both esters' masses in each rinse volume,

(b) Accumulated (acc.) mass in grams of each ester and the sum of both esters' masses in the accumulated rinse volume, and

(c) Fraction of accumulated mass of each ester and sum of both esters' masses in the accumulated rinse volume as a percent of the accumulated ester(s) removed in all three rinses.

(2) These reduced data as well as statistical qualities on them are presented in Tables F-2 through F-5. The data points were highly variable with many standard deviations large when compared to a mean value. Whenever possible, statistical comparisons were performed on the data to determine the significance between data sets at or above the 90% confidence level.

(3) TCDD was not analyzed in the rinse samples, but the samples were saved should any need arise. Since TCDD has similar solubility to 2,4-D and 2,4,5-T esters in organic solvents, its removal from the drums was based on the removal efficiencies found for 2,4-D and 2,4,5-T.

### b. Relative Removals of Each Ester.

(1) Review of the data in Tables F-2 through F-5 revealed that the 2,4-D mass in a rinse was almost always greater than the 2,4,5-T mass in the rinse. This was expected since the blended herbicide analyses, Table G-1, showed that nb 2,4-D and nb 2,4,5-T esters, respectively, averaged 50.90 and 43.78 percent of the herbicide total weight. Figure F-1 considers the 2,4-D and 2,4,5-T nb esters to be 100 percent of the total herbicide in the rinse and presents the average mass percentage of each of these esters in each rinse for all drums. Also shown is the mass percent of these esters when they are considered to be 100 percent of the herbicide total mass rather than their average 94.68 percent. Similarly,

TABLE F-2: SUMMARY OF HERBICIDE MASS IN RINSE SOLUTION - DRUM SET A

Drum Set "A" EHL(K) Drum Numbers 63/64/74/75/76/77/91				Rinses			Date			Collectors: DiLorenzo/Knerl Chemists: Hodgkinson/Rodriguez									
				Gal/Rinse	1	2	3	Collected: 3-4 Dec 73	17 Dec 73										
				5	5	5	5	Analyzed: 8 Jan 74											
SAMPLE NO.	Drain OF Drip Time (Min)	nb 24D ester						nb 245T ester						nb Total Esters					
		gm/rinse			Acc. gm/rinse % Total			gm/rinse			Acc. gm/rinse % Total			gm/rinse			Acc. gm/rinse % Total		
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
A-63	9	179.4	32.17	16.45	178.4	211.6	228.0	173.7	27.82	9.88	173.7	201.5	211.4	353.1	60.0	26.3	353.1	413.1	439.4
					78.7	92.8					82.2	95.3					80.4	94.0	
A-64	7	162.4	41.07	1.10	162.4	203.5	204.6	153.3	33.50	0.62	153.3	186.8	187.4	315.7	74.6	1.7	315.7	390.3	392.0
					79.4	99.5					81.8	99.7					80.5	99.6	
A-74	8	176.0	19.49	6.25	176.0	195.5	201.7	166.9	10.03	2.21	166.9	176.9	179.1	342.9	29.5	8.5	342.9	372.4	380.9
					87.2	96.9					93.2	98.8					90.0	97.8	
A-75	7	128.3	10.22	7.12	128.3	138.5	145.6	131.7	4.92	2.63	131.7	136.6	139.3	260.0	15.1	9.8	260.0	275.1	284.9
					88.1	95.1					94.6	98.1					91.3	96.6	
A-76	8	173.7	15.52	6.66	173.7	189.2	195.9	169.2	7.38	2.42	169.2	176.6	179.0	342.9	22.9	9.1	342.9	365.8	374.9
					88.7	96.6					94.5	98.6					91.5	97.6	
A-77	8	156.7	43.53	27.73	156.7	200.2	228.0	151.0	30.66	15.29	151.0	181.7	197.0	307.7	74.2	43.0	307.7	381.9	424.9
					68.7	87.8					76.7	92.2					72.4	89.9	
A-91	8	135.1	12.11	7.31	135.1	147.2	154.5	139.7	6.06	2.78	139.7	145.8	148.5	274.8	18.2	10.1	274.8	293.0	303.1
					87.4	95.3					94.0	98.1					90.7	96.7	
Ave ( $\bar{x}$ )		158.8	24.87	10.37	158.8	183.7	194.0	155.1	17.19	5.12	155.1	172.3	177.4	313.9	42.1	15.5	313.87	355.9	371.4
Std D. ( $\delta$ )		20.2	13.89	8.90	20.2	28.8	32.6	15.8	12.80	5.38	15.8	23.0	25.6	35.8	26.6	14.2	35.8	51.6	58.0
Ave ( $\bar{x}$ )					82.6	94.8					88.1	97.3					85.3	96.0	
Std D. ( $\delta$ )					7.4	3.7					7.6	2.6					7.5	3.2	

USAF EHL(K)

TABLE F-3: SUMMARY OF HERBICIDE MASS IN RINSE SOLUTION - DRUM SET B

Drum Set "B" EHL(K) Drum Numbers 62/66/68/73/82/85/90								Rinses			1	2	3	Date Collected: 3-4 Dec 73 Date 17 Dec 73- Analyzed: 8 Jan 74		Collectors: DiLorenzo/Knerl Chemists: Hodgkinson/Rodriguez					
SAMPLE NO.	Drain or Drip Time (Min)	nb 24D ester						nb 245T ester						nb Total Esters							
		gm/rinse			Acc. gm/rinse % Total			gm/rinse			Acc. gm/rinse % Total			gm/rinse			Acc. gm/rinse % Total				
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3		
B-62	9	68.8	8.86	4.66	68.8	77.7	82.3	68.1	4.66	1.67	68.1	72.8	74.4	136.9	13.5	6.3	136.9	150.4	156.8		
					83.6	94.3					91.5	97.8					87.3	96.0			
B-66	8	94.0	7.04	0.90	94.0	101.0	101.9	81.8	4.20	0.49	81.8	86.0	86.5	175.8	11.2	1.4	175.8	187.0	188.4		
					92.2	99.1					94.6	99.4					73.3	99.3			
B-68	7	158.1	36.00	5.45	158.1	194.1	199.6	149.9	22.14	2.46	149.9	172.0	174.5	308.0	58.1	7.9	308.0	366.1	374.1		
					79.2	97.3					85.9	98.6					82.3	97.9			
B-73	8	103.6	5.34	0.65	103.6	108.9	109.6	97.4	3.18	0.41	97.4	100.6	101.0	201.0	8.5	1.1	201.0	209.5	210.6		
					94.5	99.4					96.4	99.6					95.5	99.5			
B-82	6	81.8	4.20	0.78	81.8	86.0	86.8	86.5	2.73	0.39	86.5	89.2	89.6	168.3	6.9	1.2	168.3	175.2	176.4		
					94.3	99.1					96.5	99.6					95.4	99.3			
B-85	7	62.7	15.22	3.12	62.7	77.9	81.0	65.4	8.29	1.23	65.4	73.7	74.9	128.1	23.5	4.4	128.1	151.6	156.0		
					77.4	96.2					87.3	98.4					82.1	97.2			
B-90	8	122.6	11.24	0.41	122.6	133.8	134.3	110.4	6.70	0.23	110.4	117.1	117.3	233.0	17.9	0.6	233.0	250.9	251.6		
					91.3	99.7					94.1	99.8					92.6	99.7			
Ave (x̄)		98.8	12.56	2.28	98.8	111.4	113.6	94.2	7.41	0.98	94.2	101.6	102.6	193.0	20.0	3.3	193.0	212.9	216.3		
Std D. (s)		33.2	10.99	2.11	32.2	41.6	42.3	29.1	6.78	0.84	29.2	34.7	35.1	62.1	17.8	2.7	62.1	76.0	77.2		
Ave (x̄)					87.5	97.9					92.3	99.0					89.8	98.4			
Std D. (s)					7.3	2.0					4.3	0.8					5.9	1.4			

USAF EHL(K)

