A STUDY OF PESTICIDE DISPOSAL IN A SEWAGE SLUDGE INCINERATOR

Copies will be available from the
National Technical Information Service
U.S. Department of Commerce
Springfield, Virginia 22151

U.S. ENVIRONMENTAL PROTECTION AGENCY
1975

TABLE OF CONTENTS

TABLE OF CONTENTS (Con't)

LIST OF TABLES

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES

1.0 PROGRAM SUMMARY

Removal from general use of certain refractory pesticide compounds
has resulted in large excess stocks of these materials. These stocks con-
stitute a potential hazard to the environment, and environmentally adequate
methods for their disposal are being sought by the United States Environmental
Protection Agency. A significant portion of the problem may be attributed to
DDT, millions of pounds of which are currently stored in military depots
throughout the United States. Conventional solid waste incineration methods
and other low-cost disposal methods do not appear to be environmentally ade-
quate because of the relative chemical stability of these types of materials
and the large amounts requiring disposal. Thus, less conventional methods
of disposal, having both high and low relative cost compared to conventional
incineration, are under study.

The rapidly accumulating evidence that a larger fraction of the omni-
present polychlorinated biphenyls (PCB) are effectively destroyed incident
to sewage sludge incineration suggests the possibility that co-incineration
of other refractory compounds with sewage sludge might provide effective
disposal. On the basis of this premise, the program was designed to demon-
strate that a modern sewage sludge incinerator, fitted with the appropriate
air pollution control devices, could be used to successfully destroy typical
organic pesticides under conditions that assure that the emissions from the
incinerator remain well within established effluent standards.

EPA selected 2,2, bis (p-chlorophenyl) 1,1,1-trichlorethane (DDT) and
2,4,5-trichlorophenoxy-acetic acid (2,4,5-T) as the primary test materials.
DDT was selected because it represented a high priority disposal problem as
a result of the ban. The cancellation of the 2,4,5-T registration was being
considered at hearings during the planning stage of this contract and there-

1

fore also appeared to represent a potentially high priority disposal problem. (The hearings have since been concluded and the 2,4,5-T registration was not cancelled).

In order to obtain the maximum amount of information the demonstration program was conducted in two phases:

Phase 1 - prototype experiments on the Envirotech Corporation

76 cm. six-hearth furnace at Brisbane, California; and

Phase 2 - full scale experiments on the Palo Alto, California

municipal multiple hearth sewage sludge incinerator.

The Phase 1 experiments were designed to test the effect on destruction of a range of variables including pesticide type, pesticide preparation (powder or solution), feed rate, location of feed mechanism, hearth temperature and afterburner temperature. The Phase 2 experiments were subsequently designed to provide a field test to verify the results of the Phase I study.

The six Phase 1 experiments utilized the following pesticide feeds:

Experiment	Pesticide Feed	Feed Ratio[*]
1	DDT powder, 75% active ingredient	2 g /100 g sludge solids
2	DDT powder, 75% active ingredient	5 g /100 g sludge solids
3	DDT in kerosene, 20% active ingredient	2 g /100 g sludge solids
4	DDT in kerosene, 20% active ingredient	5 g /100 g sludge solids
5	Weedon™ solution, 20% 2,4,5-T	2 g /100 g sludge solids
6	Weedon™ solution, 20% 2,4,5-T	5 g /100 g sludge solids

The above feed ratios were computed on the basis of the total pesticide preparation per dry sludge. The sludge contained variable

---

*All experiments were originally planned such that the feed ratios would be two and five percent. However, these varied slightly in some cases due to changes in the solids content of the sludge and the lack of precision in the feed mechanism.

solids contents on the order of 20 per cent by weight. The total feed rate of the sewage sludge was maintained at 45.4 kg/hr (100 lb/hr) in all six experiments.

For each prototype experiment, the furnace was allowed to reach steady state with the afterburner at 760 C (1400 F), pesticide feed was initiated and another hour was allowed for steady state conditions to be reestablished before sampling. One hour elapsed between the first and the second set of samples. Subsequently, the afterburner temperature was increased to 955 C (1750 F), two sample sets were taken as per the above schedule, and then the afterburner was shut down and two additional sample sets were taken at the same one hour intervals. Each set of samples included product (ash), scrubber water, sludge feed, exhaust particulates and exhaust gases.

Detailed laboratory studies were made to determine sample concentrations and injection rates of the test materials into the various effluent streams from the furnace. Since some concern had been expressed about the possible conversion of DDT to 2-2-bis(p-chlorophenyl)-1,1-dichloroethane (DDD) and 2-2-bis(p-chlorophenyl)-1,1-dichloroethylene (DDE), the analytical studies included analyses for these compounds in addition to DDT. A similar concern about the possible formation of significant amounts of tetrachlorodioxin during the combustion of 2,4,5-T, required that the 2,4,5-T samples also be analysed for the dioxin. Analyses were, in every case, carried out by standard methods and verified by the frequent interposition of standard and calibration samples.

The results of the prototype experiments allowed the following conclusions to be drawn:

1. Detectable quantities of DDD and DDE were found in the incineration system, but no trace of the dioxin was found;

3

2. The total of DDT, DDD and DDE in all of the effluent streams did not exceed 0.4 per cent of the DDT feed under any operating condition, and did not exceed 0.04 per cent of the feed with the afterburner on; destruction efficiencies for DDT were thus 99.96% or greater with the afterburner operating;

3. Destruction efficiencies for 2,4,5-T were above 99.95% at all operating conditions (even with the afterburner off) and above 99.99% in many cases with no detectable tetrachlorodioxin; and

4. Variations in feed type, pesticide feed rate and sludge solids content did not affect the results over the ranges studied for these variables.

In nearly all cases the highest pesticide losses were found in the scrubber water. Since these waters are normally recycled through the facility, tne above destruction ratios appear to be conservatively low in comparison to normal operating conditions.

In view of the results from the prototype experiments, large-scale experiments were authorized at the municipal sewage sludge incinerator in Palo Alto, California. The experiments carried out in this facility followed a program similar to that of the prototype with the exception that no attempt was made to alter the afterburner operating conditions or other normal operations at the facility. In addition, only the solid formulation of DDT was tested because the DDT/kerosene solution supplied for this experiment was judged to be unfit for use in such tests.

The full-scale experiments produced results which agreed extremely well with those from the prototype tests with the afterburner on. No dioxin was found, but both DDD and DDE were formed from DDT in the process; in many cases, the samples held higher concentrations of DDE than DDT. Destruction

4

effeciencies were 99.97% or higher for DDT (including DDD and DDE) and 99.99% or higher for 2,4,5-T. No effect of pesticide feed ratio was found over the range covered. These values, too, could be considered conservatively low, since the scrubber water is returned to the treatment facility for recycling.

To simplify comparison of the prototype and full scale experiments, the significant data are summarized in Tables A and B which follow:*

TABLE A
DDT DESTRUCTION EFFICIENCY

PROTOTYPE EXPERIMENTS						FULL SCALE EXPERIMENTS					
Preparation	Feed Hearth	Feed Ratio (gm/gm)	Avg. Hearth Temp (C°)	AB* Temp (C°)	% Dest. Eff. (%)	Preparation	Feed Hearth	Feed Ratio (gm/gm)	Avg. Hearth Temp (C°)	AB* Temp (C°)	% Dest. Eff. (%)
Solid	1st	0.02	764	733	99.98	Solid	1st	0.02	629	638	99.97
Solid	1st	0.02	754	738	99.98	Solid	1st	0.02	634	649	99.98
Solid	1st	0.02	715	900	99.98	Solid	1st	0.05	628	663	99.98
Solid	1st	0.02	738	182	99.96	Solid	1st	0.05	659	649	99.98
Solid	1st	0.05	759	733	99.995						
Solid	1st	0.05	795	716	99.997						
Solid	1st	0.05	780	800	99.998						
Solid	1st	0.05	782	221	99.66						
Solution	3rd	0.02	841	672	99.79						
Solution	3rd	0.02	827	716	—						
Solution	3rd	0.02	837	983	99.99						
Solution	3rd	0.02	842	204	99.99						
Solution	3rd	0.05	838	705	—						
Solution	3rd	0.05	841	727	99.99						
Solution	3rd	0.05	810	830	99.98						
Solution	3rd	0.05	802	182	99.99						

*A.B. - Afterburner

TABLE B
2,4,5-T DESTRUCTION EFFICIENCY

PROTOTYPE EXPERIMENTS						FULL SCALE EXPERIMENTS					
Preparation	Feed Hearth	Feed Ratio (gm/gm)	Avg. Hearth Temp (C°)	AB* Temp (C°)	% Dest. Eff. (%)	Preparation	Feed Hearth	Feed Ratio (gm/gm)	Avg. Hearth Temp (C°)	AB* Temp (C°)	% Dest. Eff. %
Solution	3rd	0.02	792	711	99.98	Solution	3rd	0.02	700	677	99.99
Solution	3rd	0.02	809	711	99.99	Solution	3rd	0.02	677	655	99.99
Solution	3rd	0.02	781	1005	99.99	Solution	3rd	0.05	691	644	99.996
Solution	3rd	0.02	749	216	99.98	Solution	3rd	0.05	698	663	99.99
Solution	3rd	0.05	774	694	99.99						
Solution	3rd	0.05	793	727	99.99						
Solution	3rd	0.05	780	1010	99.99						
Solution	3rd	0.05	784	227	---						

*A.B. - Afterburner

*The feed ratios varied slightly from the amounts shown above in some cases. The feed ratios for the solid DDT in the prototype experiments were actually .026 and .066. The feed ratios for the liquid 2,4,5-T in the full-scale experiments were actually .012 and .038.

5

Several other observations should be made regarding the full-scale experiments. A small amount of the finer particulates in the DDT powder did escape during the feeding process. Members of the research team experienced slight and temporary upper respiratory irritation, apparently from this source. This, of course, could be prevented if the powder were fed in as a prepared solution in kerosene. The test results indicate no loss of effectiveness between top hearth feed of solids and third hearth feed of kerosene solutions. The education of operating personnel would be very important to the effective use of this method in municipal facilities. The Palo Alto operating crew were uncooperative until they had been fully informed of the purposes of and the minimal hazards from the tests.

The results of this study indicate that DDT and 2,4,5-T can be safely destroyed by co-incineration with sewage sludge in a multiple hearth furnace. It appears probable that other pesticides with a similar chemical nature to DDT or 2,4,5-T could also be safely destroyed via this technique. The possible application of this co-incineration disposal method to other pesticides and other MHF installations is discussed in Section 6 of this report. The stack sampling procedures used during this study are described in detail in Appendix E.

2.0 GLOSSARY OF ABBREVIATIONS AND SYMBOLS

A.I. = active ingredient contained in preparation

DDD = dichlorodiphenyl-dichloroethane

DDE = dichlorodiphenyl-ethylene

DDT = dichlorodiphenyl-trichloroethane

2,4,5-T = 2,4,5-trichlorophenoxyacetic acid

$C_{Cl}^{-}(t)$ = chloride ion concentration at time t (gm/gm)

C_i = chloride ion concentration of make up feed (gm/gm)

C_o = chloride ion concentration at time t = o (gm/gm)

M_m = make up water input rate (gm/min)

M_t = total mass of water in the scrubber (gm)

Q = rate of injection of Cl^{-} ions due to DDT combustion (gm/min)

t_i = time at which DDT feed began

t_o = initial fire up time

7

3.0 INTRODUCTION

Pesticide use has increased explosively in recent years, resulting in greater yields and higher quality products from American agriculture. However, these pesticides have also resulted in a legacy of pollution problems in addition to these benefits. Most recently, the banning of some persistent pesticides such as DDT (dichlorodiphenyl-trichloroethane) and Herbicide Orange has focused attention on the problem of pesticide disposal. The amounts involved are large. Approximately 100 pesticide manufacturers produce some 1000 basic chemicals for use in registered commercial pesticide products, with production of these materials in 1971 estimated at 600 million kilograms (1320 million pounds). In addition, over 10 million kilograms (22 million pounds) are on hand for disposal by government agencies, including pesticides involved in regulatory actions and surplus military material. This problem has been investigated by the Federal Working Group on Pesticide Management (FWGPM) and the EPA Task Force on Excess Chemicals (TFEC).

Materials to be disposed of include the following general types:

(1) Inorganic pesticides in various forms;

(2) Organic pesticides in solid form;

(3) Organic pesticides in liquid form (solutions, slurries, suspensions, emulsions, etc.); and

(4) Organic pesticides in aerosol cans containing various propellants and other ingredients.

Organic pesticides (items 2 and 3 above) comprise the bulk of the disposal problem at this time. For these materials incineration as recommended by the TFEC is a very desirable form of disposal.

In analyzing how best to meet this requirement, Versar, in a paper to EPA, Office of Solid Waste Management Programs, used the following criteria:

(1) The disposal plan should utilize existing and available facilities, if possible, or commercially-available equipment if appropriate facilities do not exist;

8

(2)   The recommended type of facility and equipment should be capable
      of disposing of the widest possible range of pesticides provided
      product streams (to air, water, landfills, etc.) meet local
      standards and codes;

(3)   If an existing type of facility is chosen, such facilities should
      be generally available throughout the contiguous 48 states; and

(4)   If existing facilities appear to be unavailable, then the designated
      equipments must be capable of being operated successfully and within
      code in any of the contiguous 48 states.

The Versar study concluded that the most attractive general type of incinerator
for this purpose (providing high temperatures, long residence times, and
closed-cycle collection of effluent species) appears to be a rotary kiln or
a multiple-hearth furnace. Both of these are designed primarily for solid feeds
and provide mixing and turning of the charge during a relatively long residence
time. Additionally, both appear to have been used for the incineration of
pesticides. The rotary kiln, used primarily for calcining or roasting ores,
consists of a revolving tube inclined so that the material moves downward by
gravity as the hot combustion gases move through the tube (usually) counter-
current to the feed. The rotary motion stirs the solid materials and constantly
exposes new surfaces. Incineration is a relatively new, but growing, use for
rotary kilns.

Multiple hearth furnaces also provide counter-current exposure of solids
to the hot gases. Revolving rakes mix the charge and move it so that it falls
by gravity from one hearth to another. These furnaces are generally cylindrical,
and an air-cooled central shaft is revolved to provide the raking motion. This
type of furnace has been used to incinerate sewage sludge since the early 1930's.
The mixing and turning action is much more positive than that of the rotary kiln,
and semi-liquid tars, gums, etc., can be incinerated by controlled introduction
to avoid slugs which create hot spots. The rotating hearth furnace, employing
rotation of the hearth against a stationary rake, is a simpler but less effective
version of the same general technique used in the multiple hearth furnaces.

The multiple-hearth furnace incinerator appears to be the logical first
choice for an incineration system, with the rotary kiln second. The basis for
this selection was as follows:

(1) Multiple hearth systems have been used for incineration for many years, and thus would appear to be more available in a wide geographical distribution; and

(2) The more positive mixing and turning action of the multiple hearth furnace compared to the rotary kiln seems desirable.

This information, plus other investigations carried out by the TFEC, indicate that a modern design sewage sludge incinerator may have the potential to destroy organic pesticides, and thus formed the basis for the study discussed in this report.

The present program was designed to verify that a modern sewage sludge incinerator, fitted with the appropriate air pollution control devices, could be used to successfully destroy typical organic pesticides under conditions that assure that the emissions from the incinerator remain well within established effluent standards.

5.1 Experimental Design

In order to determine the applicability and safety of co-incineration as a method for disposing of refractory pesticides it was decided to conduct a study using the banned pesticide DDT and the still approved 2,4,5-T (trichlorophenoxyacetic acid) as test materials. A program was designed to determine the effect of such parameters as pesticide feed rate, pesticide form (that is, as a water wettable solid and as a normal hydrocarbon solution) and afterburner temperature. In the original program it was proposed to also examine the effects of below normal hearth temperatures, but the possible dangers of injecting large amounts of pesticide into the environment prohibited such an experiment.

In order to allow the gathering of the maximum amount of information in the least amount of time, it was further decided to conduct the parametric variation experiments on a prototype multiple hearth furnace available in the laboratories of Envirotech Corporation in Brisbane, California. Only after these prototype experiments were completed and the results evaluated would a full scale experiment be carried out.

10

The experiments at Brisbane were designed as follows:

1. Powdered DDT preparation pre-mixed in dewatered sludge to
    be fed into the top hearth. The emergent DDT to be measured
    in each effluent stream under three afterburner conditions.
    In addition, the concentration of DDT in the sludge was to
    be 2 per cent and/or 5 per cent by weight.

2. Kerosene solution of DDT mixed with sludge to be injected
    into the grease port (scum port) on the third hearth. The
    DDT emergent in each of the effluent streams was to be measured
    under three afterburner conditions. There were to be two
    separate concentrations of DDT — 2 per cent and/or 5 per cent.

3. Standard preparation of 2,4,5-T solution mixed with sludge to
    be injected into the grease port on the third hearth. The
    emergent 2,4,5-T in each effluent stream was to be measured
    under three afterburner conditions. There were to be two sep-
    arate concentrations of pesticide preparation, 2 per cent
    and/or 5 per cent.

4. In each of the above experiments sampling should be delayed
    for a sufficient length of time after initial injection to allow
    equilibrium to be established.

5. In order to insure greater accuracy and sensitivity, it was
    decided that no attempt would be made to accomplish analyses
    in the field, but that all samples would be returned to the
    laboratory where only standard methods of sample treatment and
    analysis would be used.

If the results of the prototype experiments showed successful inciner-
ation with effluent levels well below existing regulations, the experiments
would be repeated in a full scale operating multiple hearth incinerator. The
full scale experiments would be conducted in a manner similar to the prototype
experiments except that no attempt would be made to alter the normal afterburner
temperature.

4.0 PROTOTYPE EXPERIMENTS

The experiments conducted at the 76.2 cm. (30 in.) diameter pilot multiple hearth furnace at Envirotech Corporation in Brisbane, California, were designed to discover the effects of such variables as the formulation of the test compound, method of feed, feed ratio and afterburner conditions on the effectiveness of the destruction of the two representative pesticides (DDT and 2,4,5-T). The tests were divided into six separate experiments, each conducted with a specified pesticide, specified formulation and feed method and a specified feed ratio. Each experiment involved sampling at each of three temperature conditions of the afterburner --- normal temperature of 760 C (1400F), highest attainable temperature 955 C (1750 F) and with the afterburner off. In all experiments the sludge feed rate was maintained at 45.4 kg/hr (100 lb/hr) throughout the experiment.

4.1 Experiments

Experiment A:

Dry DDT preparation (75 per cent active ingredient) mixed with sludge feed in the ratio of 2 grams preparation per 100 grams of the sludge and fed to the top hearth by screw pump.

Test 1 & 2   Taken with afterburner at 760 C (1400 F)

Test 3   Taken with afterburner at 955 C (1750 F)

Test 4   Taken with afterburner off

Experiment B:

Dry DDT preparation (75 per cent active ingredient) mixed with sludge feed in the ratio of 5 grams preparation per 100 grams of the sludge and fed to the top hearth by screw pump.

Test 5 & 6   Taken with afterburner at 760 C (1400 F)

12

Test 7   Taken with afterburner at 955 C (1750 F)

Test 8   Taken with afterburner off

Experiment C:

DDT in kerosene solution (20 per cent active ingredient) mixed with sludge feed at third hearth in the ratio of 2 grams preparation per 100 grams sludge.

Test 9 & 10   Taken with afterburner at 760 C (1400 F)

Test 11   Taken with afterburner at 955 C (1750 F)

Test 12   Taken with afterburner off

Experiment D:

DDT in kerosene solution (20 per cent active ingredient) mixed with sludge feed at third hearth in the ratio of 5 grams preparation per 100 grams sludge.

Test 13 & 14 Taken with afterburner at 760 C (1400 F)

Test 15   Taken with afterburner at 955 C (1750 F)

Test 16   Taken with afterburner off

Experiment E:

2,4,5-T in polyalcohol solution (20 per cent active ingredient) mixed with sludge feed at third hearth in the ratio of 2 grams preparation per 100 grams sludge.

Test 17 & 18 Taken with afterburner at 760 C (1440 F)

Test 19   Taken with afterburner at 955 C (1750 F)

Test 20   Taken with afterburner off

Experiment F:

2,4,5-T in polyalcohol solution (20 per cent active ingredient) mixed with sludge feed at third hearth in the ratio of 5 grams preparation per 100 grams sludge.

Test 21 & 22 Taken with afterburner at 760 C (1400 F)

Test 23   Taken with afterburner at 955 C (1750 F)

Test 24   Taken with afterburner off

13

As indicated above, all feed ratios were to have been .02 and .05. However, due to changes in the solids content these varied slightly in some cases. The feed ratios in the solid DDT experiments (A and B) were actually .026 and .066 rather than .02 and .05.

4.2 Prototype Furnace Operations

A schematic diagram of the Envirotech Corporation prototype 76.2 cm. (30 in.) multiple hearth furnace shown in Figure 1 represents the normal configuration of the system. For the purposes of this series of experiments, the cyclone was by-passed and the scrubber was arranged for closed circuit operation by the addition of a reservoir approximately 1.22 m x 0.91 m x 0.91 m (4 ft x 3 ft x 3 ft) fitted with a surface closure and an access port to allow periodic sampling. The major purpose of recycling the scrubber water was to minimize escape of unburned pesticide to the environment; however, it also provided samples for a chloride production analysis.

Provisions were made to allow a continuous measurement of the individual hearth temperatures, the afterburner and exhaust temperatures and the oxygen and carbon dioxide content of the emergent gas stream. Provisions were also made to collect the product (ash) and to impound the scrubber water pending the outcome of the analyses.

Tables 1 through 6 contain discrete hourly temperature and gas analysis data taken during each experiment. These tables also show the time intervals during which the pesticide feed was continued and also those time intervals during which sampling was carried out. In the interests of the widest possible utilization of the data within this report, Tables 1-A through 6-A are repetitious of the corresponding Tables 1 through 6 except that the hearth temperatures are given in degrees Fahrenheit — this seems appropriate since most current instrumentation in the field is calibrated in English units. In addition, these tables indicate that sampling was delayed for one hour after initial injection of the pesticide in order to allow equilibrium residence time of the order of 45 minutes.

The combustion conditions within the furnace can be inferred by measurement of the composition of the emergent exhaust gases. In the studies conducted at the prototype furnace at Brisbane, it has been found that under conditions wherein the O_2 content of the stack gases is greater than several per cent and the CO content very low (not detectable in the experiments reported herein). The conditions are such as to indicate excess air as per the following discussion.

15
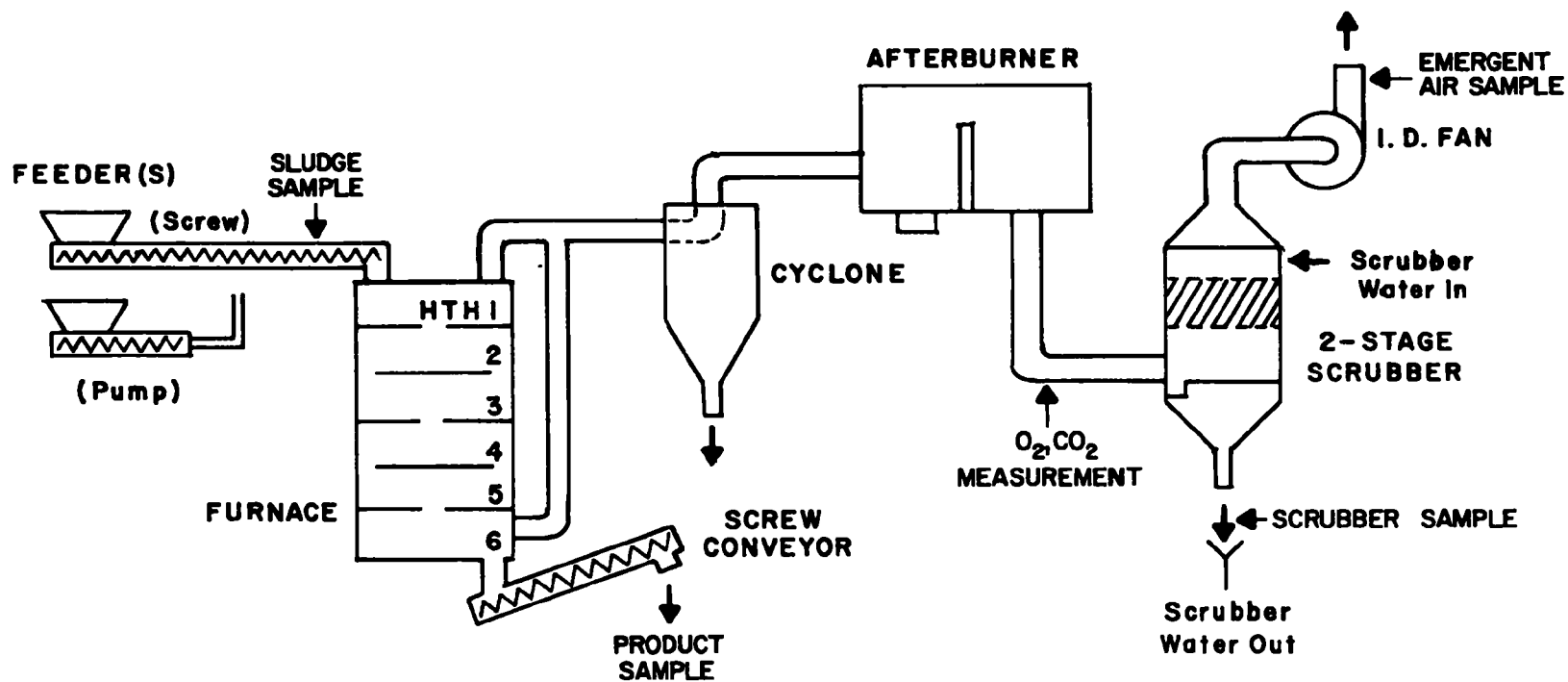
FIGURE I

30" I.D. x 6 HTH PILOT FURNACE SYSTEM

Table I
FURNACE CONDITIONS - 2% DDT SOLID EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Temperature (°C)						A.B.* (°C)	Stack (°C)	Stack Gas Analysis			Sample
		T_1	T_2	T_3	T_4	T_5	T_6			$\%O_2$	$\%CO_2$	$\%N_2$	
Sludge only	1050	549	805	838	861	894	861	494	93				
"	1230	405	633	872	894	905	861	738	99				
"	1320	394	738	850	838	872	827	738	99	13.5	5	81.5	
"	1430	271	572	672	838	872	827	827	121				
"	1555	127	527	872	872	905	894	538	99				
"	1650	383	771	861	861	872	872	661	93				
Sludge & DDT	1705	433	783	872	872	872	872	722	93				
"	1730	349	733	866	894	872	872	733	96	15	2.3	82.7	#1
"	1830	316	761	838	861	894	872	772	116				
"	1930	405	705	838	872	872	866	705	93	14	4.0	82.0	
"	2010	483	749	827	838	883	872	749	93				
"	2100	471	744	827	844	861	883	705	93				
"	2150	394	777	816	827	838	872	738	93	15.2	2.1	82.7	#2
"	2230	405	683	816	850	861	883	716	93				
"	2300	260	677	794	838	838	883	894	116	13.4	1.6	85	#3
"	2400	338	694	827	861	861	861	905	110	18.5	1.5	81	
"	0040	366	688	805	827	850	894	182	63	20	0.6	79.4	#4

Notes:
a. Entire run plagued by clogging of #1 drop hole.
b. Sludge feed @ rate of 45 kg/hr (100 lb/hr).
c. DDT (solid) feed @ rate of 0.91 kg/hr (2 lb/hr) began @ 1705.
d. Sludge/DDT fed to hearth #1.
* A.B. = Afterburner

17

Table 2
FURNACE CONDITIONS - 5% DDT SOLID EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Temperatures (°C)						A.B.* (°C)	Stack (°C)	Stack Gas Analysis			Sample
		T_1	T_2	T_3	T_4	T_5	T_6			%O_2	%CO_2	%N_2	
Sludge	0900	538	761	816	888	894	838	683	93				
"	1000	427	761	838	894	900	850	705	99				
"	1030	427	711	827	883	894	850	683	105				
"	1100	515	761	794	883	894	872	683	105				
"	1130	583	738	788	894	905	877	699	105				
"	1200	560	738	772	888	916	866	711	349				
"	1220	583	749	794	888	916	861	716	405				
"	1240	405	761	833	894	916	866	716	93				
"	1340	371	772	850	894	905	872	733	99				
Sludge & DDT	1400	394	755	850	883	894	872	716	93	13.5	2.0	84.5	
"	1430	327	761	850	872	883	866	716	93				
"	1515	338	738	855	872	894	866	727	93				
"	1600	271	705	905	905	894	872	733	93	13.5	1.9	84.6	5
"	1630	316	705	905	900	894	861	716	93				
"	1645	399	761	927	905	905	872	716	93	13.0	1.8	85.2	6
"	1715	366	749	927	900	894	866	705	93				
"	1800	416	705	905	888	900	866	800	93	10.5	1.9	87.6	7
"	1830	427	772	905	883	872	827	794	93				
"	1900	427	738	905	872	872	877	221	71	14.5	1.3	84.2	8

Notes:
a. Sludge feed began 0900 - completed 1900@rate of 45 kg/hr (100 lb/hr).
b. DDT (solid) feed @rate of 2.25 kg/hr (5 lb/hr) began @ 1400 discontinued @ 1900.
c. Brief shut-down @ 1045 - 1200 to fix rake arm # 3 hearth.
d. Sludge/DDT fed to hearth #1.
* A.B. = Afterburner

18

Table 3
FURNACE CONDITIONS - 2% DDT SOLUTION EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Temperature (°C)						A.B.* (°C)	Stack (°C)	Stack Gas Analysis			Sample
		T_1	T_2	T_3	T_4	T_5	T_6			$\%O_2$	$\%CO_2$	$\%N_2$	
Sludge	1140	727	716	622	761	872	865	143	38	10.5	4	85.5	
"	1415	733	772	516	865	894	872	483	60				
Sludge & DDT	1500	727	772	583	872	883	865	666	105				
"	1530	772	816	722	916	950	844	661	93	13.5	5	81.5	
"	1600	783	833	699	916	939	883	672	93	13.0	5	82.0	9
"	1630	777	833	694	905	916	883	716	93				
"	1700	760	794	649	888	894	871	716	93	19	3	78	
"	1715	783	821	677	916	894	871	716	93	13	3	84	10
"	1800	772	827	694	894	916	871	727	93	11	4	85	
"	1830	772	855	716	727	905	866	738	93				
"	1850	783	855	683	916	911	871	983	99	10.5	1.5	88	11
"	1925	772	850	705	905	905	871	850	93				
Sludge Only	1950	794	833	722	905	905	866	427	99				
"	2040	783	850	738	916	900	866	204	71	10.5	1.5	88	12

Note:

a. Sludge feed began 1140 @ rate of 45 kg/hr (100 lb/hr), discontinued @ 2020. Fed on third hearth.
b. 2% DDT solution feed @ rate of 0.91 kg/hr (2 lb/hr) of preparation began @ 1515 on third hearth - feed discontinued @ 1950.
c. Several minor leaks developed in the DDT feed line.
d. Sludge/DDT fed to hearth #3.
* A.B. = Afterburner

Table 4
FURNACE CONDITIONS - 5% DDT SOLUTION EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	T1	T2	T3	T4	T5	T6	A.B.* (°C)	Stack (°C)	Stack Gas Analysis %O2	%CO2	%N2	Sample
Sludge Only	1115	772	805	638	888	894	872	705	93				
Sludge & DDT	1200	772	805	638	888	900	883	716	93				
"	1230	777	833	672	894	916	8/2	711	93				
"	1300	816	861	699	649	671	694	705	93				
"	1320	783	838	738	894	883	883	722	93	12.5	6.1	81.4	
"	1345	761	838	761	894	883	872	722	93	10.5	4.0	85.5	
"	1400	749	838	738	900	883	872	705	93				
"	1415	755	844	761	905	888	872	705	93				13
"	1435	749	844	788	916	872	883	727	93	13.5	5	81.5	
"	1500	749	858	783	894	883	883	727	93				
"	1525	755	850	794	894	883	872	727	93				14
"	1540	749	844	761	894	888	883	727	93				
"	1600	722	816	722	900	900	872	805	93	13	5	82	
"	1635	716	805	672	894	900	872	805	104				15
"	1640	716	800	649	888	894	888	838	516**				
"	1700	705	805	694	872	894	883	316	116	19	1	80	
"	1730	705	794	672	850	894	888	205	82				
"	1750	711	788	672	861	888	894	182	71				16
"	1830	705	772	649	850	894	888	171	60				

Notes:
a. Sludge feed @ rate of 45 kg/hr (100 lb/hr) began @ 1115, discontinued @ 1800. Fed on third hearth.
b. DDT feed @ rate of 2.25 kg/hr (5 lb/hr) of solution began @ 1200, discontinued 1725. Fed on third hearth.
c. Scrubber feed pump lost @ 1630 - replaced 1650.
d. A series of hearth bed temperatures vs nominal temperatures gave the following results:

Hearth	Bed	Nominal
6	677 °C	882 °C
5	860 °C	893 °C
4	849 °C	893 °C
3	449 °C	804 °C

* A.B. = Afterburner
** Scrubber water level control failed - immediately replaced