TABLE F-4: SUMMARY OF HERBICIDE MASS IN RINSE SOLUTION - DRUM SET C

Drum Set "C" EHL(K) Drum Numbers 71/81/83/86/88/89/92								Rinses			1			2			3			Date Collected: 3-4 Dec 73 Date 17 Dec 73 Analyzed: 8 Jan 74			Collectors: DiLorenzo/Knerl Chemists: Hodgkinson/Rodriguez					
SAMPLE NO.	Drain or Drip Time (Min)	nb 24D ester						nb 245T ester						nb Total Esters														
		gm/rinse			Acc. gm/rinse % Total			gm/rinse			Acc. gm/rinse % Total			gm/rinse			Acc. gm/rinse % Total											
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3									
C-71	6	82.2	6.59	0.81	82.2 91.7	88.8 99.1	89.6	75.9	3.86	0.43	75.9 94.7	79.8 99.5	80.2	158.1	10.5	1.2	158.1 93.1	168.6 99.3	169.8									
C-81	7	55.0	5.00	1.20	55.0 89.9	60.0 98.0	61.2	49.5	2.80	0.64	49.5 93.5	52.3 98.8	52.9	109.5	7.8	1.8	109.5 91.6	112.3 98.4	114.1									
C-83	8	105.4	9.84	2.45	105.4 89.6	115.2 97.9	117.7	99.0	5.83	1.26	99.0 93.3	104.8 98.8	106.1	204.4	15.7	3.7	204.4 91.3	220.1 98.3	223.8									
C-86	7	104.5	15.29	1.76	104.5 86.0	119.8 98.6	121.6	97.7	9.24	0.91	97.7 90.6	106.9 99.2	107.9	202.2	24.5	2.7	202.2 88.1	226.7 98.8	229.4									
C-88	6	80.8	7.80	1.70	80.8 89.5	88.6 98.1	90.3	74.0	4.47	0.90	74.0 93.2	78.5 98.9	79.4	154.8	12.3	2.6	154.8 91.2	167.1 98.5	169.7									
C-89	8	125.8	18.17	1.42	125.8 86.5	144.0 99.0	145.4	119.9	16.35	0.74	119.9 87.5	136.3 99.5	137.0	245.7	34.5	2.2	245.7 87.0	280.2 99.2	282.4									
C-92	7	107.2	13.93	1.70	107.2 87.3	121.1 98.6	122.8	102.2	8.93	0.90	102.2 91.2	111.1 99.2	112.0	209.4	22.9	2.6	209.4 89.2	232.3 98.9	234.9									
Ave ( $\bar{x}$ )		94.4	10.94	1.58	94.4	105.4	106.9	88.3	7.35	0.83	88.3	95.7	96.5	182.7	18.3	2.4	182.7	201.0	203.4									
Std D. ( $\delta$ )		23.3	4.92	0.51	23.3	27.9	28.1	23.3	4.67	0.26	23.3	27.5	27.6	46.6	9.5	0.8	46.6	55.3	55.6									
Ave ( $\bar{x}$ )					88.6	98.5					92.0	99.1					90.2	98.8										
Std D. ( $\delta$ )					2.1	0.5					2.4	0.3					2.2	0.4										

USAF EHL(K)

TABLE F-5: SUMMARY OF HERBICIDE MASS IN RINSE SOLUTION - DRUM SET D

Drum Set "D" EHL(K) Drum Numbers 65/69/70/78/80/84/87								Rinses		1	2	3	Date Collected: 3-4 Dec 73 Date 17 Dec 73 Analyzed: 8 Jan 74			Collectors: DiLorenzo/Knerl Chemists: Hodgkinson/Rodriguez					
SAMPLE NO.	Drain or Drip Time (Min)	nb 24D ester						nb 245T ester						nb Total Esters							
		gm/rinse			Acc. gm/rinse % Total			gm/rinse			Acc. gm/rinse % Total			gm/rinse			Acc. gm/rinse % Total				
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3		
D-65	8	109.0	3.97	1.20	109.0 95.5	113.0 98.9	114.2 100.0	102.2	2.38	0.63	102.2 97.1	104.6 99.4	105.2	211.2	6.4	1.8	211.2 96.3	217.6 99.2	219.4		
D-69	7	138.5	8.40	0.60	138.5 93.9	146.9 99.6	147.5	127.2	4.88	0.28	127.2 96.1	132.1 99.8	132.4	265.7	13.3	0.90	265.7 94.9	279.0 99.7	279.9		
D-70	6	98.8	13.85	1.43	98.8 86.6	112.7 98.7	114.1	93.1	7.84	0.76	93.1 91.5	100.9 99.3	101.7	191.9	21.7	2.2	191.9 88.9	213.6 99.0	215.8		
D-78	6	118.1	7.04	0.89	118.1 93.7	125.1 99.3	126.0	109.0	4.20	0.48	109.0 95.9	113.2 99.6	113.7	227.1	11.2	1.4	227.1 94.7	238.3 99.4	239.7		
D-80	6	163.5	11.24	1.49	163.5 92.8	174.7 99.2	176.2	156.7	6.70	0.78	156.7 95.4	163.4 99.5	164.2	320.2	17.9	2.3	320.2 94.1	338.1 99.3	340.4		
D-84	7	159.0	26.57	1.46	159.0 85.0	185.6 99.2	187.0	149.9	16.81	0.77	149.9 89.5	166.7 99.5	167.5	308.9	43.4	2.2	308.9 87.1	352.3 99.4	354.5		
D-87	8	120.4	55.64	1.45	120.4 67.8	176.0 99.2	177.5	117.0	51.32	0.79	117.0 69.2	168.3 99.5	169.1	237.4	107.0	2.2	237.4 68.5	344.4 99.4	346.6		
Ave ( $\bar{x}$ )		129.6	18.10	1.22	129.6	147.7	149.0	122.1	13.45	0.64	122.2	135.6	136.3	251.8	31.0	1.9	251.8	283.3	285.2		
Std D. (s)		24.8	18.08	0.35	24.8	31.4	31.5	23.9	17.34	0.20	23.9	30.2	30.3	48.6	35.8	0.5	48.6	61.5	61.7		
Ave ( $\bar{x}$ )					87.9	99.2					90.7	99.5					89.2	99.3			
Std D. (s)					9.7	0.3					9.9	0.2					9.7	0.2			

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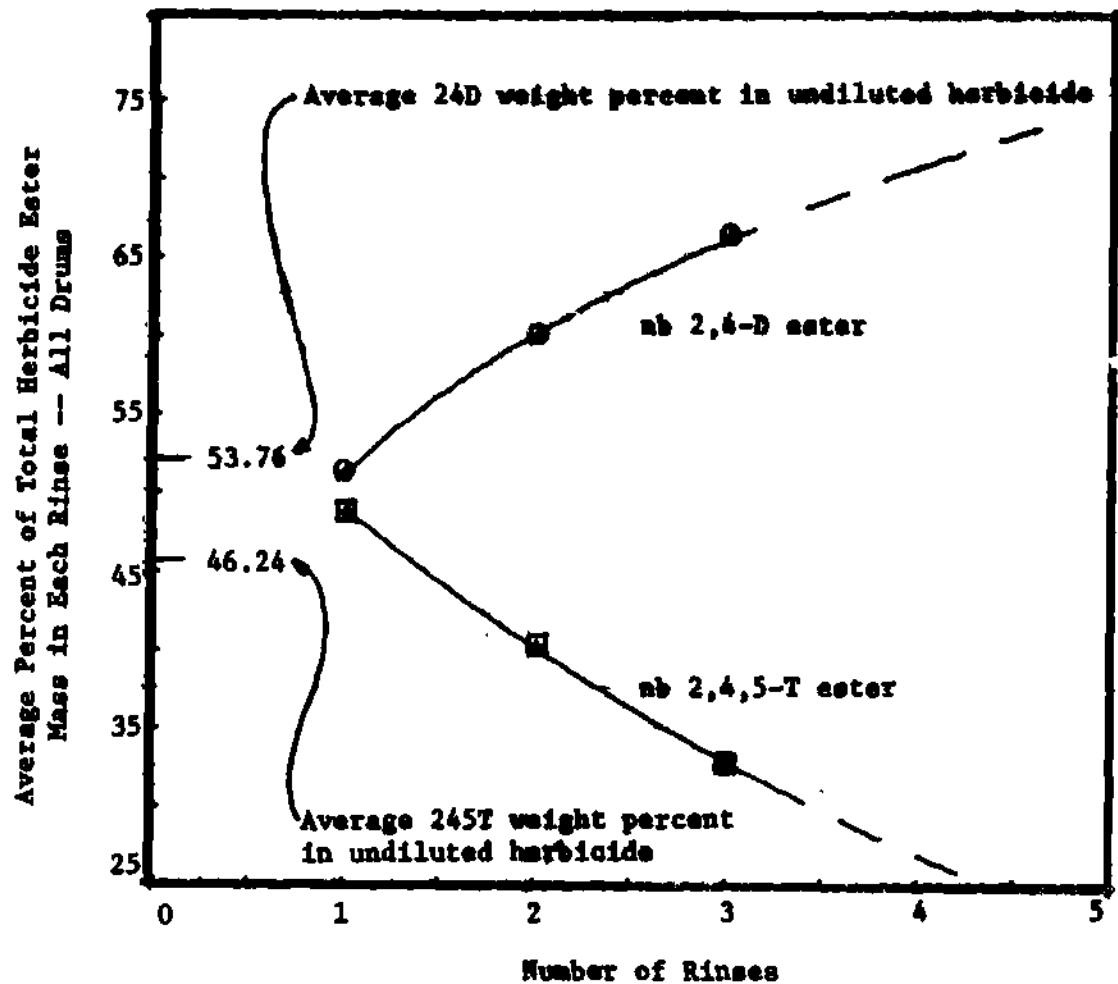


FIGURE F-1: WEIGHT PERCENT OF 2,4-D AND 2,4,5-T ESTERS OF TOTAL HERBICIDE IN EACH RINSE

USAF EHL(K)

Figure F-2 gives, for all drums, the average accumulative mass percentage of each of these esters in the accumulative rinses.

(2) An evaluation of Figures F-1 and F-2 indicated that slightly more of an original mass of nb 2,4,5-T ester was removed from a drum during its first rinse than was the nb 2,4-D ester. This better proportional removal of an original 2,4,5-T mass appeared independent of the solvent volume used in the initial rinse. Apparently, in the competing solubilities, 2,4,5-T was absorbed more rapidly than 2,4-D in an initial rinse of JP-4. The proportion of 2,4,5-T decreased markedly in successive rinses because a larger fraction of it had already been removed. The accumulative three-rinse effect of this phenomenon was less dramatic than the individual rinses but still showed a proportionately higher average removal (106%) of original masses of 2,4,5-T than 2,4-D, respectively, from the drums.

#### c. Estimate of Herbicide Mass in Drum.

(1) The average accumulative mass of total esters in the accumulative rinses and the average mass of total esters in each rinse are plotted for each drum set in Figures F-3 and F-4, respectively. The curves in both figures were fitted by regression analyses and found to best fit power equations (Figure F-3) and exponential decay equations (Figure F-4). Data in both figures indicated that ester mass removal in the rinses was controlled by a first order absorption isotherm. There was no significant difference in the total herbicide mass in drum set "B" and "C" rinses which was only 70 to 80 percent of the mass in drum set "A" and "D" rinses.

(2) Drum set "A" rinses contained significantly higher amounts of total herbicide mass on a per rinse basis and on an accumulative basis. Drum set "A" rinses removed more herbicide from the drums and this set's data were used to estimate the average total herbicide mass originally in the drums. Applying the principle of first order decay, the seventh rinse or 35th accumulative gallon of rinse should remove an estimated 99 plus percent of the drum's herbicide mass. The equations of best fit were then used for the seventh rinse and 450 ( $\pm 25$ ) grams of herbicide were concluded to be the best estimate of original mass of herbicide in drum.

#### d. Herbicide Removal Per Gallon of Rinse Used.

(1) Table F-6 presents the accumulative herbicide mass per gallon of accumulative rinse for each drum in all drum sets. The data in Table F-6 were statistically compared with each other for herbicide mass per accumulated gallon of rinse. At the 95% confidence level, these comparisons showed that:

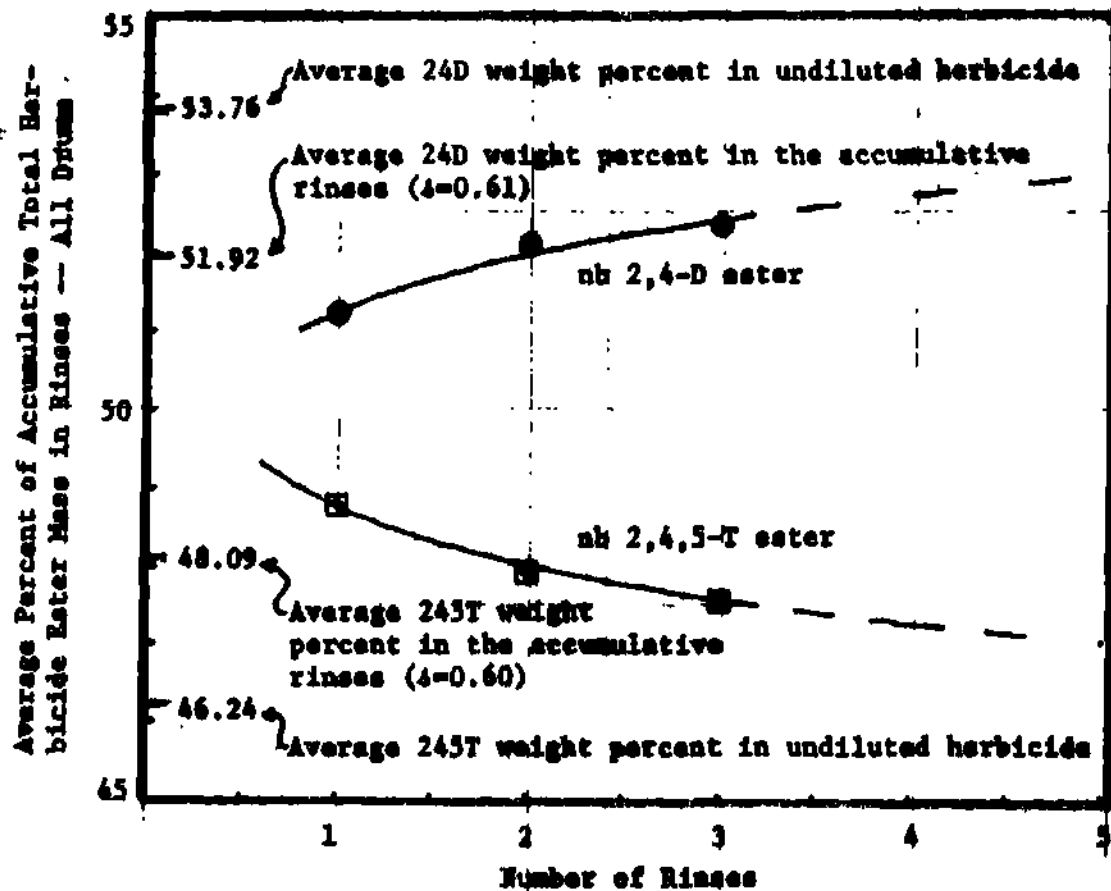


FIGURE F-2: WEIGHT PERCENT OF 2,4-D and 2,4,5-T ESTERS OF TOTAL HERBICIDE IN ACCUMULATED DRUM RINSINGS.

USAF EHL(K)



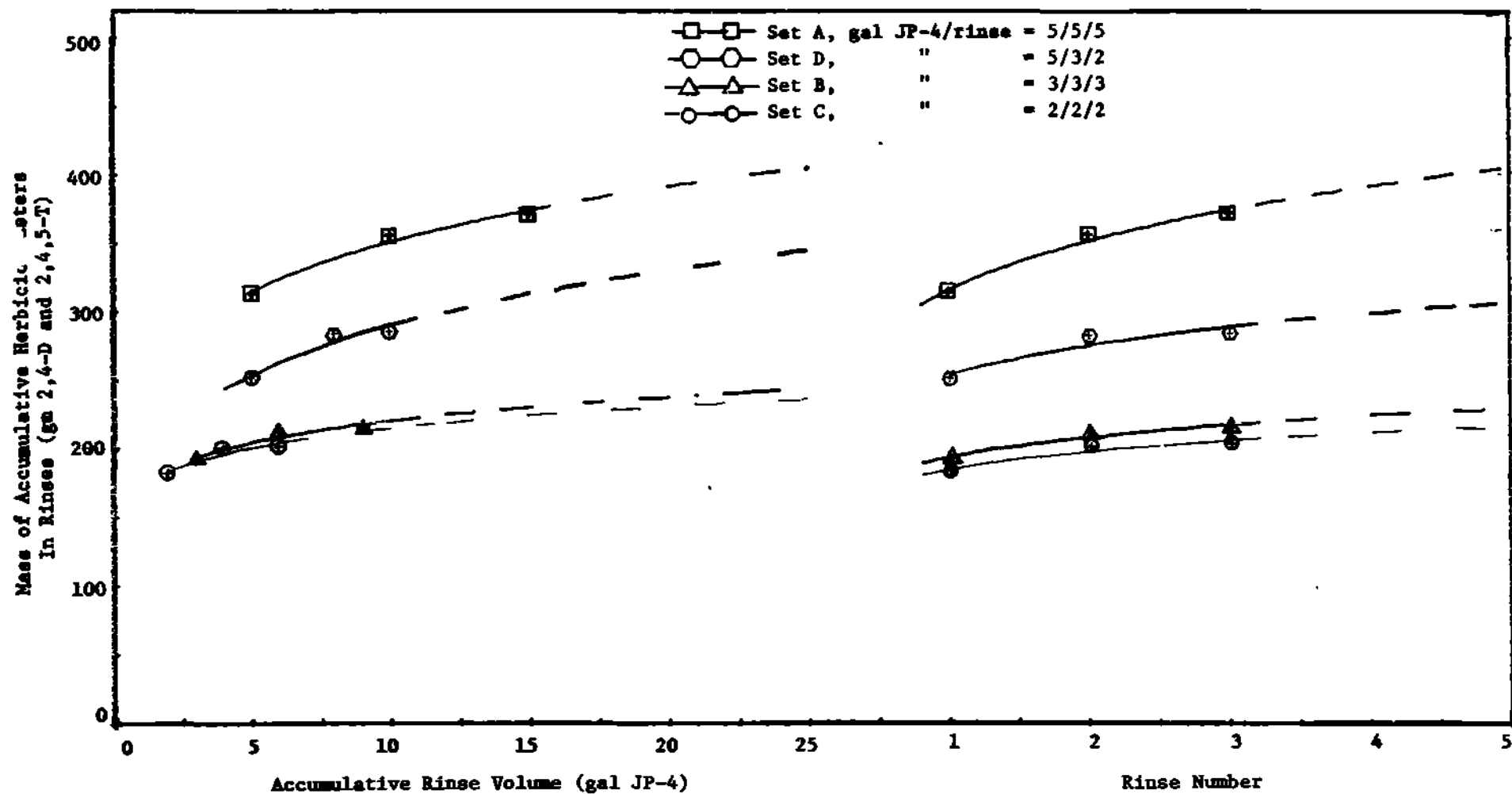


FIGURE F-3: MASS OF ACCUMULATIVE HERBICIDE ESTERS IN RINSES vs ACCUMULATIVE RINSE VOLUMES AND RINSE NUMBERS

USAF EHL(K)