Table 5
FURNACE CONDITIONS - 2, 4, 5-T 2% SOLUTION EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Temperatures (°C)						A.B.* (°C)	Stack (°C)	Stack Gas Analysis			Sample
		T_1	T_2	T_3	T_4	T_5	T_6			%O_2	%CO_2	%N_2	
Sludge	1100	788	783	683	816	933	861	583	99				
Sludge & Solvent	1130	850	794	716	816	888	850	705	116				
Sludge & 2,4,5-T	1200	761	738	632	805	894	872	683	93				
"	1300	766	816	694	838	872	872	694	88	16.0	3.5	80.5	
"	1400	755	777	694	844	888	872	705	93	16.5	2.0	81.5	
"	1430	761	794	572	844	911	872	711	77				17
"	1500	761	805	644	844	894	816	711	88	15.0	115	83.5	18
"	1530	761	822	583	850	900	872	738	93				
"	1600	749	761	588	816	872	872	861	99	14	4	82.0	
"	1625	749	772	572	816	883	894	1005	96				19
"	1640	749	772	572	805	888	894	1061	105				
"	1700	705	761	538	827	872	872	216	60	13	6	81.0	
Sludge	1730	705	727	538	788	844	894	216	60				20
Shut Down	1800	705	783	588	805	861	316	193	60				

Notes:
a. Sludge feed @ rate of 45 kg/hr (100 lb/hr) began @ 1100, discontinued @ 1725. Fed on third hearth.
b. Solvent only injection @ rate of 0.91 kg/hr (2 lb/hr) began @ 1130, discontinued @ 1200. Fed on third hearth.
c. 2,4,5-T Solution injection @ rate of 0.91 kg/hr (2 lb/hr) began @ 1200, discontinued @ 1735. Fed on third hearth.
* A.B. = Afterburner

Table 6
FURNACE CONDITIONS - 2, 4, 5-T 5% SOLUTION EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Conditions (°C)						A.B.* (°C)	Stack (°C)	Stack Gas Analysis			
		T_1	T_2	T_3	T_4	T_5	T_6			$\%O_2$	$\%CO_2$	$\%N_2$	
Sludge Feed	1110	638	733	672	761	872	872	143	49				
Sludge & Solvent	1130	705	761	594	805	872	872	594	77				
Sludge & 2,4,5-T	1145	711	761	594	838	916	872	661	93				
"	1230	733	783	594	811	872	872	733	93				
"	1330	727	783	555	827	872	883	694	93				
"	1430	716	777	577	827	872	872	694	82	16	2	82	21
"	1510	727	794	605	827	877	861	705	93				
"	1530	738	772	616	833	872	872	705	88	16	2	82	
'	1555	749	783	627	855	872	872	727	88				22
"	1615	761	816	661	872	883	872	972	88				
"	1630	747	761	638	838	872	872	1010	88	14	4.5	81.5	
"	1655	749	782	588	816	872	872	788	93				23
"	1700	749	782	599	816	872	872	761	93				
"	1735	749	772	622	816	872	872	227	71				24
Sludge	1800	983	772	616	816	872	872	205	49	17	1	82	

Notes:
a. Sludge feed @ rate of 45 kg/hr (100 lb/hr) began @ 1110, discontinued @ 1750. Fed on third hearth.
b. Solvent only injection @ rate of 2.25 kg/hr (5 lb/hr) began @ 1130, discontinued @ 1145. Fed on third hearth.
c. 2,4,5-T solution feed @ rate of 2.25 kg/hr (5 lb/hr) began @ 1145, discontinued @ 1735. Fed on third hearth.
* A.B. = Afterburner

Table I -A
FURNACE CONDITIONS - 2% DDT SOLID EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Temperature ($^\circ$F)						A.B.* ($^\circ$F)	Stack ($^\circ$F)	Stack Gas Analysis			Sample
		T_1	T_2	T_3	T_4	T_5	T_6			%O_2	%CO_2	%N_2	
Sludge only	1050	1020	1480	1540	1580	1640	1580	920	200				
"	1230	760	1460	1600	1640	1660	1580	1360	210				
"	1320	740	1360	1560	1540	1600	1520	1360	210	13.5	5	81.5	
"	1430	520	1060	1240	1540	1600	1520	1520	250				
"	1555	260	980	1600	1600	1660	1640	1000	210				
"	1650	720	1420	1580	1580	1600	1600	1220	200				
Sludge & DDT	1705	810	1440	1600	1600	1600	1620	1330	200				
"	1730	660	1350	1590	1640	1600	1600	1350	205	15	2.3	82.7	#1
"	1830	600	1400	1540	1580	1640	1600	1420	240				
"	1930	760	1300	1540	1600	1600	1590	1300	200	14	4.0	82.0	
"	2010	900	1380	1520	1540	1620	1600	1380	200				
"	2100	880	1370	1520	1550	1580	1620	1300	200				
"	2150	740	1430	1500	1520	1540	1600	1360	200	15.2	2.1	82.7	#2
"	2230	760	1260	1500	1560	1580	1620	1320	200				
"	2300	500	1250	1460	1540	1540	1620	1640	240	13.4	1.6	85	#3
"	2400	640	1280	1520	1580	1580	1580	1660	230	18.5	1.5	81	
"	0040	690	1270	1480	1520	1560	1640	360	145	20'	0.6	79.4	#4

Notes:
a. Entire run plagued by clogging of #1 drop hole.
b. Sludge feed @ rate of 45 kg/hr (100 lb/hr).
c. DDT (solid) feed @ rate of 0.91 kg/hr (2 lb/hr) began @ 1705.
d. Sludge/DDT fed to hearth #1.
* A.B. = Afterburner

Table 2-A
FURNACE CONDITIONS-5% DDT SOLID EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Temperatures (°F)						A.B.* (°F)	Stack (°F)	Stack Gas Analysis			Sample
		T_1	T_2	T_3	T_4	T_5	T_6			%O_2	%CO_2	%N_2	
Sludge	0900	1000	1400	1500	1630	1640	1540	1260	200				
"	1000	800	1400	1540	1640	1650	1560	1300	210				
"	1030	800	1310	1520	1620	1640	1560	1260	220				
"	1100	960	1400	1460	1620	1640	1600	1260	220				
"	1130	1080	1360	1450	1640	1660	1610	1290	220				
"	1200	1040	1360	1420	1630	1680	1590	1310	660				
"	1220	1080	1380	1460	1630	1680	1580	1320	760				
"	1240	760	1400	1530	1640	1680	1590	1320	200				
"	1340	700	1420	1560	1640	1660	1600	1350	210				
Sludge & DDT	1400	740	1390	1560	1620	1640	1600	1320	200	13.5	2.0	84.5	
"	1430	620	1400	1560	1600	1620	1590	1320	200				
"	1515	640	1360	1570	1600	1640	1590	1340	200				
"	1600	520	1300	1660	1660	1640	1600	1350	200	13.5	1.9	84.6	5
"	1630	600	1300	1660	1650	1640	1580	1320	200				
"	1645	750	1400	1700	1660	1660	1600	1320	200	13.0	1.8	85.2	6
"	1715	690	1380	1700	1650	1640	1590	1300	200				
"	1800	780	1300	1660	1630	1650	1590	1470	200	10.5	1.9	87.6	7
"	1830	800	1420	1660	1620	1600	1520	1430	200				
"	1900	800	1360	1660	1600	1600	1610	430	160	14.5	1.3	84.2	8

Notes:
a. Sludge feed began 0900 - completed 1900 @ rate of 45 kg/hr (100 lb/hr).
b. DDT (solid) feed @ rate of 2.25 kg/ hr (5 lb/hr) began @ 1400 discontinued @ 1900.
c. Brief shut-down @ 1045 - 1200 to fix rake arm #3 hearth.
d. Sludge/DDT fed to hearth # 1.

* A.B. = Afterburner

24

Table 3-A
FURNACE CONDITIONS-2% DDT SOLUTION EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Temperature (°F)						A.B.* (°F)	Stack (°F)	Stack Gas Analysis			Sample
		T_1	T_2	T_3	T_4	T_5	T_6			$\%O_2$	$\%CO_2$	$\%N_2$	
Sludge	1140	1340	1320	1150	1400	1600	1560	290	100	10.5	4	85.5	
"	1415	1350	1420	960	1560	1640	1600	900	140				
Sludge & DDT	1500	1340	1420	1080	1600	1620	1560	1230	220				
"	1530	1420	1500	1330	1680	1740	1550	1220	200	13.5	5	81.5	
"	1600	1440	1530	1290	1680	1720	1620	1240	200	13.0	5	82.0	9
"	1630	1430	1530	1280	1660	1680	1620	1320	200				
"	1700	1400	1460	1200	1630	1640	1600	1320	200	19	3	78	
"	1715	1440	1480	1250	1680	1640	1600	1320	200	13	3	84	10
"	1800	1420	1520	1280	1640	1680	1600	1340	200	11	4	85	
"	1830	1420	1570	1320	1630	1660	1590	1360	200				
"	1850	1440	1570	1260	1680	1670	1600	1800	210	10.5	1.5	88	11
"	1925	1420	1560	1300	1660	1660	1600	1560	200				
Sludge Only	1950	1460	1530	1330	1660	1660	1590	800	210				
	2040	1440	1560	1360	1680	1650	1590	400	160	10.5	1.5	88	12

Notes:
a. Sludge feed begun 1140 @ rate of 45 kg/hr (100 lb/hr), discontinued @ 2020. Fed on third hearth.
b. 2% DDT solution feed @ rate of 0.91 kg/hr (2 lb/hr) of preparation began @ 1515 on third hearth – feed discontinued @1950.
c. Several minor leaks developed in the DDT feed line.
d. Sludge/DDT fed to hearth #3.
* A.B. = Afteburner

Table 4-A
FURNACE CONDITIONS-5% DDT SOLUTION EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Temperatures (°F)						A.B.* (°F)	Stack (°F)	Stack Gas Analysis			Sample
		T_1	T_2	T_3	T_4	T_5	T_6			%O_2	%CO_2	%N_2	
Sludge Only	1115	1420	1480	1180	1630	1640	1600	1300	200				
Sludge & DDT	1200	1420	1480	1180	1630	1650	1620	1320	200				
"	1230	1430	1530	1240	1640	1680	1600	1310	200				
"	1300	1500	1580	1290	1200	1240	1280	1300	200				
"	1320	1440	1540	1360	1640	1620	1620	1330	200	12.5	6.1	81.4	
"	1345	1400	1540	1400	1640	1620	1600	1330	200	10.5	4.0	85.5	
"	1400	1380	1540	1360	1650	1620	1600	1300	200				
"	1415	1390	1550	1400	1660	1630	1600	1300	200				437-13
"	1435	1380	1550	1450	1680	1600	1620	1340	200	13.5	5	81.5	
"	1500	1380	1575	1440	1640	1620	1620	1340	200				
"	1525	1390	1560	1460	1640	1620	1600	1340	200				437-14
"	1540	1380	1550	1400	1640	1630	1620	1340	200				
"	1600	1330	1500	1330	1650	1650	1600	1480	200	13	5	82	
"	1635	1320	1480	1240	1640	1650	1600	1480	220				437-15
"	1640	1320	1470	1200	1630	1640	1630	1540	960**				
"	1700	1300	1480	1280	1600	1640	1620	600	240	19	1	80	
"	1730	1300	1460	1240	1560	1640	1630	400	180				
"	1750	1310	1450	1240	1580	1630	1640	360	160				437-16
	1830	1300	1420	1200	1560	1640	1630	340	140				

Notes:
a. Sludge feed @ rate of 45 kg/hr (100 lb/hr) began @ 1115, discontinued @ 1800. Fed on third hearth.
b. DDT feed @ rate of 2.25 kg/hr (5 lb/hr) of solution began @ 1200, discontinued 1725. Fed on third hearth.
c. Scrubber feed pump lost @ 1630 - replaced 1650.
d. A series of hearth bed temperatures vs nominal temperatures gave the following results.

Hearth	Bed	Nominal
6	1250° F	1620° F
5	1580°F	1640° F
4	1560°F	1640° F
3	840°F	1480° F

* A.B. = Afterburner
** Scrubber water level control failed - immediately replaced.

Table 5-A
FURNACE CONDITIONS - 2, 4, 5-T 2% SOLUTION EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Temperatures (°F)						A.B* (°F)	Stack (°F)	Stack Gas Analysis			Sample
		T_1	T_2	T_3	T_4	T_5	T_6			$\%O_2$	$\%CO_2$	$\%N_2$	
Sludge	1100	1450	1440	1260	1500	1710	1580	1080	210				
Sludge & Solvent	1130	1560	1460	1320	1500	1630	1560	1300	240				
Sludge & 2,4,5-T	1200	1400	1360	1170	1480	1640	1600	1260	200				
"	1300	1410	1500	1280	1540	1600	1600	1280	190	16.0	3.5	80.5	
"	1400	1390	1430	1280	1550	1630	1600	1300	200	16.5	2.0	81.5	
"	1430	1400	1460	1060	1550	1670	1600	1310	170				17
"	1500	1400	1480	1190	1550	1640	1500	1310	190	15.0	115	83.5	18
"	1530	1400	1510	1080	1560	1650	1600	1360	200				
"	1600	1380	1400	1090	1500	1600	1600	1580	210	14	4	82.0	
"	1625	1380	1420	1060	1500	1620	1640	1840	205				19
"	1640	1380	1420	1060	1480	1630	1640	1940	220				
"	1700	1300	1400	1000	1520	1600	1600	420	140	13	6	81.0	
Sludge	1730	1300	1340	1000	1450	1550	1640	420	140				20
Shut down	1800	1300	1440	1090	1480	1580	1600	380	140				

Notes:
a. Sludge feed @ rate of 45 kg/hr (100 lb/hr) began @ 1100, discontinued @ 1725. Fed on third hearth.
b. Solvent only injection @ rate of 0.91 kg/hr (2 lb/hr) began at 1130, discontinued @ 1200. Fed on third hearth.
c. 2,4,5-T Solution injection @ rate of 0.91 kg/hr (2#/hr) began @ 1200, discontinued @ 1735. Fed on third hearth.

Table 6-A
FURNACE CONDITIONS - 2, 4, 5-T 5% SOLUTION EXPERIMENT
PROTOTYPE FURNACE

Feed	Time	Hearth Conditions (°F)						A.B.* (°F)	Stack (°F)	Stack Gas Analysis			Sample
		T_1	T_2	T_3	T_4	T_5	T_6			%O$_2$	%CO$_2$	%N$_2$	
Sludge Feed	1110	1180	1350	1240	1400	1600	1600	290	120				
Sludge & Solvent	1130	1300	1400	1100	1480	1600	1600	1100	170				
Sludge & 2,4,5-T	1145	1310	1400	1100	1540	1680	1600	1220	200				
"	1230	1350	1440	1100	1490	1600	1600	1350	200				
"	1330	1340	1440	1030	1520	1600	1620	1280	200				
"	1430	1320	1430	1070	1520	1600	1600	1280	180	16	2	82	21
"	1510	1340	1460	1120	1520	1610	1580	1300	200				
"	1530	1360	1420	1140	1530	1600	1600	1300	190	16	2	82	
"	1555	1380	1440	1160	1570	1600	1600	1310	190				22
"	1615	1400	1500	1220	1600	1620	1600	1780	190				
"	1630	1375	1400	1180	1540	1600	1600	1850	190	14	4.5	81.5	
"	1655	1380	1440	1090	1500	1600	1600	1450	200				23
"	1700	1380	1440	1110	1500	1600	1600	1400	200				
"	1735	1380	1420	1150	1500	1600	1600	440	160				24
Sludge	1800	1340	1420	1140	1500	1600	1600	400	120	17	1	82	

Notes:
a. Sludge feed @ rate of 45 kg/hr (100 lb/hr) began @ 1110, discontinued @ 1750. Fed on third hearth.
b. Solvent only injection @ rate of 2.25 kg/hr(5 lb/hr) began @ 1130, discontinued @ 1145. Fed on third hearth.
c. 2,4,5-T solution feed @ rate of 2.25 kg/hr (5 lb/hr) began @ 1145, discontinued @ 1735. Fed on third hearth.
* A.B. = Afterburner

28

As a typical experiment involving the prototype furnace at Brisbane, consider the 5 per cent solid DDT burn. The furnace and emergent air stream analysis are given in Table 2(2A) along with the total run time of 10 hours. During this experiment producer gas was consumed at an average rate of 4.4 m^3/min (155 ft^3/min) [total gas consumption of 2.65 x 10^3 m^3 (9.36 x 10^4 ft^3) in an elapsed time of 600 minutes]. At the same time, the dry sludge input rate of 151 gms/min (dry weight) was maintained. If it is assumed that the sludge contains approximately 20 per cent carbon as the most significant combustible (the hydrogenous components would produce water which is removed by the scrubber) contained within the sludge, and further,that the producer gas contains 60 per cent nitrogen, then it is possible to compute the level of oxygen excess in the system during this experiment. The flue gas analysis, from Table 2, is:

$$CO_2 = 1.78\%$$
$$O_2 = 13\ \%$$
$$N_2 = 85.22\%$$

computed and measured on a dry basis. Following Baumeister[1], to totally combust 4.4 m^3 of producer gas requires the consumption of 4.4 x 0.198 = 0.87 m^3 O_2 and produces 4.4 x 0.31 = 1.36 m^3 CO_2 in the process. Thus, taking the volumetric composition of air to be 21 per cent O_2, this requires 4.14 m^3/min of air for total combustion of the input producer gas.