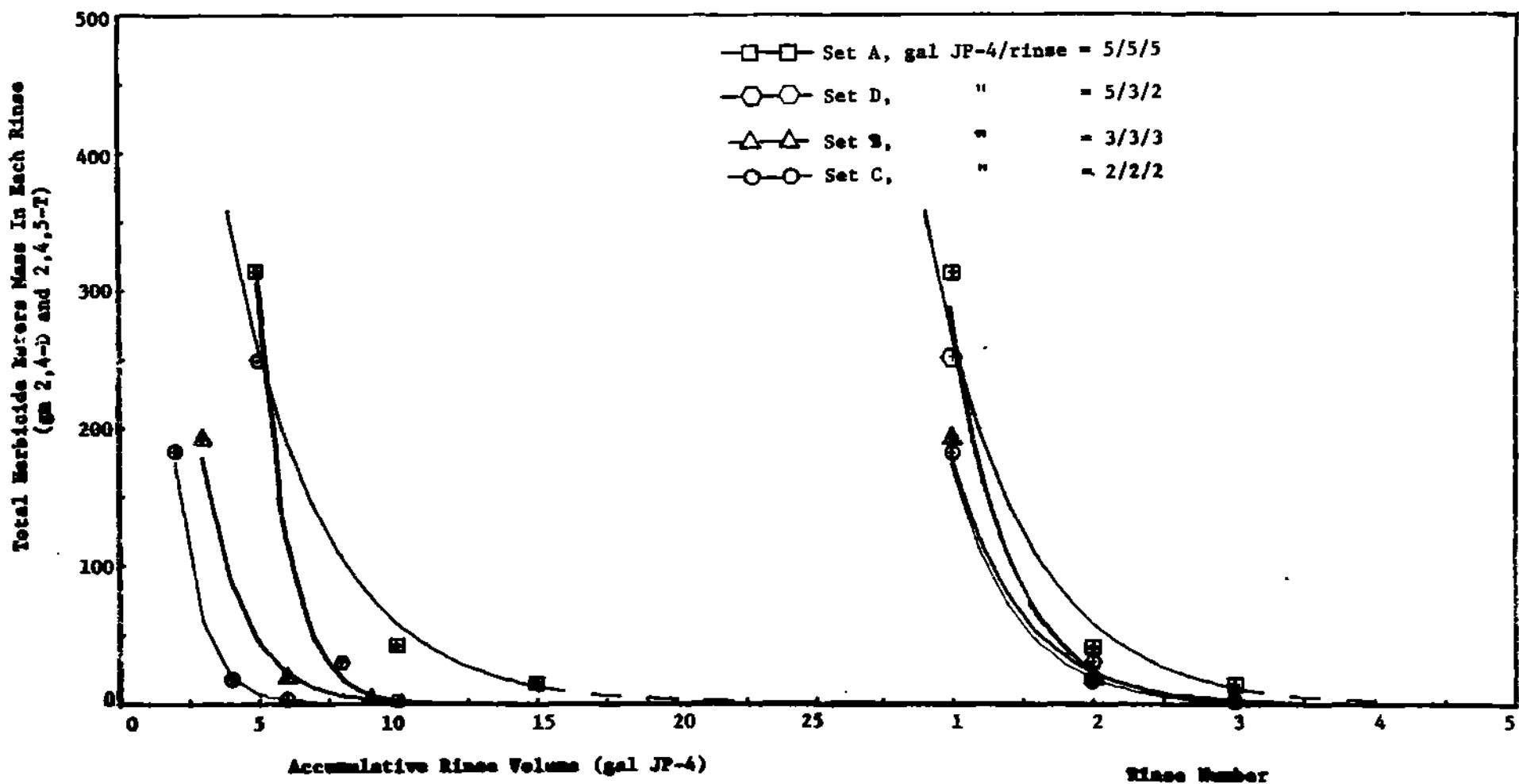


FIGURE F-4: MASS OF TOTAL HERBICIDE ESTERS IN EACH RINSE vs ACCUMULATIVE RINSE VOLUMES AND RINSE NUMBERS

USAF FHI (K)

(a) Variances of herbicide mass per accumulated gallon of rinse for the following cases were:

1 Equal for rinse gallon combinations of 5,3,5, and 2/2 and the pooled variance of these rinse gallon combinations was unequal to any other single or pooled variances. Note range of rinse gallons: 3 to 5 gallons.

2 Equal for rinse gallon combinations of 5/5, 3/3, 5/3, and 2/2/2 and the pooled variance of these rinse gallon combinations was unequal to any other single or pooled variances. Note range of rinse gallons: 6 to 10 gallons.

3 Equal for rinse gallons combinations of 5/5/5, 3/3/3, and 5/3/2 and the pooled variance of these rinse gallon combinations was unequal to any other single or pooled variances. Note range of rinse gallons: 9 to 15 gallons.

4 Unequal for any rinse gallon combinations or their pooled variances when compared to the single rinse of 2 gallons.

(b) Means of herbicide mass per accumulated gallon of rinse for the following cases were:

1 Equal for rinse gallon combinations of 5,3,5, and 2/2 and the pooled mean of these rinse gallon combinations was unequal to any other single or pooled mean. Note range of rinse gallons: 3 to 5 gallons.

2 Equal for rinse gallon combinations of 5/5, 3/3, 5/3, and 2/2/2 and the pooled mean of these rinse gallon combinations was unequal to any other single or pooled means. Note range of rinse gallons: 6 to 10 gallons.

3 Equal for rinse gallon combinations of 5/5/5, 3/3/3, and 5/3/2 and the pooled mean of these rinse gallon combinations was unequal to any other single or pooled means. Note range of rinse gallons: 9 to 15 gallons.

4 Unequal for any rinse gallon combinations or their pooled means when compared to the single rinse of 2 gallons.

(c) Rinses with smaller volumes caused significantly higher variances in performance. The three gallon rinses had dramatically less variance than the two gallon rinses.

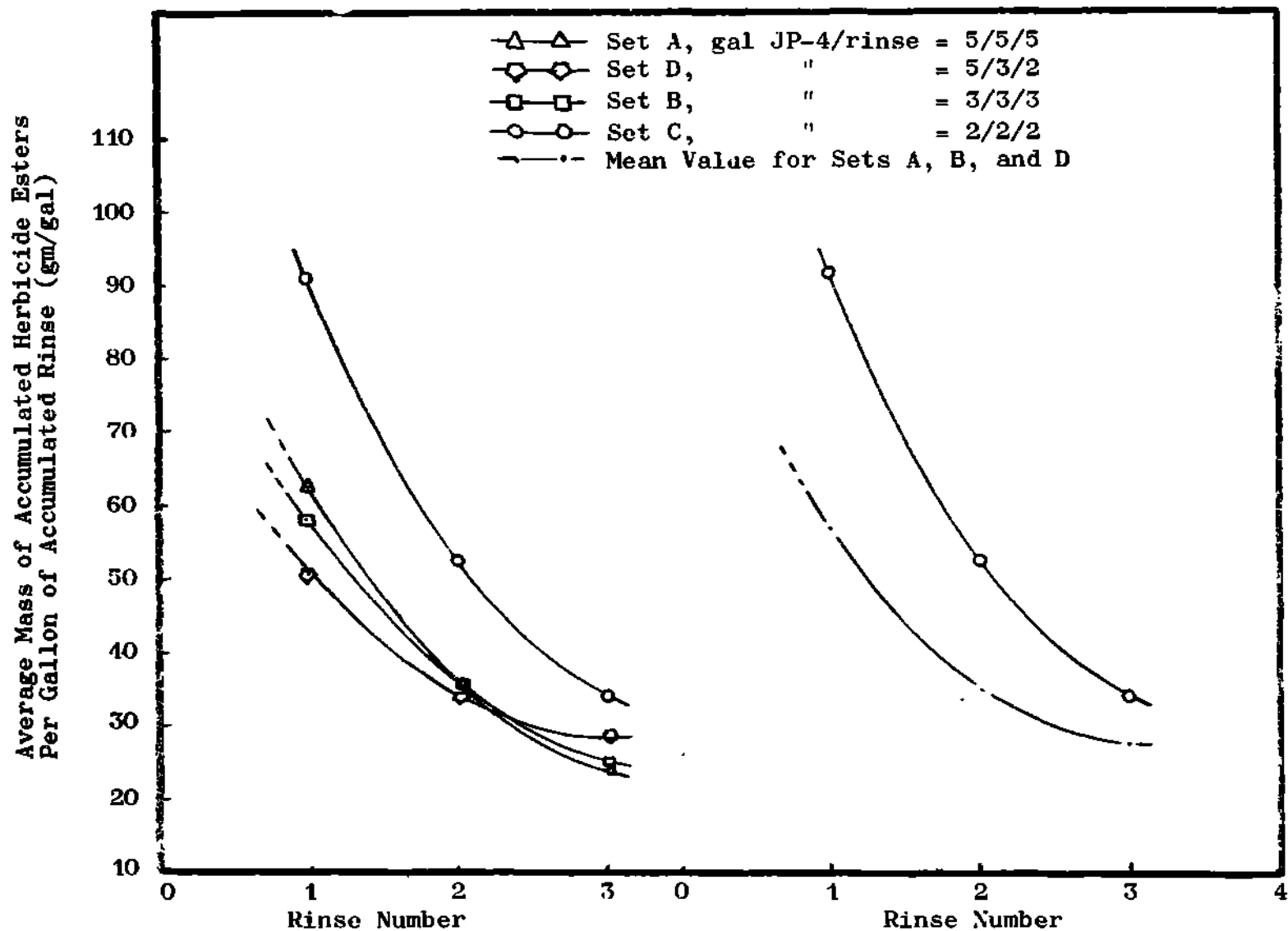
(2) Considering these statistical evaluations, the data of Table F-6 were plotted in Figure F-5 against rinse number and in Figure F-6 against accumulative rinse volume. Interpretation of these figures indicated that:

TABLE F-6: Accumulative Herbicide Mass Per Gallon of Rinse

Drum Set	Acc. Mass of Herbicide Esters Per Acc. Gal. Rinse (gm/gal)			Drum Set	Acc. Mass of Herbicide Esters Per Acc. Gal. Rinse (gm/gal)		
	Rinse Number/ Acc. Rinse Volume (gal JP-4)				Rinse Number/ Acc. Rinse Volume (gal JP-4)		
A	1/5	2/10	3/15	C	1/2	2/4	3/6
	70.62 63.14 68.58 52.00 68.58 61.54 54.96	41.31 39.03 37.24 27.51 36.58 38.19 29.30	29.29 26.13 25.39 18.99 24.99 28.33 20.21		79.05 52.25 102.20 101.10 77.40 122.85 104.70	42.15 28.08 55.03 56.68 41.78 70.05 58.08	28.30 19.02 37.30 38.23 28.28 47.07 39.15
$\bar{x}$ $s$ $s^2$	62.77 7.16 51.30	35.59 5.16 26.64	24.76 3.86 14.93	$\bar{x}$ $s$ $s^2$	91.36 23.30 542.99	50.26 13.82 191.09	33.91 9.27 85.95
B	1/3	2/6	3/9	D	1/5	2/8	3/10
	45.63 58.60 102.67* 67.00 56.10 42.70 77.67	25.07 31.17 61.02* 34.92 29.20 25.27 41.82	17.42 20.93 41.57* 23.40 19.60 17.33 27.96		42.24 53.14 38.38 45.42 64.04 61.78 47.48	27.20 34.88 26.70 29.79 42.26 44.04 43.05	21.94 27.99 21.58 23.97 34.04 35.45 34.66
$\bar{x}$ $s$ $s^2$	57.95 13.11 171.79	31.24 6.38 40.67	21.10 4.06 16.48	$\bar{x}$ $s$ $s^2$	50.35 9.72 94.57	35.42 7.69 59.15	28.52 6.17 38.11

\*Considered to be a possible outlier and not used in statistical calculation.

FIGURE F-5: Average Mass of Accumulated Herbicide Esters Per Gallon of Accumulated Rinse vs Rinse Numbers



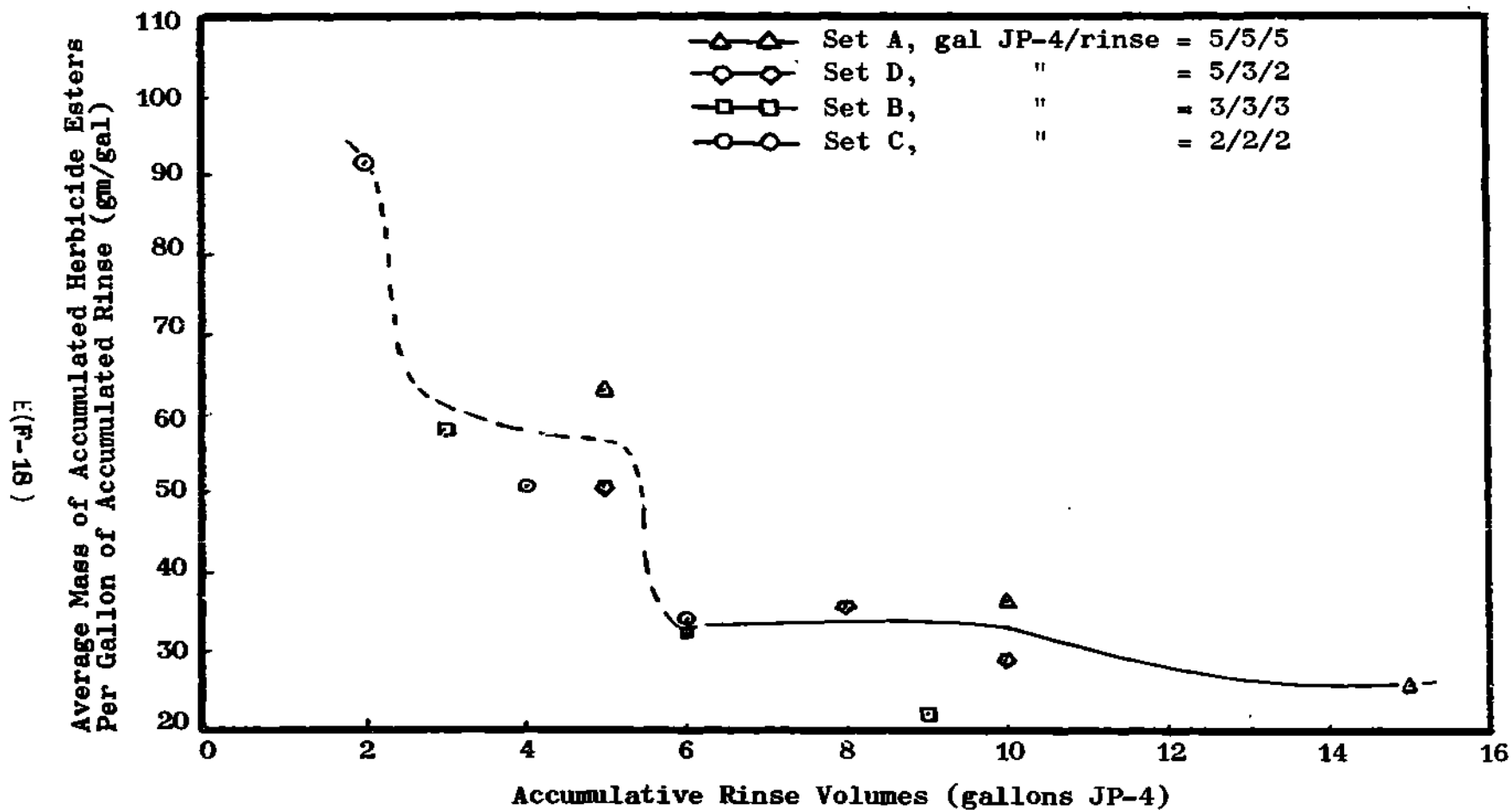


FIGURE F-6: Average Mass of Accumulated Esters Per Gallon of Accumulative Rinse vs Accumulated Rinse Volumes

(a) Herbicide removal per gallon of solvent was essentially independent of any two applied rinse volumes whose accumulative total volume was <5 gallons, 6 to 10 gallons, and 11 to 15 gallons. However, a more consistently average performance could be expected if volume per rinse were maximized within each of these volumetric groupings, i.e., use a single rinse of 5 gallons if total rinse volume is <5 gallons; use two rinse volumes of 3/3, 4/4, or 5/5 gallons if total rinse volume is between 6 and 10 gallons; etc.

(b) The difference in average performance diminished between rinse sets on the third rinse because  $\approx 50\%$  of the herbicide had been removed from the drum and each rinse set had approached its respective plateau for herbicide removal per rinse (see Figures F-3 and F-4).

c. Estimate of Herbicide Removal Efficiency.

(1) The accumulative mass of total herbicide in each rinse volume was compared to the estimated 450 grams of total herbicide in each drum. Percent removal of this estimated amount of herbicide after two rinses was 79.1% for "A", 63.0% for "D", 47.3% for "B", and 44.7% for "C." Regardless of rinse volume used, the third rinse improved the overall herbicide removal efficiency by less than 3%.

(2) Percents of original herbicide remaining in the drum were calculated for each drum set and plotted against accumulative rinse volume in Figure F-7. The five gallon rinses left 15 to 30 percent less herbicide in the drums than did any other rinses. It was thus concluded that given two or three rinses whose total volume was less than 10 gallons, the optimal removal efficiency (79.1% for the total gallons used) was achieved using two rinses of five gallons each.

6. Conclusions and Recommendations

a. Herbicide mass removal from the drums using JP-4 appeared to be dependent upon the applied rinse volume and to follow a first order absorption isotherm.

b. Accumulative mass of herbicide in the accumulative JP-4 rinses were fitted quite well to exponential curves which were used to estimate the original mass of total herbicide in the drained drums: 450 ( $\pm 25$ ) grams.

c. Based upon the original weights of 2,4-D and 2,4,5-T esters in the herbicide, proportionately more 2,4,5-T ester mass than 2,4-D ester mass was removed in the first JP-4 rinse. These proportions reversed during the following rinses, but the accumulative effect was that about 106 percent more 2,4,5-T ester mass was removed than was the 2,4-D ester mass.