From the data given above, the carbon input from sludge is 28 gm/min which, for complete combustion requires, according to the relation:

$$C + O_2 \rightarrow CO_2$$
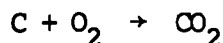
74 gms O_2/min which then requires a volume (STP) of O_2 on the order of 1.85 m^3/min and which produces 1.87 m^3/min of CO_2. The air input for sludge decomposition is then 1.87/0.21 = 8.90 m^3/min.

Thus, the total air input required is:

8.90 + 4.14 = 13.04 m^3/min

The total CO_2 produced is 1.36 x 1.87 = 3.23 m^3/min.

From the N_2 in stack gas we may compute the total input N_2 from all sources as 35.2 m^3/min x 0.85 = 29.92 m^3/min which is derived partially from the input air (79 per cent N_2) and from the producer gas (60 per cent N_2) as follows:

N_2 producer gas = 4.4 x 0.6 = 2.64 m^3/min

N_2 from input air = 29.92 − 2.64 = 27.28 m^3/min

Input air volume rate = $\frac{27.28}{.79}$ = 34.53 m^3/min

To compute the expected O_2 content of the emergent gases, the total O_2 input = 34.53 x .21 = 7.25 m^3/min of which 0.87 + 1.85 = 2.72 m^3/min is consumed. Hence residual O_2 in emergent stack gases should be 4.53 m^3/min which suggests an O_2 concentration on the order of 13 per cent. On the other hand, the total CO_2 produced by the assumed model is 1.87 + 1.36 = 3.23 m^3/min which should correspond to a concentration in the emergent stream on the order of 9 per cent. Several points may be made dealing with the discrepancy between the computed CO_2 concentration in the exhaust gases and the actual measured values as given in Table 2(2A).

If we add the nitrogen volume rate (29.92 m^3/min) plus the expected O_2 volume rate (4.53 m^3/min) and the CO_2 generation rate (3.23 m^3/min), the total is 37.66 m^3/min which is to be compared to the measured 35.2 m^3/min. It is interesting to note that if the difference of 2.46 m^3/min were assumed to be due to the absorption of CO_2 in the scrubber, then there remains 0.77 m^3/min CO_2 in the stack gases. This corresponds to a level of 2 per cent CO_2 which compares favorably to the measured levels as shown in Table 2(2A).

The average scrubber water temperature was on the order of 50 C (122 F) and the average scrubber flow rate on the order of 150 l/min (40 gal/min) so that, in order to absorb 2.46 m^3/min CO_2 which is 147 gm CO_2/min, it is necessary that the solubility of CO_2 in water at 50 C be on the order of 0.98 gms/liter or 9.8 x 10^{-4} gm/ml ~ 9.8 x 10^{-4} gms/gm. From the table values (Reference 2), the solubility of CO_2 in water at 50 C is given as 7.61 x 10^{-4} gms/gm which compares favorably with the computed value above.

In view of the discussion above and the fact that the CO_2/O_2 ratio in all the reported experiments is of the same order, one is safe in concluding that the combustion conditions are in fact such that excess air is present in the system.

4.2.1 Pesticides; Sources and Analysis

For the purposes of these experiments, a wettable DDT powder preparation containing 75 per cent active ingredient was supplied by the Army Material Command from the Sierra Base Depot in northern California. In addition, a solution of 20 per cent DDT in kerosene was also supplied by the Army. Laboratory analyses of both these preparations indicated that the labeled concentrations were correct and further that the active ingredient was an exceptionally pure DDT (ratio of o-p' DDT to p-p' DDT ≈ 1 to 4) with no trace of such decomposition products as DDD (dichlorodiphenyl-dichloroethane) or DDE (dichlorodiphenyl-ethylene).

The 2,4,5-T was only available as a solution containing 20 per cent active ingredient. The preparation used in these experiments was a commercial weed killer known as Weedon^{TM}, which is available through commercial channels. Analysis of the material used indicated very low (below detection limits) levels of tetrachlorodioxin and further that the concentration of 2,4,5-T was correctly given by the manufacturer.

4.2.2 Pesticide Mixing and Feed

In those experiments where the wettable powder preparation was used, mixing was accomplished by adding the appropriate amount of the preparation to a 207.9 liter (55 gallon) drum of sludge. Mixing was accomplished using a slow speed paddle arrangement. The mixing operations were carried out within a plastic glove bag to avoid contamination of the area. The mixed sludge-pesticide was introduced into a vibrator hopper which in turn fed a screw pump. The resulting mixture was then introduced into the top hearth.

The solution feed was accomplished by metering the test solution into a 5.1 cm. (2 in.) feedline with the sludge. The mixed sludge-pesticide was then introduced into the third hearth. In these experiments the upper two hearths served as additional afterburners.

In all the experiments conducted at the prototype furnace, the sludge feed was regulated at 45.4 kg/hour (100 lbs/hour) — a rate fixed by the size of the inter-hearth drop holes within the prototype furnace.

31

4.3   Gas Stream Sampling

The emergent gas stream was sampled at the output of the scrubber
(Figure 1) using the standard EPA Method 5 for air stream particulates (Appendix A
& E. The physical layout of the stack was such that it was not possible to con-
duct separate traverses of the stack along perpendicular paths so a single
traverse was conducted for each run. The heated probe (at 95 C or 203 F) was
inserted into the 7.6 cm. (3.0 in.) sampling port (see Figure 1 for location
of port) at the beginning of each sampling run. The collected sample was passed
through the 0.45 micron filter prior to its introduction into the bubbler
as shown in the schematic Figure 2. For DDT (and its combustion products) the
first two impinger tubes contained 100 ml spectro grade hexane each; for the
2,4,5-T, the first two impingers contained 100 ml ethylene glycol each. The
third impinger was empty while the fourth contained 150 grams Dryrite^{TM} — the
whole train being maintained at ice temperatures.

Isokinetic sampling was accomplished by first calibrating the S
Pitot tube in the probe against a calibrated Dwyer Pitot tube with a slant guage
manometer. Adjustments were made in the pumping speed as needed to compensate
for variation in air stream velocity during a sampling run or when the sampling
probe was moved during a traverse. Each traverse was conducted so as to collect
approximately 0.15 m^3 at each of four sampling points per traverse.

At the completion of each sampling run, the probe and the connected
sampling train assembly were removed from the stack, taken to a clean room and
the samples removed. In the case of DDT sampling, the filter, along with the
hexane rinsings of the probe, cyclone and associated fittings were combined into
the particulate sample. The hexane impinger samples were combined with the
hexane rinsings of the first two impingers and their connecting fitting to
form the impinger sample. The same procedure was used for the 2,4,5-T samples,
except that ethylene glycol was used in the rinsing.

After each run, the sampling train, probe and associated glassware
were washed in hot detergent solution, rinsed with distilled water, rinsed with
de-ionized water, dried with anhydrous ethyl alcohol and finally rinsed with
spectro grade hexane.

33

STACK
WALL

20

1

19

17

2

3

4

5   5   5   5

6   7

8

16

6   6

11

9

10

14

15

12

13

18

17

21

1) PROBE
2) CYCLONE
3) FLASK
4) PARTICULATE FILTER
5) IMPINGERS (Greenbug-
      Smith)
6) THERMOMETER
7) CHECK VALVE
8) UMBILICAL CORD
9) VACUUM GAGE
10) COURSE FLOW ADJUST VALVE
11) FINE FLOW ADJUST VALVE
12) OILER
13) VACUUM PUMP
14) FILTER
15) DRY GAS METER
16) ORIFICE TUBE

17) INCLINE MANOMETER
18) SOLENOID VALVES
19) PITOT
20) THERMOCOUPLE
21) PYROMETER

FIGURE 2
STACK SAMPLER SCHEMATIC

The detailed data from each of the 24 runs are displayed in Table 7 after being converted to metric units (nearly all commercial sampling trains still present data in English units). Also included in Table 7 is the corrected (to standard conditions) sample volume and the calculated gas flow rate averaged over each run (the method of correction is outlined in Appendix A).

4.3.1 Other Samples

At the end of each gas sampling run representative samples were taken of the scrubber water, the product (ash) and the input sludge. During the experimental run, the total product was collected so that each product sample, approximately 100 grams, was a composite of the product collected over the period during which the gas stream sample was taken. As is indicated in Section 4.2, the scrubber system was arranged to be a closed system in order to attempt to measure the rate of HCl production — an attempt that was not successful as will be discussed below. Scrubber samples, approximately 1 liter, were taken from the holding tank at the end of each gas sampling run. Because of the turbulence within the holding tank, it was assumed that adequate uniformity would be assured and thus a simple surface sample was taken.

The sludge samples, taken at the end of each gas sampling run, were taken from the vibratory feed hopper and stored in a refrigerator until they were analyzed.

The sample bottles had been washed and rinsed according to the same scheme outlined for the sampling train. When the cleaned bottles were dry, they were sealed with teflon lined plastic caps and held in this condition until the sample was introduced.

4.4   Analytical Methods and Results - DDT and Products

The samples, product, scrubber water with particulates and gas stream samples were returned to the laboratory for analysis. Since some concern had been expressed about the possible conversion of significant amounts of DDT to the even more hazardous chlorinated hydrocarbons DDD and DDE, analytical procedures were adopted to detect all three compounds. The methods of analysis, which are described in detail in Appendix B, consisted primarily

34

Table 7
STACK SAMPLING DATA
Prototype Experiment

Sample	Collect Time (sec)	Sample Vol.(Meas) (M³)	Stack Temp (°C)	ΔP (mmH₂O)	P Stack (cmHg)	ΔH (mmH₂O)	Vel Stack (M/sec)	Corrected* Sample Vol. (M³)	Q Stack Flow (M³/min)
1	1200	0.404	102.2	21.6	75.95	31.3	20.91	0.513	40.78
2	900	0.254	107.8	20.2	75.95	56.0	20.69	0.329	40.26
3	1140	0.537	107.8	11.95	75.95	112.0	18.62	0.696	36.35
4	1140	0.528	85.6	8.9	75.95	96.6	13.28	0.640	25.82
5	960	0.386	96.7	17.8	75.90	61.0	18.99	0.495	37.04
6	840	0.258	96.7	21.6	75.90	52.6	20.91	0.324	40.78
7	900	0.271	85.6	14.2	75.90	45.7	16.82	0.343	32.79
8	600	0.217	85.6	12.2	75.90	30.5	15.45	0.267	30.07
9	900	0.267	85.6	19.6	75.90	48.3	19.60	0.337	38.23
10	1080	0.314	85.6	19.6	75.90	47.5	19.60	0.398	38.23
11	1020	0.335	85.6	14.1	75.90	45.7	16.73	0.425	32.62
12	1020	0.258	85.6	10.7	75.95	32.0	17.19	0.327	33.47
13	1080	0.368	102.2	17.8	75.95	45.7	19.17	0.463	37.38
14	1200	0.355	102.2	17.0	75.95	45.7	18.68	0.450	36.36
15	1200	0.438	102.2	14.1	75.95	35.6	17.10	0.550	33.30
16	1200	0.290	102.2	12.7	75.85	30.5	15.94	0.363	31.09
17	1080	0.402	93.9	24.9	75.85	58.5	22.34	0.479	43.66
18	1080	0.364	93.9	24.6	75.85	58.5	22.25	0.434	43.32
19	1140	0.343	93.9	15.2	75.85	38.1	17.53	0.412	34.15
20	1080	0.283	93.9	12.7	75.85	30.5	16.00	0.343	31.26
21	900	0.318	96.7	27.9	75.85	63.5	23.80	0.386	46.38
22	900	0.398	96.7	27.9	75.85	73.6	23.80	0.487	46.38
23	900	0.315	96.7	15.8	75.85	35.5	17.89	0.379	34.83
24	1140	0.312	63.3	13.0	75.85	30.5	15.51	0.346	30.07

35

Notes:

Average stack flow = $\overline{Q}=35.25 \ m^3/min$

*See Appendix A for correction formulae and for the identification of all symbols.

All data taken from the sampler are presented in English units which have been converted to metric units in this table.
Sample data form is included in Appendix A.

of extraction of the hydrocarbons, chromatographic clean-up to remove inter-
fering compounds and subsequent concentration and quantative determination using
an electron capture detector on a gas chromatograph. The frequent introduction of
reference solutions of known concentration of each of the compounds of interest
provided calibration.

The analytical results (analyses carried out by methods described
in detail in Appendix B) for the principal hazardous products, DDT, DDD and DDE,
in the individual emergent streams are displayed in Table 8-10, 12 and 13. These
data may be combined to allow the computation of the rates of emission of each
of the hazardous components and for each emergent stream; the results of these
computations are displayed in Tables 11 and 14 and summarized in Table 15.

4.5 Results of the DDT Combustion Experiments

In order to simplify the comparison of the results obtained under
various conditions of pesticide formulation, pesticide feed ratio and furnace
operation, it is appropriate to introduce the concept of the per cent destruction
efficiency using the following general definition:

$$\% \text{ efficiency of destruction} = \frac{\text{pesticide feed rate} - \text{hazardous product emission rate}}{\text{pesticide feed rate}} \times 100$$

which, for DDT takes the specific form:

$$\% \text{ efficiency of destruction} = \frac{\text{DDT feed rate} - \text{(DDT+DDD+DDE) emission rate}}{\text{DDT feed rate}} \times 100.$$

The % efficiency of DDT destruction is shown in Column 5 of Table 16 and diagram-
atically in Figure 3 wherein the effect of the various parametric variations is
illustrated. To better illustrate the significance of these data, recall that the
first eight tests were run using solid DDT fed on the top hearth. Further, note
the following:

a) Tests 1, 2, 5 and 6 were run with the afterburner at
760 C (1400 F);

b) Tests 3 and 7 were run with the afterburner at 955 C
(1950 F); and

c) Tests 4 and 8 were run with the afterburner off.

36

Table 8
DDT CONCENTRATION - PRODUCT (ASH)
Prototype Experiments

Test No.	p-p' DDT (ppb)	o-p' DDT (ppb)	Total (ppb)	Product (Ash) Production (grams/hr)	Total DDT Emission (grams/hr)	DDT Feed Rate (grams/hr)
1	6.1	522	528	680	36*.	908
2	7.5	37	44.5	"	.30x10-4	"
3	9.5	50.5	60.0	"	.41x10-4	"
4	5.35	33.8	39.2	"	.27x10-4	"
5	2.1	8.2	10.3	"	.07x10-4	2270
6	10.4	17.7	28.1	"	.19x10-4	"
7	1.4	4.4	5.8	"	.04x10-4	"
8	5.6	19.4	25.0	"	.17x10-4	"
9	2.5	7.8	10.3	"	.07x10-4	181.6
10	2.7	16.6	19.3	"	.13x10-4	"
11	13.6	38.3	51.9	"	.35x10-4	"
12	4.1	24.7	28.8	"	.195x10-4	"
13	2.0	12.3	14.3	"	.09x10-4	454
14	4.5	15.2	19.7	"	.13x10-4	"
15	9.2	35.5	44.7	"	.30x10-4	"
16	9.7	30.6	40.3	"	.28x10-4	"

Notes:

a. Analytical methods described in Appendix B.

b. Test conditions described in Section 4.1, pp. 9 and 10.

c. DDT feed rate is reported on an active ingredient basis, rather than the total formulation.
*Questionable data point.

Table 9
DDT CONCENTRATION-EMERGENT AIR STREAM
Prototype Experiments

Test No.	Impinger			Particulate			Total DDT Air Stream (ppb)	Air Flow Rate M^3/min.	DDT in Exit Air gm/M^3
	o-p' (ppb)	p-p' (ppb)	Total (ppb)	o-p' (ppb)	p-p' (ppb)	Total (ppb)			
1	1122	2060	3182	23	227	250	3422	36.3	6.7x10-6
2	40	155	195	98	450	548	743	36.3	2.26x10-6
3	103	295	398	609	2284	2893	3291	36.3	4.73x10-6
4	83	408	491	218	600	818	1309	36.3	2.05x10-6
5	288	800	1088	45	183	228	1316	36.3	2.68x10-6
6	267	1335	1602	47	278	325	1927	36.3	5.97x10-6
7	155	322	477	194	930	1124	1601	36.3	4.69x10-6
8	230	2818	3049	4666	13376	48042	55756	36.3	211.1x10-6
9	4146	12423	16569	87	447	534	17103	36.3	50.8x10-6
10	307	1780	2087	451	1780	2231	4318	36.3	10.7x10-6
11	203	1043	1246	72.5	327.5	400	1646	36.3	3.88x10-6
12	41	168	209	62.5	275	337.5	546	36.3	2.37x10-6
13	sample lost		---	8	30	38	---	36.3	----
14	258	1437	1694	100	390	490	2153	36.3	8.22x10-6
15	224	758	982	349	1308	1657	2839	36.3	5.15x10-6
16	58	199	257	40	148	188	445	36.3	2.08x10-6

Notes:

a. Analytical methods described in Appendix B.
b. Test conditions described in Section 4.1, pp. 9 and 10.