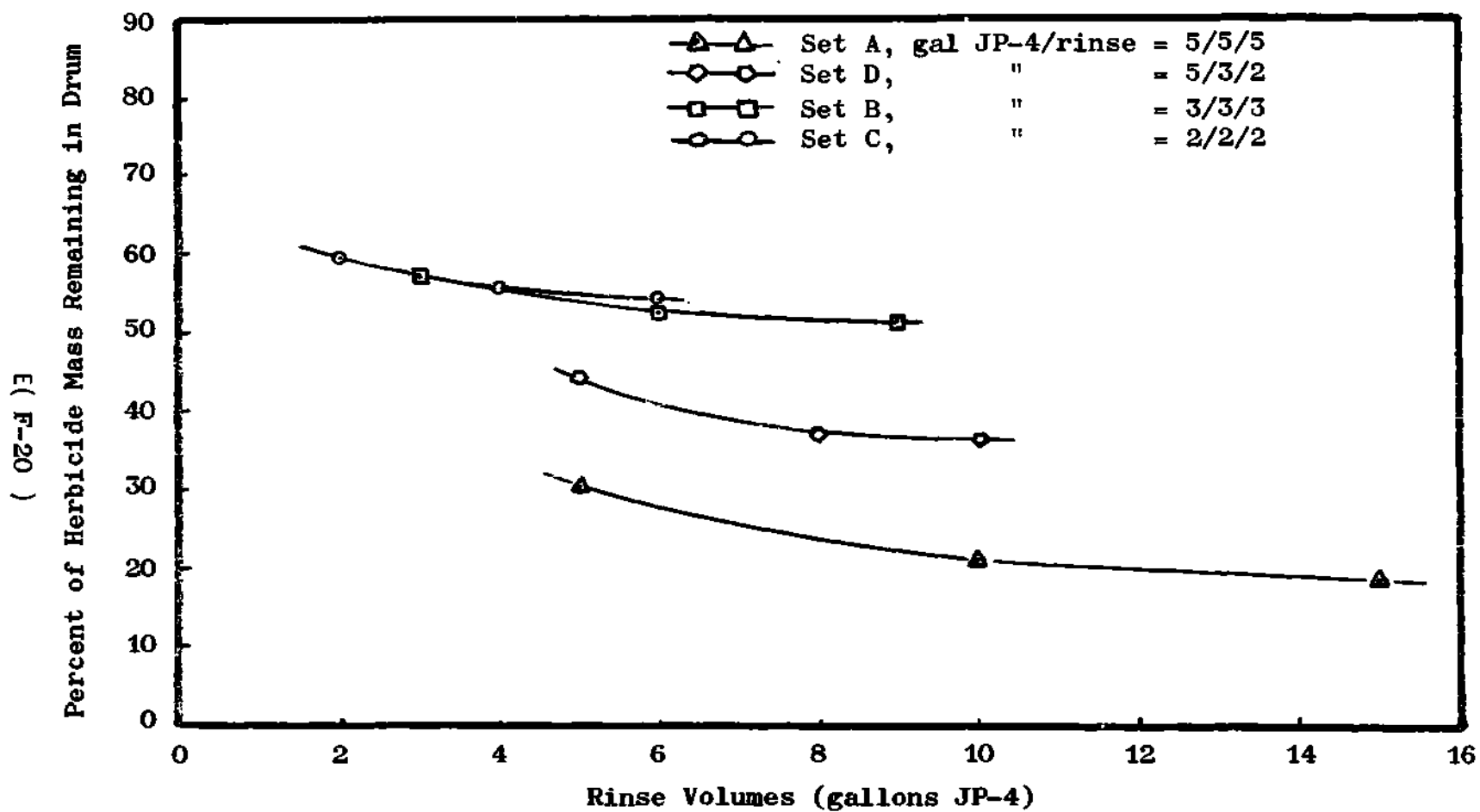


FIGURE F-7: Percent of Herbicide Mass Remaining in Drums vs Applied Rinse Volumes



d. Removing drum ends and spraying the rinse downward through an open drum would provide better herbicide removal efficiency per gallon of rinse used. This is because successive rinses could be thoroughly drained from the drum. Since such draining could not be achieved in this test program, 10 to 25 percent improved results could be expected depending on rinse volumes used.

e. Depending on ultimate drum disposal, desired drum cleanliness, and availability of rinse (JP-4), this program concluded that under the following two constraints, separate rinse procedures could be used to obtain maximum results:

(1) Limited supplies of JP-4 rinse ( $\leq 5$  gallons per drum) and some cleaning desired. Use the five gallons in a single rinse to obtain minimal variation of drum cleanliness. Any volumetric rinses totaling five gallons per drum would remove about the same herbicide mass but would be more variable in performance.

(2) Up to 10 gallons of JP-4 rinse available per drum and optimal drum cleaning required--use two rinses of 5/5 gallons to remove the most herbicide from the drum, i.e., 79% compared to 45 to 63% for the rinse volumes of 2/2/2, 3/3/3, or 5/3/2 gallons.

(3) A third JP-4 rinse equal to or less than 5 gallons would not improve the overall removal efficiency by more than 3%.

f. No evidence exists to indicate that contaminated JP-4 could not be used to achieve the same drum cleaning performance as unused JP-4.

g. Calculations based on an average TCDD concentration of 13.25 mg/kg of herbicide showed that the mass of TCDD in these drained drums was 5.96 mg. This calculation of TCDD mass in the drum before and after rinses presented the worst case for all herbicide stocks because the TCDD in these 28 drums was 7 times greater than the average TCDD concentration in the Air Force stock (see paragraph 2.2). If TCDD removal efficiency was equal to the herbicide esters, then 1.25 mg of TCDD would have been in the drums after two JP-4 rinses of 5/5 gallons. Rinse samples were not analyzed for TCDD but were saved for analyses should they be needed to select a final drum disposal method.

h. The data of this study can be used to determine the volumetric rinses of unused or contaminated JP-4 needed to meet any prescribed drum cleaning requirements.

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E (F-22)

WEST COAST TECHNICAL SERVICE, INC.

APPENDIX G

(TO APPENDIX E)

ORGANIC ANALYSES OF BLENDED HERBICIDE,  
COMBUSTION AND SCRUBBED EFFLUENT GASES,  
SPENT SCRUBBER WATER, AND RESIDUES

*E(F-23)*

## APPENDIX G

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## REPORT



(213) 921-9831  
(714) 523-9200

**date/** February 1, 1974

**job no./** 5252

**p.o. no./** 805137-1

**prepared for/**

Dr. R. P. Babbitt

The Marquardt Company  
16555 Satcoy Street  
Van Nuys, California 91409

The samples from the combustion of liquid herbicide have been analyzed by gas chromatography, combined gas chromatography-mass spectrometry, and/or atomic absorption. The various samples were processed prior to analysis by one of the procedures described below. In addition, extraction efficiency, sensitivity and detection limits for the various compounds were determined. These data are given below:

### I Procedures

#### A. Equipment

##### 1. Mass Spectrometer

A DuPont Model 490 Mass Spectrometer was used for identification of the various components. The mass spectrometer was connected to the gas chromatograph through an all glass jet separator. All spectra were taken at an ionization voltage of 70e.v. The spectra were recorded on a recording oscillograph.

##### 2. Gas Chromatograph

A Varian Model 2700 Gas Chromatography equipped with a flame ionization detector was used for separation and quantization of all volatile components. The operating parameters were as follows:

Column - 10 ft. x 1/8 inch stainless steel packed  
with 5% OV-17 on Chromsorb G (AW DMCS)  
Detector - 325°C  
Injector - 310°C  
Flow Rate - 22cc/minute  
Column Temperature - 165° - 310°C at 10°C/minute

##### 3. Atomic Absorption

A Perkin-Elmer Model 403 Atomic Absorption Spectrometer was used for determining the iron content of certain samples. The aqueous solutions were run against standard iron solutions. The iron content of the blended herbicide was determined by diluting the sample with xylene and running against an organo-iron standard dissolved in xylene.

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## II Calibration

A standard solution containing the following material was prepared in benzene. This solution was used for calibration and determination of recovery efficiency. The solution contains 500 micrograms of the following compounds per milliliter of solution.

2,4-dichlorophenoxy acetic acid  
2,4,5-trichlorophenoxy acetic acid  
2,4-dichlorophenoxy acetic acid butylester  
2,4,5-trichlorophenoxy acetic acid butylester  
2,4,5-trichlorophenoxy acetic acid octylester  
2,4-dichlorophenol

In addition, the standard contained 51 micrograms of 2,3,7,8-tetrachlorodibenzo-p-dioxin per milliliter of solution. The standard solution was treated with diazomethane to convert the acids and phenol to the esters and ether. The sample was then diluted to volume and injected into the gas chromatograph, and the response of the various components determined. The detection limit for these compounds was determined. Since all test samples were taken to a final volume of 25 microliters, the absolute detection limits for the various components were calculated based on this volume. These limits are, therefore, the limit for the quantity present in the total sample.

The detection limits for the components of the standard solution were as follows:

	<u>Detection Limit</u> <u>Nanograms/Total Sample</u>
2,4-dichlorophenoxy acetic acid (methylester)	22
2,4,5-trichlorophenoxy acetic acid (methylester)	21
2,4-dichlorophenoxy acetic acid butylester	23
2,4,5-trichlorophenoxy acetic acid butylester	21
2,4,5-trichlorophenoxy acetic acid octylester	19
2,4-dichlorophenol (methylether)	29
2,3,7,8-tetrachlorodibenzo-p-dioxin	22

Previous calibration and stability tests show the detection limit to be valid to  $\pm 10\%$  of the value.

### III Recovery Efficiency

The efficiency of extraction for the various compounds from a water solution was determined as follows: 1.00ml of the standard solution described in II above was pipetted into a 1 liter beaker. The benzene was removed under a nitrogen stream at 40°C. 500ml of tap water was added and the solution mixed. The water solution was then added to a separating funnel, made acid-pH-2, and extracted four (4) times with 50ml portions of diethylether. The ether extracts were combined, dried over anhydrous sodium sulfate, filtered and evaporated to a volume of 5cc. Excess diazomethane in ether was added and allowed to stand for 15 minutes as the solution evaporated under nitrogen at 40°C. The extract was then diluted to 1.00ml with benzene and analyzed by gas chromatography.

A 1.00ml volume of the standard solution was evaporated to dryness and treated with excess diazomethane for 15 minutes. The ether was then removed and the mixture diluted to 1.00ml with benzene. This solution was then analyzed by gas chromatography.

The recovery efficiency was calculated as the percentage of the standard components extracted from the water solution relative to that from the esterified standard solution.

The recovery efficiency of the standard components were found to be as follows:

	<u>Efficiency of Recovery</u>
2,4-dichlorophenoxy acetic acid	92%
2,4,5-trichlorophenoxy acetic acid	92%
2,4-dichlorophenoxy acetic acid butylester	96%
2,4,5-trichlorophenoxy acetic acid butylester	98%
2,4,5-trichlorophenoxy acetic acid octylester	97%
2,4,-dichlorophenol	72%
2,3,7,8-tetrachlorodibenzo-p-dioxin	93%

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**The Marquardt Company  
Dr. R. P. Babbitt**

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**IV Work Up and Analysis of Sample**

**A. Analysis of blended herbicide samples**

0.5ml of the blended herbicide was tested with excess diazomethane to convert any acid or phenol present to the more volatile methyl derivation. The ether was removed at 40°C under a stream of nitrogen. The samples were then chromatographed and the composition of the mixture determined. The identity of the various components was determined on the first sample by a use of the combined gas chromatography-mass spectrometry. Subsequent samples were analyzed by gas chromatography only using the retention time from the original gas chromatography-mass spectrometry run for identification.

**B. Analysis of combustion, scrubbed effluent, and miscellaneous gas impinger samples**

The quantity of the benzene solutions was determined and recorded. The benzene was removed by distillation. The residue was treated with excess diazomethane in ether for 15 minutes and the ether removed at 40°C under a stream of nitrogen. The residue was then diluted to 25 microliters with methylenechloride and analyzed by gas chromatography. Combined gas chromatography-mass spectrometry was used to identify the various compounds in the first sets of samples. Subsequent samples were analyzed by gas chromatography using the retention time data for identification.

The water layer from those samples which contained water were acidified to pH-2 with hydrochloric acid and extracted four (4) times with ether. The ether was dried over anhydrous sodium sulfate. The ether extract was then added to the corresponding benzene solution or treated with diazomethane and processed in a corresponding manner.



C. Analysis of fresh and spent scrubber waters

500ml of the scrubber water sample was acidified (pH-2) with concentrated hydrochloric acid. The water solution was then extracted four (4) times with ether. The ether was then dried and evaporated. The extract was treated with excess diazomethane after which the solvent was evaporated and the residue diluted to 25 microliters with methylenechloride and analyzed by gas chromatography. Combined gas chromatography-mass spectrometry was used to identify the various components from the first runs. Subsequent samples were analyzed by gas chromatography using the retention time data for identification. The presence of 2,3,7,8-tetrachlorodibenzo-p-dioxin in sample III SSW TBC was confirmed by gas chromatography-mass spectrometry.

D. Analysis of combustion chamber residues

The hard carbonaceous residue was pulverized. A 100 gram sample was then extracted four (4) times with a boiling mixture of 75% benzene -25% methanol. The extracts were combined and the solvents removed by distillation. The residues were treated with excess diazomethane, concentrated and diluted to 25 microliters with methylenechloride. The residues were analyzed by gas chromatography. Combined gas chromatography-mass spectrometry was used to identify the various components. Five grams of the carbon residues were ignited in a platinum crucible. The ash was treated with hydrochloric acid and diluted to 25ml. The acid solution was then analyzed for iron by atomic absorption.

The ash content was determined by thermogravimetric analysis in air. The sample began to lose weight (undergo oxidation) at approximately 525°C. The carbon was completely oxidized by 725°C.

E. Analysis of spent scrubber water sediment

The dark precipitate from the scrubber water sample was separated by filtration through one micron glass filter and washed with 60ml of deionized water. The residue was air dried and weighed. The residue was then treated in the same manner as the combustion chamber deposit.

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**F. Analysis of particulate filter samples**

The filters were extracted four (4) times with hot benzene. The benzene was then removed by distillation. The residue was treated with excess diazomethane and the solvent evaporated. The residue was then diluted to 25 microliters with methylenechloride and analyzed by gas chromatography. Combined gas chromatography-mass spectrometry was used to identify the various components.

The benzene insoluble material was then extracted with hot 5% hydrochloric acid. The extract was then diluted to 25ml and analyzed for iron by atomic absorption.

**V General Comments**

The presence of Ionol and didecylphthlate in several of the samples is most probably due to contamination. Since these compounds are used extensively as an anti-oxidant and plasticizer, respectively, in plastics, their presence is quite frequently encountered. These compounds could have been picked up from the sample bottles, screw caps, plastic tubing or from the work area atmosphere.

The absence of biphenyl in the combustion gas and scrubber water while seen in other samples, raises certain questions. It is possible that the biphenyl was not observed in the combustion chamber gases as a result of peak interference. Its absence from the spent scrubber water is most probably due to its being removed by the hot water vapors. Since the biphenyl has a very low solubility in water and the presence of the salt and caustic further reduce this solubility, there is no driving force to retain it in the water phase. The detected biphenyls were unchlorinated.

The presence of butylalcohol was specifically monitored in the spent scrubber water and scrubbed effluent gas since it is a hydrolysis product of the principal herbicides. It was possible that some butylesters of the herbicide would survive the combustion and react with the hot caustic solution. Saponification could then occur producing the acid salt and butylalcohol. The absence of butylalcohol therefore eliminates the possibility of the ester reaching the scrubber and being hydrolyzed.

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There was no evidence for the presence of aldehyde in the combustion gases. This was substantiated by the fact that the several peaks identified as aliphatic and aromatic hydrocarbons occurred both in the combustion gas and spent scrubber water samples. If aldehydes had been present in the combustion chamber, they would have undergone further reactions in the presence of hot aqueous caustics and not been detected in the spent scrubber water.

The bulk of the residues on the particulate sampling filters appeared by visual examination to be sodium chloride. The only analysis which was carried out on these residues was for iron and volatile organic compounds.

It is difficult to fully explain the presence of the phenoxyacetic acid in sample III RACC-2, combustion chamber residue. It would appear that it arises directly from the blended herbicide feed since it is present as the butylester in the range of 0.02% to 1.64%. It would therefore appear that the compound exhibits a higher stability than the other products in the zone where the carbon deposit occurs.

No attempt was made to identify the positional isomers of the monochlorophenol or the dichlorophenol. It is reasonable to assume that the monochloro derivative is a mixture of ortho and para isomers, since these are the normal products from the preparation of chlorophenol. It is also reasonable to assume that the dichlorophenol is 2,4-dichlorophenol since it is a reactant in the preparation of 2,4-dichlorophenoxy acetic acid.

The identity of specific aromatic and aliphatic hydrocarbon was not undertaken. The mass spectrometry of these materials showed them to contain no chlorine. The aromatic hydrocarbons were distributed around the C<sub>4</sub> substituted benzene derivation. These compounds also appeared to have saturated sidechain. The amount of these aromatic hydrocarbons was therefore calculated as butylbenzene. The aliphatic hydrocarbons in the system spanned the range of C<sub>7</sub> through C<sub>15</sub>. The preponderance of them was centered at C<sub>10</sub>. These compounds were therefore calculated as C<sub>10</sub>H<sub>22</sub> even though many of them appear to be unsaturated.