Table 10
DDT CONCENTRATIONS — SCRUBBER WATER
Prototype Experiments

Test No.	Scrubber Water			Scrubber Particulates			Total DDT in Scrubber (ppb)
	o-p' (ppb)	p-p' (ppb)	Total (ppb)	o-p' (ppb)	p-p' (ppb)	Total (ppb)	
1	0.025	0.10	0.125	0.125	0.435	0.56	0.685
2	0.02	0.12	0.140	0.075	0.38	0.46	0.595
3	0.075	0.13	0.21	0.07	0.23	0.307	0.507
4	1.37	4.50	5.87	146	371	517	523
5	0.25	0.63	0.88	0.08	0.27	0.35	1.23
6	0.06	0.13	0.19	0.73	2.18	2.91	3.09
7	0.07	0.25	0.32	2.0	31.0	33.0	33.3
8	0.27	1.01	1.28	210	638.2	859.4	860.0
9	0.08	0.23	0.31	0.4	1.7	2.1	2.41
10	0.05	0.32	0.37	0.14	0.54	0.68	1.05
11	0.06	0.10	0.16	0.1	0.45	0.55	0.71
12	0.06	0.19	0.25	0.1	0.38	0.48	0.74
13	0.04	0.10	0.14	0.026	0.127	0.153	0.29
14	0.02	0.12	0.14	0.115	0.39	0.500	0.64
15	0.05	0.17	0.22	0.15	0.41	0.56	0.76
16	0.025	0.102	0.127	0.02	0.11	0.129	0.255

Notes:

a. Analytical methods described in Appendix B.

b. Test conditions described in Section 4.1, pp. 9 and 10.

Table 11
SUMMARY OF DDT COMBUSTION EXPERIMENTS*

Prototype Experiments — DDT Emission Rates Various Streams

Test No.	Product DDT (Total) gm/hr	Air Stream DDT (Total) gm/hr	Scrubber DDT (Total) gm/hr	Total Losses DDT (Total) gm/hr	DDT Feed Rate (gm/hr)
1	3.6×10^{-3}	1.46×10^{-2}	3.9×10^{-4}	1.86×10^{-2}	908 (Solid)
2	0.3×10^{-4}	0.49×10^{-2}	3.4×10^{-4}	4.96×10^{-3}	
3	0.41×10^{-4}	1.03×10^{-2}	2.9×10^{-4}	1.06×10^{-2}	
4	0.27×10^{-4}	0.45×10^{-2}	0.3	0.340	
5	0.07×10^{-4}	0.58×10^{-2}	2.05×10^{-4}	6.5×10^{-3}	2270 (Solid)
6	0.04×10^{-4}	1.30×10^{-2}	1.75×10^{-3}	1.48×10^{-2}	
7	0.04×10^{-4}	1.02×10^{-2}	1.90×10^{-2}	2.92×10^{-2}	
8	0.17×10^{-4}	4.59×10^{-1}	0.49	0.949	
9	0.07×10^{-4}	0.111	1.37×10^{-3}	0.112	181.6 (Solution)
10	0.13×10^{-4}	0.0234	6.0×10^{-4}	0.024	
11	0.35×10^{-4}	0.84×10^{-2}	4.0×10^{-4}	8.84×10^{-3}	
12	0.195×10^{-4}	0.515×10^{-2}	4.30×10^{-4}	5.6×10^{-3}	
13	0.09×10^{-4}	(lost sample)	1.65×10^{-4}	-----	454 (Solution)
14	0.13×10^{-4}	1.79×10^{-2}	3.64×10^{-4}	1.83×10^{-2}	
15	0.30×10^{-4}	1.12×10^{-2}	4.32×10^{-4}	1.16×10^{-2}	
16	0.28×10^{-4}	0.45×10^{-2}	1.45×10^{-4}	$-.48 \times 10^{-2}$	

40

Notes:

a. Analytical methods described in Appendix B.

b. Test conditions described in Section 4.1, pp. 9 and 10.

c. DDT feed rate is reported on an active ingredient basis, rather than the total formulation.

*Product Emission Rate = Product DDT Concentration x Product Production Rate.

  Air Stream Emission Rate = Air Stream DDT Concentration x Air Stream Flow Rate.

  Scrubber Emission Rate = Scrubber DDT Concentration x Scrubber Flow Rate.

Table 12
PRODUCTION & DISTRIBUTION OF DDT COMBUSTION PRODUCT: DDD

Prototype Experiments

| | Air Stream | | | | | Scrubber | | | Product (Ash) | | |
| | Impinger | | Filter | | | | | | | | |
Test	op' (ppb)	pp' (ppb)	op' (ppb)	pp' (ppb)	Total (ppb)	op' (ppb)	pp' (ppb)	Total (ppb)	op' (ppb)	pp' (ppb)	Total (ppb)
1		1315	19	33	2967	0.104	0.70	0.804	--	413	413
2	32.5	108.0	61.8	125.5	327.8	0.142	0.118	0.255	1.18	1.18	3.15
3	108	127	388	2354	2977	0.28	0.119	0.399	7.30	45.4	52.7
4	20.5	165	455	2300	2941	6.68	0.-1	6.69	1.10	2.67	3.77
5	325	2059	7.8	159	2551	1.53	0.131	1.66	0.43	2.92	3.35
6	133	1050	0.8	53	1237	0.18	3.42	3.6	0.59	6.29	6.88
7	11	104	6.5	205	327	0.47	5.82	6.29	0.36	1.85	2.21
8	53	262	3774	25417	45383	2.25	0.33	2.59	4.17	33.6	37.77
9	2600	12300	13	965	15878	0.5	0.62	1.12	0.85	3.19	4.04
10	95	760	--	--	--	0.2114	0.31	0.52	0.28	1.97	2.25
11	10.4	52.2	5.2	198	266	0.058	0.34	0.398	9.87	84.0	93.87
12	4.8	25	17	92	139	0.28	0.16	0.44	0.63	1.59	2.22
13	--	--	7.0	23.0	--	0.21	0.35	0.56	0.79	8.37	9.16
14	68	827	69	111	1075	0.16	0.28	0.44	1.45	4.25	5.70
15	74	183	202	1076	1535	0.19	0.18	0.37	1.29	69.2	70.5
16	12	115	15	42	184	0.20	0.08	0.28	2.30	51.8	54.1

Notes:

a. Analytical methods described in Appendix B.
b. Test conditions described in Section 4.1, pp. 9 and 10.

41

Table 13
PRODUCTION & DISTRIBUTION OF DDT COMBUSTION PRODUCTS: DDE

Prototype Experiments

Test	Air Stream					Scrubber			Product		
	Impinger		Filter								
	o-p' (ppb)	p-p' (ppb)	o-p' (ppb)	p-p' (ppb)	Total (ppb)	o-p' (ppb)	p-p' (ppb)	Total (ppb)	o-p' (ppb)	p-p' (ppb)	Total (ppb)
1	1850	1040	60	53	3003	.6	3.75	4.35	6.1	39.3	45.4
2	45	55	113	70	283	.56	1.92	2.48	3.9	14.4	18.3
3	165	120	1820	1308	3413	.74	3.88	4.62	45.5	78	124
4	386	385	1050	265	2086	8.0	4.2	12.2	2.5	11.4	13.9
5	338	3155	190	255	3938	.89	3.2	4.09	1.02	2.6	3.62
6	1720	3277	232	338	5567	4.1	4.2	8.3	6.29	1.2	7.5
7	73	105	103	160	341	7.7	4.3	12.0	1.99	3.98	6.0
8	353	420	6758	11133	18664	1518	1707	3225	27.3	15.8	43.1
9	106	160	650	1240	2156	1.3	1.9	3.2	2.42	17.3	19.7
10	230	520	No sample		---	1.2	3.6	4.8	0.98	9.03	10.0
11	30	68	80	129	307	1.48	1.9	3.38	60.8	43.7	104.5
12	93	113	70	80	356	1.1	4.1	5.2	1.65	10.3	11.95
13	No sample		56	16	---	1.1	3.95	5.05	5.18	5.34	10.52
14	500	552	150	105	1307	1.15	3.88	5.03	1.77	3.90	5.67
15	1630	2145	580	1265	5620	1.16	3.73	4.89	3.11	6.48	9.59
16	188	240	103	54	585	0.26	4.1	4.36	6.84	1.09	7.93

42

Notes:

a. Analytical methods described in Appendix B.
b. Test conditions described in Section 4.1, pp. 9 and 10.

Table 14
DISTRIBUTION OF DDT COMBUSTION PRODUCTS*

DDT & DDE Emission Rates — Prototype Experiments

Test	Product		Air Stream		Scrubber	
	DDD (gm/hr)	DDE (gm/hr)	DDD (gm/hr)	DDE (gm/hr)	DDD (gm/hr)	DDE (gm/hr)
1	2.81×10^{-2}	3.08×10^{-3}	1.27×10^{-2}	1.28×10^{-2}	4.56×10^{-4}	2.47×10^{-3}
2	2.15×10^{-4}	1.24×10^{-3}	2.17×10^{-3}	1.87×10^{-3}	1.45×10^{-4}	1.41×10^{-3}
3	3.6×10^{-3}	8.43×10^{-3}	9.32×10^{-3}	1.08×10^{-2}	2.26×10^{-4}	2.63×10^{-3}
4	2.57×10^{-4}	9.45×10^{-4}	1×10^{-2}	7.17×10^{-3}	3.8×10^{-3}	6.94×10^{-3}
5	2.28×10^{-4}	2.46×10^{-4}	1.2×10^{-2}	1.73×10^{-2}	9.42×10^{-4}	2.33×10^{-3}
6	4.69×10^{-4}	5.1×10^{-4}	8.32×10^{-3}	3.76×10^{-2}	2.04×10^{-3}	4.72×10^{-3}
7	1.51×10^{-4}	4.0×10^{-4}	2.10×10^{-3}	2.17×10^{-3}	3.57×10^{-3}	6.82×10^{-3}
8	2.57×10^{-3}	2.93×10^{-3}	3.76×10^{-1}	1.53×10^{-1}	1.47×10^{-3}	1.83
9	2.75×10^{-4}	1.34×10^{-3}	1.03×10^{-1}	1.39×10^{-2}	6.36×10^{-4}	1.82×10^{-3}
10	1.53×10^{-4}	6.8×10^{-4}	----	----	2.95×10^{-4}	2.73×10^{-3}
11	6.39×10^{-3}	7.11×10^{-3}	1.36×10^{-3}	1.57×10^{-3}	2.25×10^{-4}	1.92×10^{-3}
12	1.51×10^{-4}	8.13×10^{-4}	0.93×10^{-3}	3.36×10^{-3}	2.50×10^{-4}	2.96×10^{-3}
13	6.24×10^{-4}	7.15×10^{-4}	----	----	3.18×10^{-4}	2.87×10^{-3}
14	3.85×10^{-4}	3.84×10^{-4}	5.2×10^{-3}	1.09×10^{-2}	2.50×10^{-4}	2.86×10^{-3}
15	4.8×10^{-3}	6.52×10^{-4}	6.08×10^{-3}	2.22×10^{-2}	2.10×10^{-4}	2.78×10^{-3}
16	3.68×10^{-3}	5.39×10^{-4}	1.10×10^{-3}	5.92×10^{-3}	1.59×10^{-4}	2.48×10^{-3}

Notes:

a. Analytical methods described in Appendix B.
b. Test conditions described in Section 4.1, pp. 9 and 10.

*Product Emission Rate = Product DDT Concentration x Product Production Rate.
 Air Stream Emission Rate = Air Stream DDT Concentration x Air Stream Flow Rate.
 Scrubber Emission Rate = Scrubber DDT Concentration x Scrubber Flow Rate.

Table 15
DDT & COMBUSTION PRODUCTS - TOTAL EFFLUENT STREAMS EMISSION RATES

DDT & DDD & DDE —— Prototype Experiments

Test No.	DDT Feed Rate (gm/hr)		DDT Emission Rate (gm/hr)	DDD Emission Rate (gm/hr)	DDE Emission Rate (gm/hr)
1	908	(Solid)	1.86×10^{-2}	4.126×10^{-2}	1.84×10^{-2}
2	908	(Solid)	6.27×10^{-2}	2.53×10^{-3}	4.52×10^{-3}
3	908	(Solid)	1.06×10^{-2}	1.31×10^{-2}	2.186×10^{-2}
4	908	(Solid)	0.34	1.41×10^{-2}	1.51×10^{-2}
5	2270	(Solid)	6.5×10^{-2}	1.32×10^{-2}	1.99×10^{-2}
6	2270	(Solid)	1.48×10^{-2}	1.08×10^{-2}	4.28×10^{-2}
7	2270	(Solid)	2.92×10^{-2}	5.8×10^{-3}	9.39×10^{-3}
8	2270	(Solid)	0.949	0.380	1.99
9	181.6	(Solution)	0.112	1.05×10^{-1}	1.71×10^{-2}
10	181.6	(Solution)	2.4×10^{-2}	----	----
11	181.6	(Solution)	8.84×10^{-3}	7.98×10^{-3}	1.06×10^{-2}
12	181.6	(Solution)	5.6×10^{-3}	1.33×10^{-3}	7.13×10^{-3}
13	454	(Solution)	----	----	----
14	454	(Solution)	1.83×10^{-2}	5.84×10^{-3}	1.414×10^{-2}
15	454	(Solution)	1.16×10^{-2}	1.11×10^{-2}	2.56×10^{-2}
16	454	(Solution)	0.48×10^{-2}	4.94×10^{-3}	8.94×10^{-3}

Notes:

a. Analytical methods described in Appendix B.
b. Test conditions described in Section 4.1, pp. 9 and 10.
c. DDT feed rate is reported on an active ingredient basis, rather than the total formulation.

Table 16
SUMMARY DDT COMBUSTION EXPERIMENTS

Test No.	DDT Feed Rate (gm/hr)	Prototype Experiments Feed Form	Emission Rate for Total Effluents (DDT & DDD & DDE) (gm/hr)	Eff. of Destruction* %
I	908	Solid	0.0783	99.981
2	908	Solid	0.0698	99.983
3	908	Solid	0.115	99.980
4	908	Solid	0.369	99.·96
5	2270	Solid	0.098	99.995
6	2270	Solid	0.068	99.997
7	2270	Solid	0.044	99.998
8	2270	Solid	7.76	99.66
9	181.6	Solution	0.388	99.79
10	181.6	Solution	---	---
11	181.6	Solution	0.027	99.986
12	181.6	Solution	0.0141	99.993
13	454	Solution	---	---
14	454	Solution	0.033	99.993
15	454	Solution	0.086	99.982
16	454	Solution	0.0273	99.994

Average   99.949%

Summary of test conditions displayed in Figure 3 which follows.

Notes:

a. Analytical methods described in Appendix B.

b. Test conditions described in Section 4.1, pp. 9 and 10.

c. DDT feed rate is reported on an active ingredient basis, rather than the total formulation.

*Efficiency of Destruction = $\dfrac{\text{DDT Feed Rate} - \text{(DDT + DDD + DDE) Emission Rate}}{\text{DDT Feed Rate}}$
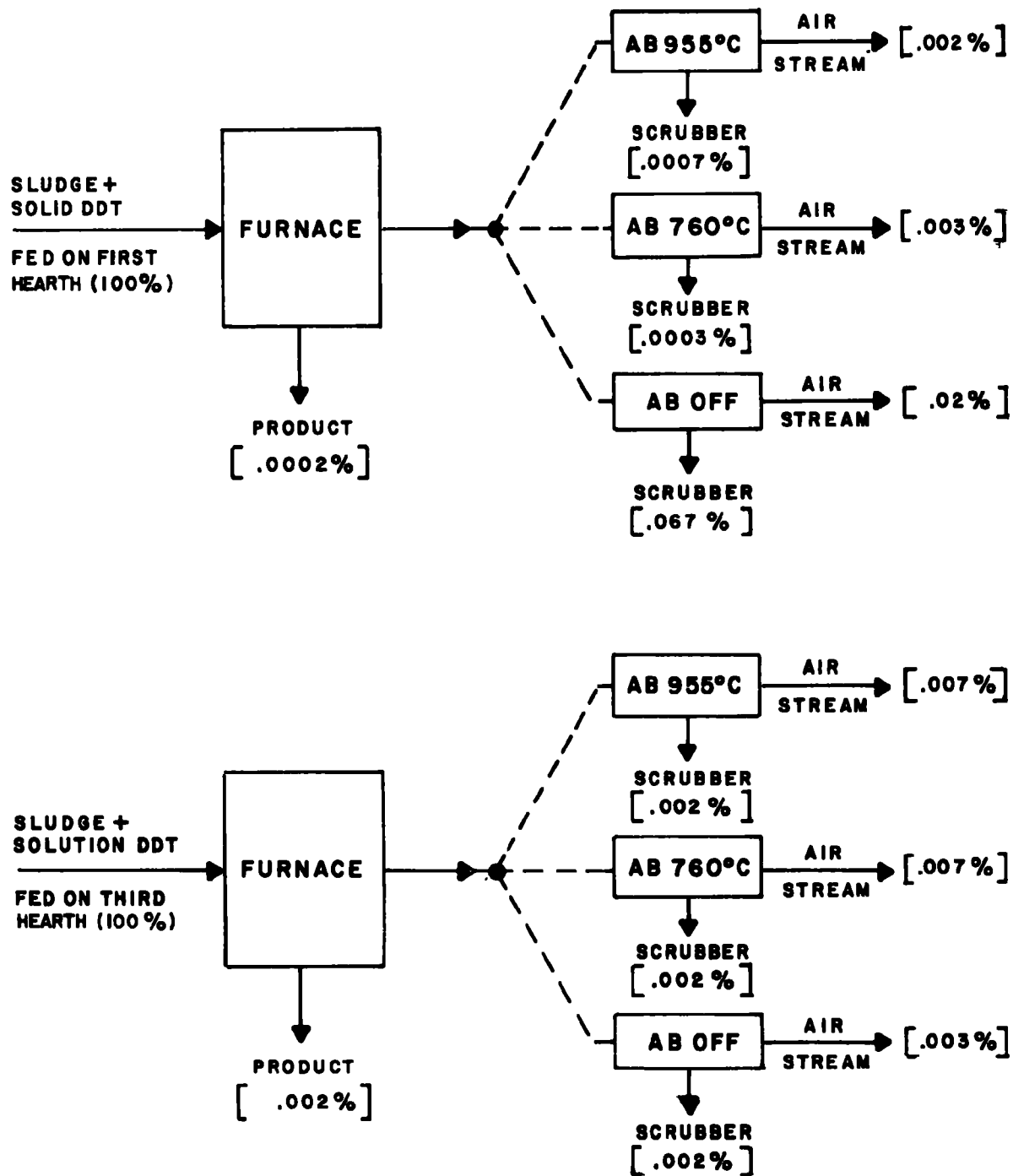
45

FIGURE 3
MASS BALANCE DDT COMBUSTION EXPERIMENTS
SHOWING EFFECT OF VARIOUS AFTERBURNER (AB) TEMPERATURES
FOR PROTOTYPE EXPERIMENTS

On consideration of Column 5 of Table 16 in light of the above, the significantly lower efficiency associated with tests 4 and 8 is striking. On the other hand, the variations among tests 1, 2, 3, 5, 6 and 7 are much smaller and show no definite trend. Clearly when solid DDT is mixed with sludge and fed on the top hearth, the afterburner is essential (See Figure 3).