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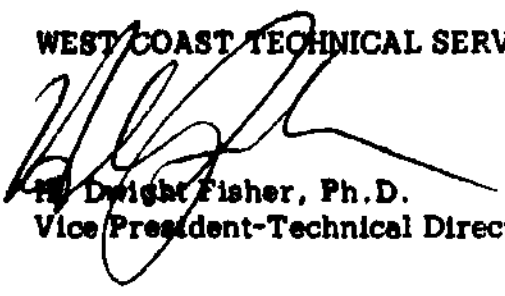
**VI Results**

**The results of the various analyses are given in the following tables.**

**If we can be of any further assistance, please do not hesitate to contact us.**

**Respectively submitted,**

**WEST COAST TECHNICAL SERVICE INC.**



**Dwight Fisher, Ph.D.  
Vice President-Technical Director**

**HDF/lp**

**P.S.**

**Reported values were not adjusted for analytical recovery efficiencies but all the reported detection limits were.**

TABLE G-1

COMPOSITION OF BLENDED HERBICIDE FEED  
(weight percent except as noted)

	I BH 62/63 64/65	II BH 76/77/91	III BH 78/80/ 89/92	IV BH 86/87/90	V BH 71/81 82/84	VI BH 66/83 85/88	VII BH 69/73	VIII BH 68/70 74/75
Dichlorophenol	1.86	.63	.78	.82	.52	2.97	2.00	2.13
Trichlorophenol	.61	.03	.08	.09	.55	1.64	1.16	1.12
Phenoxy acetic acid - butylester	.02	.08	.33	.38	.28	1.27	.85	.79
2,4-dichlorophenoxy acetic acid	.53	.44	.33	.33	.14	1.47	1.64	.96
2,4,5-trichlorophenoxy acetic acid	.48	.37	.28	.32	.24	.94	.72	.82
2,4-dichlorophenoxy acetic acid-butylester	50.35	52.02	53.14	52.99	52.71	47.59	49.25	49.15
Monochlorophenoxy acetic acid-octylester	.43	.34	.27	.29	.00	.76	.66	.60
2,4,5-trichlorophenoxy acetic acid-butylester	44.46	45.30	44.41	44.29	45.21	43.21	41.23	42.15
2,4,-dichlorophenoxy acetic acid-octylester	.77	.73	.32	.31	.32	.06	1.24	1.13
2,4,5-trichlorophenoxy acetic acid - octylester	.49	.06	.04	.19	.00	.09	1.25	1.15
2,3,7,8-tetrachlorodibenzo- p-dioxin	12ppm*	14ppm*	11ppm*	16ppm*	14ppm*	12ppm*	13ppm*	14ppm*
Iron	7.2ppm*	6.7ppm*	8.2ppm*	14.3ppm*	7.6ppm*	12.3ppm*	6.2ppm*	9.1ppm*
Total	100.00	100.00	99.98	100.01	99.97	100.00	100.00	100.00

\* ppm by weight (mg/kg)

WEST COAST TECHNICAL SERVICE INC.

TABLE G-2

COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN  
IMPINGER SAMPLES

(micrograms per total sample as compound except as noted)

	<u>ICG-1</u>	<u>ICG-2</u>	<u>ICG-3</u>	<u>ICG-4</u>	<u>Detection Limits*</u> <u>nanograms/liter</u>
Aromatic hydrocarbons (1)	382	3.2	51.9	2.9	0.18
Aliphatic hydrocarbons (2)	83	4.1	2.1	2.7	0.18
Chlorinated aromatic hydrocarbons (3)	ND	ND	ND	ND	0.18
Chlorinated aliphatic hydrocarbons (4)	ND	ND	ND	ND	0.18
Chlorophenol	146	ND	ND	ND	0.22
Dichlorophenol	ND	ND	ND	ND	0.22
2,4-dichlorophenoxy acetic acid (methylester)	ND	ND	ND	ND	0.16
2,4,5-trichlorophenoxy acetic acid (methylester)	ND	ND	ND	ND	0.15
2,4,-dichlorophenoxy acetic acid - butylester	ND	ND	ND	ND	0.17
2,4,5-trichlorophenoxy acetic acid - butylester	ND	ND	ND	ND	0.15
Ionol	1.67	3.2	4.3	4.9	0.18
Didecylphthlate	14	1.5	1.5	0.6	0.18
Biphenyl	ND	ND	ND	ND	0.18
2,3,7,8-tetrachlorodibenzo-p-dioxin	ND	ND	ND	ND	0.16
Total volume of solution (ml)	647	249	272	213	

- (1) calculated as butylbenzene  
 (2) calculated as decane  
 (3) calculated as dichlorobenzene  
 (4) calculated as  $C_2H_4Cl_2$

\* Based on flow data  
 furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.

(TABLE G-2 cont'd on following seven pages)

TABLE G-2 (cont'd)

COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN  
IMPINGER SAMPLES  
(micrograms per total sample as compound except as noted)

	<u>IICG-1</u>	<u>IICG-2</u>	<u>IICG-3</u>	<u>IICG-4</u>	<u>Detection Limits*</u> <u>nanograms/liter</u>
Aromatic hydrocarbons (1)	314	8.2	6.1	0.6	0.74
Aliphatic hydrocarbons (2)	29.3	6.2	1.2	1.0	0.74
Chlorinated aromatic hydrocarbons (3)	ND	ND	ND	ND	0.74
Chlorinated aliphatic hydrocarbons (4)	ND	ND	ND	ND	0.74
Chlorophenol	ND	ND	ND	ND	0.88
Dichlorophenol	ND	ND	ND	ND	0.88
2,4 dichlorophenoxy acetic acid (methylester)	ND	ND	ND	ND	0.65
2,4,5-trichlorophenoxy acetic acid (methylester)	ND	ND	ND	ND	0.62
2,4,-dichlorophenoxy acetic acid - butylester	ND	ND	ND	ND	0.67
2,4,5-trichlorophenoxy acetic acid - butylester	ND	ND	ND	ND	0.62
Ionol	121.2	37.3	67.2	1.2	0.94
Didecylphthlate	223	2.2	7.3	1.4	0.74
Biphenyl	ND	ND	ND	ND	0.74
2,3,7,8-tetrachlorodibenzo-p-dioxin	ND	ND	ND	ND	0.65
Total volume of solution (ml)	781	368	320	324	

- (1) calculated as butylbenzene  
(2) calculated as decane  
(3) calculated as dichlorobenzene  
(4) calculated as  $C_2H_4Cl_2$

\* Based on flow data  
furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC

c-(G-11)

TABLE G-2 (cont'd)

**COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN  
IMPINGER SAMPLES**  
(micrograms per total sample as compound except as noted)

	<u>IECG-1</u>	<u>IECG-2</u>	<u>IECG-3</u>	<u>IECG-4</u>	<u>Detection Limits*</u> <u>nanograms/liter</u>
Aromatic hydrocarbons (1)	100.	3.2	4.3	2.5	0.11
Aliphatic hydrocarbons (2)	201.	27.1	11.2	5.9	0.11
Chlorinated aromatic hydrocarbons (3)	ND	ND	ND	ND	0.11
Chlorinated aliphatic hydrocarbons (4)	ND	ND	ND	ND	0.11
Chlorophenol	ND	ND	ND	ND	0.13
Dichlorophenol	ND	ND	ND	ND	0.13
2,4-dichlorophenoxy acetic acid (methylester)	ND	ND	ND	ND	0.10
2,4,5-trichlorophenoxy acetic acid (methylester)	ND	ND	ND	ND	0.10
2,4,-dichlorophenoxy acetic acid - butylester	ND	ND	ND	ND	0.10
2,4,5-trichlorophenoxy acetic acid - butylester	ND	ND	ND	ND	0.10
Ionol	12.5	0.6	0.5	0.6	0.11
Didecylphthlate	16.2	0.3	3.1	0.2	0.11
Biphenyl	ND	ND	ND	ND	0.11
2,3,7,8-tetrachlorodibenzo-p-dioxin	ND	ND	ND	ND	0.10
Total volume of solution (ml)	446	360	352	410	

- (1) calculated as butylbenzene  
 (2) calculated as decane  
 (3) calculated as dichlorobenzene  
 (4) calculated as C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>

\* Based on flow data  
furnished by EHL/M

WEST COAST TECHNICAL SERVICE INC.



TABLE G-2 (cont'd)  
COMPOSITION OF COMBUSTION GAS SAMPLING TRAIN  
IMPINGER SAMPLES  
(micrograms per total sample as compound except as noted)

	<u>IVCG-1</u>	<u>IVCG-2</u>	<u>IVCG-3</u>	<u>IVCG-4</u>	<u>Detection Limits*</u> <u>nanograms/liter</u>
Aromatic hydrocarbons (1)	0.7	0.4	0.3	0.2	0.10
Aliphatic hydrocarbons (2)	0.27	0.45	0.23	0.2	0.10
Chlorinated aromatic hydrocarbons (3)	ND	ND	ND	ND	0.10
Chlorinated aliphatic hydrocarbons (4)	ND	ND	ND	ND	0.10
Chlorophenol	ND	ND	ND	ND	0.12
Dichlorophenol	ND	ND	ND	ND	0.12
2,4-dichlorophenoxy acetic acid (methylester)	ND	ND	ND	ND	0.09
2,4,5-trichlorophenoxy acetic acid (methylester)	ND	ND	ND	ND	0.09
2,4,-dichlorophenoxy acetic acid - butylester	ND	ND	ND	ND	0.09
2,4,5-trichlorophenoxy acetic acid - butylester	ND	ND	ND	ND	0.09
Ionol	0.3	0.9	36.2	1.4	0.10
Didecylphthlate	2.4	0.6	8.2	16.9	0.10
Biphenyl	ND	ND	ND	ND	0.10
2,3,7,8-tetrachlorodibenzo- p-dioxin	ND	ND	ND	ND	0.09
Total volume of solution (ml)	524	286	228	388	

- (1) calculated as butylbenzene  
(2) calculated as decane  
(3) calculated as dichlorobenzene  
(4) calculated as C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>

\* Based on flow data  
furnished by EHL/M

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