To further verify this conclusion, note that for the solution feed experiments, the top two hearths of the furnace act as afterburners, since the feed was on the third hearth. In these experiments, the effect of the afterburner should be conspiciously less than in the solid feed experiments. Comparison of the efficiency factors in Column 5 of Table 16 for tests 9-16 with tests 1-3 and test 5-7 shows that, indeed, the presence or absence of the afterburner is of markedly less significance in those experiments where the third hearth feed was used.

4.6 Analytical Results on 2,4,5-T Experiments

The analysis of the 2,4,5-T content of the various samples taken in tests 17-24 was accomplished by standard methods, as discussed in Appendix C. Essentially, the active ingredient was extracted, cleaned up to remove interfering substances, concentrated and subsequently analyzed by electron capture detection with a gas chromatograph. The results of these analyses are displayed in Table 17.

Again using the data from Table 7, Figure 1 and Table 17, we may compute the discharge rates for 2,4,5-T in each of the emergent streams. The results of these calculations are shown in Table 18 (carried out exactly as for the prototype experiments).

4.7 Results of 2,4,5-T Experiments

If we again assume that the efficiency of destruction is given by the expression:

$$\% \text{ Efficiency of destruction} = \frac{\text{Feed rate} - \text{emission rate}}{\text{Feed rate}} \times 100$$

Table 17
EFFLUENT STREAMS - 2,4,5-T CONCENTRATIONS $(gm/gm \times 10^9 = ppb)*$
Prototype Experiments

No.	Scrubber			Air Stream			Product (Ash) (ppb)
	Water (ppb)	Particulate (ppb)	Total (ppb)	Impinger (ppb)	Particulate (ppb)	Total (ppb)	
17	4.9	0.315	5.22	0.268	0.73	1.0	0.432
18	0.32	3.52	3.84	0.034	0.126	0.16	19.54
19	0.071	1.97	2.04	0.23	0.44	0.67	49.50
20	0.124	0.30	0.42	0.009	0.28	0.29	35.80
21	0.131	0.03	0.16	0.038	0.015	0.05	15.93
22	0.388	1.16	1.55	0.322	0.29	0.01	65.0
23	0.206	5.9	6.11	0.225	0.252	0.48	44.8
24	0.132	2.39	2.52	sample lost	0.04	---	8.2

*Tetrachlorodioxin not found in any sample.

where the feed and emission rates are measured on the basis of the active ingredient, 2,4,5-T, then we may compute the destruction efficiencies for each test in Table 18. The results of these calculations are displayed in Table 19 and Figure 4.

The results in Column 5 of Table 19 show a remarkable lack of variation especially when it is noted that three different sets of afterburner conditions are included as before. Recalling that in tests 17-24, the injection of the active ingredient was through the third hearth, it is again found that the first and second hearth serve as afterburners, thus alleviating the need for the additional afterburner.

There was some concern about the possibility of producing tetra-chlorodioxin as a by-product of the co-incineration of 2,4,5-T with sewage sludge. In no case in the present work has this compound been found even at trace levels.

4.8 Summary of Prototype Experiments

The results of the prototype experiments are best summarized in the following table.

DDT DESTRUCTION EFFICIENCY

Prototype Experiments

Preparation	Feed Hearth	Feed Ratio (gm/gm)	Avg. Hearth Temp (C°)	AB* Temp (C°)	% Dest. Eff. (%)
Solid	1st	0.02	764	733	99.98
Solid	1st	0.02	754	738	99.98
Solid	1st	0.02	715	900	99.98
Solid	1st	0.02	738	182	99.96
Solid	1st	0.05	759	733	99.995
Solid	1st	0.05	795	716	99.997
Solid	1st	0.05	780	800	99.998
Solid	1st	0.05	782	221	99.66
Solution	3rd	0.02	841	672	99.79
Solution	3rd	0.02	827	716	---
Solution	3rd	0.02	837	983	99.99
Solution	3rd	0.02	842	204	99.99
Solution	3rd	0.05	838	705	---
Solution	3rd	0.05	841	727	99.99
Solution	3rd	0.05	810	830	99.98
Solution	3rd	0.05	802	182	99.99

*AB - Afterburner

NOTE: The feed ratios for the solid DDT experiments were actually .026 and .066 rather than .02 and .05.

49

2,4,5-T DESTRUCTION EFFICIENCY

Prototype Experiments

Preparation	Feed Hearth	Feed Ratio (gm/gm)	Hearth Temp (C°)	AB* Temp (C°)	% Dest. Eff. (%)
Solution	3rd	0.02	792	711	99.98
Solution	3rd	0.02	809	711	99.99
Solution	3rd	0.02	781	1005	99.99
Solution	3rd	0.02	749	216	99.98
Solution	3rd	0.05	774	694	99.99
Solution	3rd	0.05	793	727	99.99
Solution	3rd	0.05	780	1010	99.99
Solution	3rd	0.05	784	227	---

*AB - Afterburner

Table 18
MASS BALANCE 2,4,5-T EXPERIMENTS*
Prototype Experiments

Test No.	Emission Rate Air Stream (gm/hr)	Emission Rate Scrubber (gm/hr)	Emission Rate Product (gm/hr)	Total Emission Rate (gm/hr)	2, 4, 5-T Feed Rate (gm/hr)
17	0.0026	0.024	5.8×10^{-7}	0.027	183.0
18	0.00041	0.017	2.7×10^{-5}	0.017	183.0
19	0.0017	0.009	6.7×10^{-5}	.0108	183.0
20	0.0074	0.019	4.9×10^{-3}	.0313	183.0
21	0.00013	0.001	2.1×10^{-5}	0.0011	454.0
22	0.0016	0.007	8.8×10^{-5}	0.0086	454.0
23	0.0012	0.028	6.1×10^{-5}	0.029	454.0
24	---	0.014	1.1×10^{-4}	---	454.0

*Air Stream Emission Rate = Air Stream Concentration x Air Stream Flow Rate.
 Scrubber Emission Rate = Scrubber Concentration x Scrubber Flow Rate.
 Product Emission Rate = Product Concentration x Product Production Rate.

2,4,5-T feed rate is reported on an active ingredient basis, rather than the total formulation.

Table 19
SUMMARY 2,4,5-T COMBUSTION EXPERIMENTS

Test No.	2,4,5-T Feed Rate (gm/hr)	Feed Form	2,4,5-T Emission Rate (gm/hr)	Eff. of Destruction*
17	183.0	Liquid	0.027	99.98
18	183.0	Liquid	0.017	99.99
19	183.0	Liquid	.0108	99.99
20	183.0	Liquid	.0313	99.98
21	454.0	Liquid	0.0011	99.99
22	454.0	Liquid	0.0086	99.99
23	454.0	Liquid	0.029	99.99
24	454.0	Liquid	---	---

*Efficiency of Destruction $= \dfrac{2,4,5\text{-T Feed Rate} - 2,4,5\text{-T Emission Rate}}{2,4,5\text{-T Feed Rate}}$

Operating conditions summarized in diagramatic form in Figure 4.

2,4,5-T feed rate is reported on an active ingredient basis, rather than the total formulation.
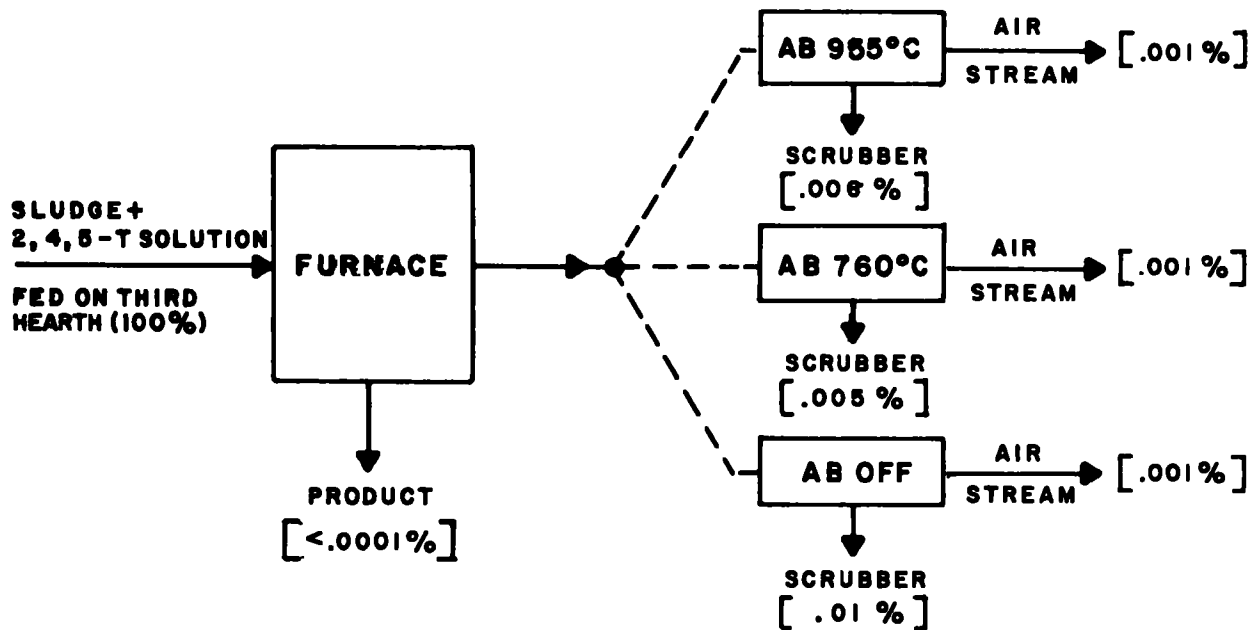
52

FIGURE 4
MASS BALANCE 2,4,5-T COMBUSTION EXPERIMENTS
SHOWING EFFECT OF VARIOUS AFTERBURNER (AB) TEMPERATURES
FOR PROTOTYPE EXPERIMENTS

4.9 Chloride Ion Measurements

The combustion products of a chlorinated hydrocarbon should be water, carbon dioxide and hydrogen chloride if the combustion is complete. Since DDT contains approximately 50 per cent chlorine, one should expect the production of significant amounts of HCl in these experiments. It was anticipated that using a closed scrubber water system would make it possible to follow the combustion process simply by observing the continuous increase in chloride ion in the scrubber system. With this purpose in mind additional scrubber samples were taken hourly during the two solid DDT experiments for subsequent chloride ion analysis.

The results of these measurements were uniformly disappointing in that though an increasing chloride ion concentration was observed with time, there was no discernable relationship between the increase in chloride concentration and the amount of DDT combusted. Several factors apparently enter into this result: the nature of the scrubber system; the mechanics of evaporation within the scrubber; the presence of contaminants in the scrubber water; and the nature of chloride ion determination.

The chloride ion content of a closed system scrubber could be expected to increase even without a source of HCl since it is constantly necessary to make up the water lost due to evaporation. In the actual scrubber system at Brisbane, there is apparently an additional source of water loss probably associated with the entrainment of water droplets in the emergent gas stream. This is illustrated by comparing the make up rate to the loss rate associated with the increase in absolute humidity of the emergent

54

air. The observed rates of these quantities was found to vary quite erratically during a typical furnace run. Since no provision was made to determine the chloride ion content of these emergent water droplets, no correction could be made for this loss.

An additional complication turned up in the form of a large residue of iron within the scrubber solution -- iron resulting from corrosion of the reservoir and probably of the interior structure of the scrubber. No attempt was made to clean the scrubber system prior to the test burns. The effect of ferric ions on the accuracy of electrochemical chloride ion measurements is well known. In addition, the use of hydroxyquinone as a reducing agent in such cases is well documented. Unfortunately, in the case in point, the addition of the hydroxyquinone to the scrubber samples resulted in the formation of a gel-like mass (even in samples taken from the scrubber system prior to the pesticide burns) which severely interfered with chloride ion measurements.

In an attempt to analyze the chloride ion measurements in the following manner by defining the several quantities as below:

$c_{Cl^-}(t)$ = chloride ion concentration at time t in gm/gm

c_o = chloride ion concentration at time t = o (gm/gm)

c_i = chloride ion concentration of make up feed (gm/gm)

M_m = make up rate in (gm/min)

M_t = total mass of scrubber water in gm

t_o = initial fire up time

t_i = time at which DDT feed began

Q = rate of injection of Cl⁻ ions due to DDT combustion (gm/min)

55

then,

$$C_{Cl^-}(t)M_t = C_oM_t + M_mC_i(t-t_o) + Q(t-t_i)$$

serves to relate the total chloride ion mass in the scrubber
system at time t to the various inputs. The actual values
of Cl^- concentration ranged from 500 ppm to over 1000 ppm.

Using the actual data taken on chloride ion concentration
along with the appropriate times, rates and masses, one can
assemble a set of three simultaneous equations, the solution
of which can presumable be found by conventional methods.
In point of fact, using the chloride ion concentrations
found, one can show that the equation set is indeterminate.
That is to say, only by adjusting the chloride concentration
by what appears to be a set of arbitrary constants can one
arrive at a solution to these equations. For this reason one
must conclude that the results are not especially useful for a
complex closed system such as that used at Brisbane.

5.0 FULL SCALE EXPERIMENTS

As a result of the excellent results obtained in the prototype experiments, it was agreed that it would be both safe and appropriate to attempt a full-scale experiment in a typical municipal incinerator in order to verify the prototype results. By the kind permission of Mr. Ronald N. Doty and the City Council of Palo Alto, California, the Palo Alto incinerator was made available for these experiments. The overall flow diagram of the sewage sludge treatment plant is illustrated in Figure 5.

5.1 Furnace Operating Conditions

The configuration of the furnace used is similar to that shown in Figure 1 (which will serve as reference in the following discussion) except for its much larger size and capacity. Additionally, the scrubber is a high energy venturi rather than the impingement type installed on the pilot scale unit. The furnace interior is diagrammed in Figure 6. In order to facilitate the extrapolation of the results of these experiments to other such multiple hearth incinerators, it was decided to operate the furnace in its normal mode using the permanent operational crew with minimal interference in the regular operations. A summary of the actual furnace conditions during the coincineration experiments is given in Tables 20 and 21 with the same information in English units displayed in Tables 20-A and 21-A. Note also that the oxygen content of the stack gases is given in Tables 20 and 21. As before, the existence of approximately 7-10 per cent residual oxygen indicates that the system was operating with something in excess of 100 per cent excess air. Tables 20 and 21 (20-A and 21-A) also indicate a delay of 1 hour after initiation of pesticide feed before sampling in order to allow equilibrium to be established on the assumption of a residence time in the furnace of 45 minutes.

5.1.1 Pesticides and Feed Methods

Feeding DDT in both solid and solution preparations as well as 2,4,5-T in solution had been planned in order to verify all of the individual tests conducted during the prototype experiments. As before, the DDT was obtained from Sierra Base, but the drum of what purported to be 20 per cent DDT in kerosene was so questionable that it was feared that it would be excessively dangerous to attempt to burn.[*] Thus, only solid DDT experiments were attempted. As before, the 2,4,5-T was in the form of the commercial weed control preparation Weedon^{TM}.

---

[*] The contents of the drum were under pressure, produced HCl fumes and appeared red in color.

58

FLOW DIAGRAM OF
PALO ALTO SEWAGE TREATMENT PLANT

FIGURE   . SCHEMATIC PALO ALTO MUNICIPAL
MULTIPLE HEARTH FURNACE

FIGURE 6

60

Table 20
FURNACE OPERATING CONDITIONS
Municipal Sewage MHF Incinerator - Palo Alto, Calif.
Solid DDT Feed

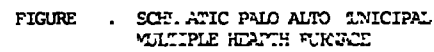| | Hearth Temperatures | | | | | | | Stack | |
Time	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	T_5 (°C)	T_6 (°C)	T_{Stack} (°C)	Gas %O_2	Notes
0900	649	705	566	811	800	288	91	7.5	
1000	658	713	638	844	794	274	91	6.75	
1100	636	705	622	797	761	269	88	9.5	
1200	638	705	591	786	772	288	93		
1300	602	682	616	791	791	330	121		
1400	597	649	591	791	794	344	93		Initial feed begun
1500	599	644	563	791	791	346	93	7.5	
1600	638	677	566	788	775	327	93	6.5	Sample #1
1700	649	711	608	802	761	274	88	9.0	
1800	649	711	608	794	766	277	88	9.0	Sample #2
1900	649	705	566	794	772	310	93	8.0	Increase feed
2000	644	705	544	794	775	310	99	9.0	⎫2100
2100	663	705	427	794	805	371	99	6.5	Sample #3 ⎭2138
2200	649	719	627	802	775	383	93	10.0	Sample #4
2300	636	711	588	794	775	344	88	10.0	Stop feed
2400	622	711	594	794	775	349	88	10.0	

There is no afterburner temperature indicated since the top hearth region serves as afterburner.

Addenda

Sludge feed - 635 #/hr/dry

DDT feed rates

| 1400 - 1800 | 6.92×10^3 gms/hr |
| 1800 - 2300 | 1.64×10^4 gms/hr |

Feed ratios $\left(\dfrac{DDT \ feed \ rate}{Solids \ feed \ rate}\right)$

| 1400 - 1800 | 2 per cent |
| 1800 - 2300 | 4.8 per cent |

Table 20-A
FURNACE OPERATING CONDITIONS
Municipal Sewage MHF Incinerator - Palo Alto, Calif.
Solid DDT Feed

	Hearth Temperatures							Stack	
Time	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	T_5 (°C)	T_6 (°C)	T_{Stack} (°C)	Gas %O_2	Notes
0900	1200	1300	1050	1490	1470	550	195	7.5	
1000	1215	1315	1180	1550	1460	525	195	6.75	
1100	1175	1300	1150	1465	1400	515	190	9.5	
1200	1180	1300	1095	1445	1420	550	200		
1300	1115	1260	1140	1455	1455	625	250		
1400	1105	1200	1095	1455	1460	650	200		Initial feed begun
1500	1110	1190	1045	1455	1455	655	200	7.5	@
1600	1180	1250	1050	1450	1425	620	200	6.5	Sample #1
1700	1200	1310	1125	1475	1400	525	190	9.0	
1800	1200	1310	1125	1460	1410	530	190	9.0	Sample #2
1900	1200	1300	1050	1460	1420	590	200	8.0	Increase feed
2000	1190	1300	1010	1460	1425	590	210	9.0	
2100	1225	1300	800	1460	1480	700	210	6.5	Sample #3
2200	1200	1325	1160	1475	1425	720	200	10.0	Sample #4
2300	1175	1310	1090	1460	1425	650	190	10.0	Stop feed
2400	1150	1310	1100	1460	1425	660	190	10.0	

Addenda

Sludge feed - 635 #/hr/dry

DDT feed rates

1400 - 1800	6.92×10^3 gms/hr
1800 - 2300	1.64×10^4 gms/hr

Feed ratios $\left(\dfrac{DDT\ feed\ rate}{Solids\ feed\ rate} \right)$

1400 - 1800	2 per cent
1800 - 2300	4.8 per cent

Table 21
FURNACE OPERATING CONDITIONS
Municipal Sewage MHF Incinerator - Palo Alto, Calif.
2,4,5-T Liquid Injection

| | Hearth Temperatures | | | | | | | Stack | |
Time	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	T_5 (°C)	T_6 (°C)	T_{Stack} (°C)	Gas %O_2	Notes
1100	616	649	572	858	838	358	88	9.5	
1200	677	705	733	900	827	368	88	12	
1300	733	727	716	827	761	266	88	6.0	Feed begun on 3rd hearth
1400	677	755	636	905	872	352	88	8.8	Sample #9
1500	655	674	602	894	866	368	88	10	Sample #10
1600	730	730	927	872	866	458	232	6.0	
1700	666	761	905	905	844	277	82	8.0	Feed changed to 5/100g sludge
1800	644	755	738	914	844	249	82	8.0	Sample #11
1900	663	761	733	942	850	238	82	7.5	Sample #12
2000	644	761	775	942	844	246	82	9.5	
2100	672	766	802	955	844	238	82	8.0	Feed stopped
2200	655	772	811	916	838	249	82	8.5	
2300	655	761	811	914	838	249	82	9.5	
2400	663	775	844	905	838	249	82	10.0	

Refer to Figure 1 for identification of temperatures/hearth.

Addenda

Sludge feed - #1 hr (dry)

2,4,5-T feed rates

| 1300 - 1700 | 1.108×10^3 gm/hr |
| 1700 - 2100 | 3.45×10^3 gm/hr |

Feed ratios $\left(\dfrac{2,4,5\text{-T feed rate}}{\text{Sludge feed rate}}\right)$

| 1300 - 1700 | 0.3 per cent |
| 1700 - 2100 | 1.1 per cent |

63

Table 21-A
FURNACE OPERATING CONDITIONS
Municipal Sewage MHF Incinerator - Palo Alto, Calif.
2,4,5-T Liquid Injection

Time	Hearth Temperatures						T_{Stack} (°C)	Stack Gas %O_2	Notes
	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	T_5 (°C)	T_6 (°C)			
0900									
1000									
1100	1140	1200	1060	1575	1540	675	190	9.5	
1200	1250	1300	1350	1650	1520	695	190	12	
1300	1350	1340	1320	1520	1400	510	190	6.0	Feed begun on 3rd hearth
1400	1250	1390	1175	1660	1600	665	190	8.8	Sample #9
1500	1210	1245	1115	1640	1590	695	190	10	Sample #10
1600	1345	1345	1700	1600	1590	855	450	6.0	
1700	1230	1400	1660	1660	1550	530	180	8.0	Feed changed to 5/100g sludge
1800	1190	1390	1360	1675	1550	480	180	8.0	Sample #11
1900	1225	1400	1350	1725	1560	460	180	7.5	
2000	1190	1400	1425	1725	1550	475	180	9.5	Sample #12
2100	1240	1410	1475	1750	1550	460	180	8.0	Feed stopped
2200	1210	1420	1490	1680	1540	480	180	8.5	
2300	1210	1400	1490	1675	1540	480	180	9.5	
2400	1225	1425	1550	1660	1540	480	180	10.0	

Addenda

Sludge feed - #1 hr (dry)

2,4,5-T feed rates

| 1300 - 1700 | 1.108 x 10^3 gm/hr |
| 1700 - 2100 | 3.45 x 10^3 gm/hr |

Feed ratios $\left(\dfrac{2,4,5\text{-T feed rate}}{\text{Sludge feed rate}}\right)$

| 1300 - 1700 | 0.3 per cent |
| 1700 - 2100 | 1.1 per cent |

The DDT feed was accomplished by a hopper arrangement placed
over the screw-feed mechanism used to conduct the de-watered
sludge from the centrifuge to the top hearth of the furnace.
The mechanical properties of the powdered DDT preparation used
were such that the simple gravity feed device was not particu-
larly satisfactory; one might elect to go to a more elaborate
vibratory feed system in practice. The feed device used did not
effect a constant feed rate, which was less serious than might
be supposed. The sludge feed was found to vary from a low on
the order of 430 kg/hr (950 lb/hr) to a high on the order of
488 kg/hr (1075 lb/hr) on a dry basis with a 24 hour average of
454 kg/hr (1000 lb/hr). This variation seems to be due to
variations in the wet sludge feed to the centrifugal pump and
to variations in the water content of the sludge fed to the
furnace. The DDT preparation was fed at an average rate of
9.2 kg/hr (20.2 lb/hr) over the initial period (1400 to 1900 -
see Table 20) computed on the basis that a total of 50 kg (109 lbs)
of the preparation was fed during the second 5 hour interval.
These feed rat   yield a pesticide preparation to sludge ratio of .02
during the initial period and .05 during the final period. The air
sampling procedure used was such that sampling was accomplished over
elapsed times ranging from a minimum of 24 minutes to a maximum of 44
minutes.

The Palo Alto furnace is equipped with a scum line feeding the
third hearth. The injection of 2,4,5-T solution was accomplished by
feeding the metered solution by gravity feed into the scum flow outside
the furnace. Variations in sludge fed to the top

hearth occurred in addition to the variation in the scum feed (not actually measured, but averaged out to about 20 kg/hr. (44 lb/hr.). Thus, the 2,4,5-T feed ratio is an average over the test period. The 2,4,5-T preparation was fed at an average rate of 5.5 kg/hr (12.1 lb/hr) over the initial period [1300 to 1700 - See Table 21] and 17.2 kg/hr (38 lb/hr) over the final period [1700 - 2100 - See Table 21]. These feed rates yield a pesticide preparation to sludge ratio of .012 during the initial period and .038 during the final period. The lack of precision in the feeding mechanism prevented matching exactly the feed ratios used during the pilot experiments (.02 and .05).

5.2 Gas Stream Sampling

The emergent (stack) gas stream was sampled by methods exactly similar to those described in Section 4.2 using a seven point traverse. The impinger solution was hexane for the DDT experiments and ethylene glycol for the 2,4,5-T experiments. The instrumental data (after being converted to MKS units) is displayed in Table 22 and the calculated data (see Appendix A) is displayed in Table 22. Appendix E describes the sampling procedures in detail.

At the end of each gas sampling run, a 1-liter sample of the scrubber water and 100 gram samples of the product were taken from the sixth hearth. In addition, composite sludge samples were made up during each experimental series.

5.3 Analytical Methods and Results of DDT and Products

The collected samples were analyzed for DDT as well as for DDD and DDE by the methods outlined in Section 4.4 and Appendix B. The results of these analyses are displayed in Tables 23 through 31 and summarized in Table 32.

66

5.4 Results of DDT Combustion Experiments

Using the results for the total rate of emission of DDT and its two principal combustion products from Table 32, the percentage of destruction may be computed as before. The results of such a calculation are displayed in Table 33.

Note that, in general, the largest portion of the effluent DDT and its products is found in the scrubber stream. A realistic analysis of the plant situation would show that this stream, the scrubber outflow, is reintroduced into the plant to be recycled. Thus, the combustion efficiencies shown in Table 33 are somewhat conservative.

The major exception to the above is found in the relatively higher concentrations of DDE found in the emergent air stream in experiments 3 and 4 (Table 32). Although not immediately obvious, there was a marked reduction in the temperature of the third hearth during the sampling interval when sample 3 was taken. From Table 20 we note that the average temperature of the third hearth was perhaps 590 C during the period of samples 1 and 2, but fell to less than 430 C during sampling period 3 (specifically at 2100 hours).

Table 22
GAS SAMPLING DATA*

Palo Alto Experiments

Sample	Collect Time (sec)	Meter Vol. (m^3)	T_{Stack} (°C)	Δp (mmH_2O)	P_{Stack} (cm Hg)	ΔH (mmH_2O)	V_s (m/min)	V_{stnd} Sample (m^3)	Q_s (m^3/hr)
1	2160	0.586	93.4	15.2	75.98	28.4	685.8	0.551	2999.7
2	2640	0.535	93.4	11.94	75.98	22.1	609.1	0.493	2666.4
3	2280	0.554	93.4	16.5	75.98	31.0	704.1	0.513	3079.7
4	1860	0.575	93.4	19.56	75.98	37.8	777.2	0.527	3399.4
9	1620	0.703	93.4	33.0	75.95	60.96	1067	0.661	4667.1
10	1440	0.498	93.4	30.2	75.95	52.58	1013.5	0.459	4433.0
11	2400	0.950	93.4	37.3	75.95	66.8	1167.4	0.868	5106.2
12	2440	0.799	93.4	36.8	75.95	67.3	1150.6	0.728	5032.7

*See Appendix A where these parameters are defined as are the appropriate calculations. For Samples 1-4 the solid DDT preparation was fed on 1st hearth and for samples 9-12 the 2,4,5-T solution was fed on 3rd hearth.

Table 23
DDT CONCENTRATIONS/PRODUCTION IN STACK GASES
Palo Alto Experiments

Test No.	SAMPLE IMPINGER DDT o-p' (gm)	DDT p-p' (gm)	DDT Total (gm)	SAMPLE PARTICULATE DDT o-p' (gm)	DDT p-p' (gm)	DDT Total (gm)	DDT TOTAL (gm)	Stack Sample (m^3)	DDT Conc. gm/m^3	Stack Flow (m^3/hr)	Emission Rate (DDT) (gm/hr)
1	5.62×10^{-7}	1.77×10^{-6}	2.3×10^{-6}	5.8×10^{-8}	3×10^{-7}	3.6×10^{-7}	2.7×10^{-6}	0.533	5.07×10^{-6}	2979	0.015
2	5.4×10^{-7}	1.32×10^{-6}	1.86×10^{-6}	2.2×10^{-7}	8.5×10^{-7}	1.07×10^{-6}	2.9×10^{-6}	0.495	5.8×10^{-6}	2649	0.0154
3	2.8×10^{-6}	5.2×10^{-6}	8.0×10^{-6}	5.6×10^{-6}	6.0×10^{-6}	11.6×10^{-6}	19.6×10^{-6}	0.515	38.1×10^{-6}	3058	0.116
4	7.2×10^{-7}	9.4×10^{-7}	1.66×10^{-6}	7.5×10^{-7}	9.7×10^{-7}	1.72×10^{-6}	3.4×10^{-6}	0.529	6.4×10^{-6}	3377	0.022

Notes: a. Analytical methods described in Appendix C.
b. Test conditions described in Section 5.2, pp 48, 53.

69

Table 24
DDD CONCENTRATIONS/PRODUCTION IN STACK GASES
Palo Alto Experiments

Test No.	SAMPLE IMPINGER DDD o-p' (gm)	DDD p-p' (gm)	DDD Total (gm)	SAMPLE PARTICULATE DDD o-p' (gm)	DDD p-p' (gm)	DDD Total (gm)	DDD TOTAL (gm)	Stack Sample (m^3)	DDD Conc. gm/m^3	Stack Flow (m^3/hr)	Emission Rate (DDD) (gm/hr)
1	6.2×10^{-8}	1.8×10^{-7}	2.4×10^{-7}	4.14×10^{-7}	1.7×10^{-8}	5.9×10^{-8}	2.99×10^{-7}	0.533	$.56 \times 10^{-6}$	2979	0.0017
2	3×10^{-10}	9×10^{-10}	1.2×10^{-9}	2.3×10^{-7}	4×10^{-9}	2.3×10^{-7}	2.3×10^{-7}	0.495	$.46 \times 10^{-6}$	2649	0.0012
3	1.1×10^{-7}	1.03×10^{-6}	1.14×10^{-6}	3.9×10^{-8}	5.2×10^{-8}	9.1×10^{-8}	1.24×10^{-7}	0.515	$.24 \times 10^{-6}$	3058	0.0007
4	9.1×10^{-8}	8.7×10^{-8}	1.8×10^{-7}	1.95×10^{-6}	1.34×10^{-6}	3.29×10^{-6}	3.47×10^{-7}	0.529	$.66 \times 10^{-6}$	3377	0.002

Notes: a. Analytical methods described in Appendix C.
b. Test conditions described in Section 5.2, pp 48, 53.

Table 25

DDE CONCENTRATIONS/PRODUCTION IN STACK GASES

Palo Alto Experiments

	SAMPLE										
	IMPINGER			PARTICULATE							Emission
Test No.	DDE o-p' (gm)	DDE p-p' (gm)	DDE Total (gm)	DDE o-p' (gm)	DDE p-p' (gm)	DDE Total (gm)	DDE TOTAL (gm)	Stack Sample (m³)	DDE Conc gm/m³	Stack Flow (m³/hr)	Rate (DDE) (gm/hr)
1	7.0×10^{-6}	16.6×10^{-6}	23.6×10^{-6}	2.5×10^{-7}	4.42×10^{-7}	6.9×10^{-7}	24.3×10^{-6}	0.533	45.6×10^{-6}	2979	0.14
2	13.8×10^{-6}	43.7×10^{-6}	57.5×10^{-6}	1.26×10^{-6}	4.63×10^{-6}	5.9×10^{-6}	63.4×10^{-6}	0.495	128×10^{-6}	2649	0.339
3	74.7×10^{-6}	90×10^{-6}	164×10^{-6}	173×10^{-6}	61×10^{-6}	235×10^{-6}	399×10^{-6}	0.515	773×10^{-6}	3058	2 360
4	42×10^{-6}	105×10^{-6}	147×10^{-6}	6.3×10^{-6}	34×10^{-6}	40.3×10^{-6}	187×10^{-6}	0.529	353×10^{-6}	3377	1.192

Notes:
a. Analytical methods described in Appendix C.
b. Test conditions described in Section 5.2, pp 48, 53.

Table 26
DDT CONCENTRATIONS/EMISSION RATE IN PRODUCT
Palo Alto Experiments

Test No.	o-p' DDT (gm/gm)	p-p' DDT (gm/gm)	Total DDT (gm/gm)	Product (Ash) Production Rate (gm/hr)	DDT* Emission Rate (gm/hr)	DDT Feed Rate (gm/hr)
1	5.1×10^{-9}	1.01×10^{-8}	1.5×10^{-8}	8.9×10^4	1.34×10^{-3}	6.92×10^3
2	3.3×10^{-9}	7.4×10^{-9}	1.07×10^{-8}	8.9×10^4	0.98×10^{-3}	6.92×10^3
3	1.38×10^{-8}	4.0×10^{-8}	5.38×10^{-8}	8.9×10^4	4.81×10^{-3}	1.635×10^4
4	5.3×10^{-9}	1.14×10^{-8}	1.67×10^{-8}	8.9×10^4	1.51×10^{-3}	1.635×10^4

*DDT Emission Rate in Product = DDT Concentration in Product × Product Production Rate.

DDT feed rate is reported on an active ingredient basis, rather than the total formulation.

Table 27

DDD CONCENTRATIONS/EMISSION RATE IN PRODUCT

Palo Alto Experiments

Test No.	o-p' DDD (gm/gm)	p-p' DDD (gm/gm)	Total DDD (gm/gm)	Product (Ash) Production (gm/hr)	DDD Emission Rate (gm/hr)	DDT Feed Rate (gm/hr)
1	1.8×10^{-9}	0.8×10^{-9}	2.6×10^{-9}	8.9×10^4	0.27×10^{-3}	6.92×10^3
2	1.2×10^{-8}	1.9×10^{-9}	1.39×10^{-8}	8.9×10^4	1.25×10^{-3}	6.92×10^3
3	1.07×10^{-8}	2.3×10^{-9}	1.30×10^{-8}	8.9×10^4	1.16×10^{-3}	1.64×10^4
4	2.7×10^{-9}	3.1×10^{-9}	5.8×10^{-9}	8.9×10^4	0.52×10^{-3}	1.64×10^4

a. DDT feed rate is reported on an active ingredient basis, rather than the total formulation.

Table 28
DDE CONCENTRATIONS/EMISSION RATE IN PRODUCT (ASH)
Palo Alto Experiments

Test No	o-p' DDE (gm/gm)	p-p' DDE (gm/gm)	Total DDE (gm/gm)	Product (Ash) Production (gm/hr)	DDT Emission Rate (gm/hr)	DDT Feed Rate gm/hr
1	5×10^{-9}	7×10^{-9}	1.2×10^{-8}	8.9×10^4	1.07×10^{-3}	6.92×10^3
2	3×10^{-9}	1.99×10^{-6}	1.99×10^{-6}	8.9×10^4	1.77×10^{-3}	6.92×10^3
3	5×10^{-8}	2.55×10^{-7}	3.0×10^{-7}	8.9×10^4	26.7×10^{-3}	1.64×10^4
4	1×10^{-9}	1×10^{-9}	2×10^{-9}	8.9×10^4	0.18×10^{-3}	1.64×10^4

a. DDT feed rate is reported on an active ingredient basis, rather than the total formulation.

73

Table 29
DDT CONCENTRATIONS/PRODUCTION IN SCRUBBER
Palo Alto Experiments

Test No.	SAMPLE SOLUTION o-p' (gm/l)	p-p' (gm/l)	Total (gm/l)	PARTICULATE o-p' (gm/l)	p-p' (gm/l)	Total (gm/l)	TOTAL (gm/l)	Scrubber Flow (l/hr)	Emission Rate DDT (gm/hr)
1	2.6×10^{-6}	6.1×10^{-7}	1.16×10^{-6}	2.7×10^{-8}	7.1×10^{-8}	1.2×10^{-7}	1.27×10^{-6}	7.5×10^{4}	0.105
2	1.2×10^{-7}	3×10^{-7}	4.2×10^{-7}	7.6×10^{-8}	4.2×10^{-7}	5×10^{-7}	9.1×10^{-7}	7.5×10^{4}	0.068
3	8×10^{-9}	5.7×10^{-7}	6.5×10^{-7}	1.3×10^{-7}	1.3×10^{-7}	2.2×10^{-7}	2.9×10^{-7}	7.5×10^{4}	0 022
4	4.8×10^{-9}	1.03×10^{-7}	1.1×10^{-7}	1.28×10^{-6}	4.9×10^{-6}	6.2×10^{-6}	6.3×10^{-6}	$7 5 \times 10^{4}$	0 47

Notes:
a. Analytical methods described in Appendix C.
b. Test conditions described in Section 5.2, pp. 53.

Table 30
DDD CONCENTRATIONS/PRODUCTION IN SCRUBBER
Palo Alto Experiments

Test No.	SAMPLE SOLUTION o-p' (gm/l)	p-p' (gm/l)	Total (gm/l)	PARTICULATE o-p' (gm/l)	p-p' (gm/l)	Total (gm/l)	TOTAL (gm/l)	Scrubber Flow (l/hr)	Emission Rate DDD (gm/hr)
1	7.1×10^{-7}	1.02×10^{-6}	1.7×10^{-6}	3.5×10^{-8}	3.5×10^{-8}	7.0×10^{-8}	1.79×10^{-6}	7.5×10^{4}	0.134
2	6.1×10^{-7}	1.1×10^{-7}	7.2×10^{-7}	2.2×10^{-7}	2.3×10^{-7}	4.5×10^{-7}	1.17×10^{-6}	7.5×10^{4}	0.087
3	3×10^{-7}	2.7×10^{-8}	3.3×10^{-7}	5.9×10^{-8}	1.2×10^{-7}	1.8×10^{-7}	5.05×10^{-7}	7.5×10^{4}	0.038
4	1.9×10^{-7}	9×10^{-9}	2×10^{-7}	2.9×10^{-8}	3.3×10^{-7}	3.6×10^{-7}	5.6×10^{-7}	7.5×10^{4}	0 042

Notes:
a. Analytical methods described in Appendix C.
b. Test conditions described in Section 5.2, pp. 53.

74

Table 31
DDE CONCENTRATIONS/PRODUCTION IN SCRUBBER
Palo Alto Experiments

Test No.	SAMPLE SOLUTION o-p' (gm/l)	p-p' (gm/l)	Total (gm/l)	PARTICULATE o-p' (gm/l)	p-p' (gm/l)	Total (gm/l)	TOTAL (gm/l)	Scrubber Flow (l/hr)	Emission Rate DDE (gm/hr)
1	3.8×10^{-7}	8.1×10^{-6}	8.4×10^{-6}	1.22×10^{-7}	8.7×10^{-6}	8.84×10^{-6}	17.3×10^{-6}	7.5×10^{4}	1.23
2	8.6×10^{-7}	1.01×10^{-6}	1.87×10^{-6}	$5\ 7 \times 10^{-7}$	11×10^{-6}	11.7×10^{-6}	13.6×10^{-6}	7.5×10^{4}	1.02
3	4.4×10^{-7}	4.8×10^{-7}	9.2×10^{-7}	4.8×10^{-6}	13.3×10^{-6}	17.1×10^{-6}	18.0×10^{-6}	7.5×10^{4}	1 21
4	5.4×10^{-7}	5.6×10^{-7}	6×10^{-7}	2.7×10^{-6}	11.4×10^{-6}	14.1×10^{-6}	14.7×10^{-6}	7.5×10^{4}	1.10

Notes:
a. Analytical methods described in Appendix C.
b. Test conditions described in Section 5.2, pp. 53.

Table 32
SUMMARY OF PALO ALTO DDT COMBUSTION EXPERIMENTS
Emission Rates in Various Streams

Test No.	PRODUCT DDT (gm/hr)	DDD (gm/hr)	DDE (gm/hr)	Total (gm/hr)	AIR STREAM DDT (gm/hr)	DDD (gm/hr)	DDE (gm/hr)	Total (gm/hr)	SCRUBBER DDT (gm/hr)	DDD (gm/hr)	DDE (gm/hr)	Total (gm/hr)	All Effluents Total (gm/hr)
1	1.34×10^{-3}	0.27×10^{-3}	1.07×10^{-3}	.0027	0.015	0.002	0.14	0.157	0.105	0.134	1.23	1.47	1.63
2	0.98×10^{-3}	1.25×10^{-3}	177×10^{-3}	.179	0.015	0.0012	0.339	0.355	0.068	0.087	1.02	1.18	1 71
3	4.81×10^{-3}	1.16×10^{-3}	26.7×10^{-3}	.033	0.116	0.0007	2.36	2.48	0.022	0.038	1.21	1.27	3.78
4	1.51×10^{-3}	0.52×10^{-3}	0.18×10^{-3}	.0029	0.022	0.002	1.192	1.22	0.47	0.042	1.10	1 61	2.83

Table 33
EFFICIENCY OF DESTRUCTION (DDT)
Palo Alto Experiments

Test No.	DDT Feed gm/hr	Emission Rate Total Effluent (DDT + DDD + DDE) gm/hr	% Efficiency of Destruction*
1	6.92×10^3	1.63	99.970
2	6.92×10^3	1.71	99.975
3	1.64×10^4	3.78	99.977
4	1.64×10^4	2.83	99.983

$$* \text{ \% Efficiency of Destruction} = \frac{\text{DDT Feed Rate} - \text{(DDT + DDD + DDE) Emission Rate}}{\text{DDT Feed Rate}} \times 100$$

a. DDT feed rate is reported on an active ingredient basis, rather than the total formulation.

One further observation can be made from the data in the last column of Table 32. In spite of the excessive excursion in the third hearth temperature mentioned above, we note that the average value for the total effluents as given for test numbers 3 and 4 is less than twice that for the average of that for test numbers 1 and 2. This result suggests that the factors responsible for the incomplete reduction of the input DDT are not seriously affected by the feed ratio at least up to a ratio of 5 grams of DDT per 100 grams of sludge.

5.5 Analytical Results of 2,4,5-T Experiments

As indicated above, 2,4,5-T solution injection was accomplished by mixing the pesticide solution into the scum feed line outside of the furnace. As before, samples were taken of the scrubber water, the exhaust air stream, the ash and the mixed scum/2,4,5-T solution. Analysis was accomplished by the methods outlined in Appendix C with results that are displayed in Tables 34 and 35. Here, as before, spot checks made to determine the presence of dioxin yielded negative results. In addition to the data in Tables 34 and 35, several typical chromatograms are included in Appendix C.

5.6 Results of 2,4,5-T Experiments

Using the results of the analyses, the efficiency of destruction shown in these experiments can be computed. Using the feed data as well as the summarized analytical results, 99.99 + destruction percentages were found as displayed in the last column of Table 36.

As for the DDT results, the principal source of throughput of 2,4,5-T seems to be in the scrubber. Since, in practice the scrubber effluent is returned to the plant for recycling, there is every reason to believe that the efficiency values shown in Table 36 are conservative. It is also reassuring to note that the efficiency of destruction does not seem to be affected by the observed feed rate.

Table 34
2,4,5-T CONCENTRATIONS VARIOUS EFFLUENT STREAMS
Palo Alto Experiments

Test No.	SCRUBBER			AIR STREAM			Product (Ash)
	Particulate (g/l)	Solution (g/l)	Total (g/l)	Particulate (g/l)	Solution (g/l)	Total (g/l)	(g/l)
9	1.28×10^{-8}	1.31×10^{-6}	1.33×10^{-6}	1.5×10^{-9}	1.88×10^{-7}	1.89×10^{-7}	6.0×10^{-10}
10	6.5×10^{-9}	1.47×10^{-6}	1.47×10^{-6}	9.8×10^{-9}	9.11×10^{-8}	1.0×10^{-7}	3.5×10^{-9}
11	2.9×10^{-9}	1.6×10^{-6}	1.63×10^{-6}	7.0×10^{-10}	5.89×10^{-7}	5.9×10^{-7}	1.1×10^{-9}
12	1.11×10^{-7}	4.74×10^{-6}	4.85×10^{-6}	3.56×10^{-7}	4.74×10^{-7}	8.30×10^{-7}	7.0×10^{-10}

Table 35
MASS BALANCE 2, 4, 5-T EXPERIMENTS*

Palo Alto Experiments

Test No.	Emission Rate 2,4,5-T in Air Stream (gm/hr)	Emission Rate 2,4,5-T in Scrubber (gm/hr)	Emission Rate 2,4,5-T in Product (gm/hr)	Total Emission Rate All Effluents (gm/hr)	Input 2,4,5-T Feed Rate (gm/hr)
9	1.33×10^{-3}	9.98×10^{-2}	5.34×10^{-5}	0.102	1.108×10^{3} gm/hr
10	9.66×10^{-4}	1.10×10^{-1}	3.1×10^{-4}	0.111	1.108×10^{3} gm/hr
11	3.47×10^{-3}	1.22×10^{-1}	9.8×10^{-5}	0.126	3.450×10^{3} gm/hr
12	5.74×10^{-3}	3.6×10^{-1}	6.2×10^{-5}	0.366	3.450×10^{3} gm/hr

*Tetrachlordioxin was not found in any sample.

2,4,5-T feed rate is reported on an active ingredient basis, rather than the total formulation.

Table 36
SUMMARY 2, 4, 5-T EXPERIMENTS
Palo Alto Experiments

Test No.	2, 4, 5-T Feed Rate (gm/hr)	Feed Form	Total Emission Rate 2, 4, 5-T in Exhaust Streams (gm/hr)	Efficiency of Destruction* (%)
9	1.108×10^3	Solution	0.102	99.991
10	1.108×10^3	Solution	0.111	99.990
11	3.45×10^3	Solution	0.126	99.996
12	3.45×10^3	Solution	0.366	99.990

Average 99.992 %

*Efficiency of Destruction $= \dfrac{2, 4, 5\text{-T Feed Rate}- 2, 4, 5\text{-T Emission Rate}}{2, 4, 5\text{-T Feed Rate}} \times 100$

2,4,5-T feed rate is reported on an active ingredient basis, rather than the total formulation.

5.7 Summary of Full Scale Experiments

DDT DESTRUCTION EFFICIENCY
Full Scale Experiments

Preparation	Feed Hearth	Feed Ratio (gm/gm)	Avg. Hearth Temp (C°)	AB* Temp (C°)	% Dest. Eff. (%)
Solid	1st	0.02	629	638	99.97
Solid	1st	0.02	634	649	99.98
Solid	1st	0.05	628	663	99.98
Solid	1st	0.05	659	649	99.98

*AB - Afterburner

2,4,5-T DESTRUCTION EFFICIENCY
Full Scale Experiments

Preparation	Feed Hearth	Feed Ratio (gm/gm)	Avg. Hearth Temp (C°)	AB* Temp (C°)	% Dest. Eff. (%)
Solution	3rd	.012	700	677	99.99
Solution	3rd	.012	677	655	99.99
Solution	3rd	.038	691	644	99.996
Solution	3rd	.038	698	663	99.99

*AB - Afterburner

5.8   References

(1)   "Mechanical Engineer's Handbook", T. Baumeister, Ed., McGraw Hill, 1958 pp. 4-69.

(2)   "Handbook of Chemistry and Physics", Chem. Rubber Pub. Co., 13th Edition pp 1396 ff., 1947.

6.0 POSSIBLE APPLICATION OF MULTIPLE HEARTH COINCINERATION OF PESTICIDES

6.1 Furnace and Feed Conditions Required

In order to put the work reported above into the proper context it is important to demonstrate the probable utility of this method of the destruction of refractory organic compounds by coincineration with sewage sludge. The results reported above suggest that such compounds as DDT and 2,4,5-T are effectively destroyed, and that the total of toxic effluents from the process is well below tolerance levels, provided that the appropriate furnace conditions are met. To briefly review the conditions under which such effects have been obtained, the following range of furnace operational parameters appear to offer effective destruction:

1. Afterburner should be operated at a temperature not below 650 C (1200 F) with the normal dwell time on the order of a few hundred milliseconds. When the feed is introduced into the scum port on the third hearth, the upper two hearths adequately serve as afterburner and thus obviate the necessity of an auxiliary afterburner. There is no evidence from this work suggesting that afterburner temperatures higher than the normal range will serve a useful purpose.

2. Individual mid-hearth temperatures should not be allowed to drop below 500 C (930 F), since there is some evidence to suggest the formation of significant amounts of intermediate products such as DDE from DDT under lower temperature conditions.

3. There is apparently no effect due to the ratio of pesticide feed to sludge feed at least up to a maximum of 5 per cent by dry weight.

4. An efficient scrubber system is mandatory, since there is evidence of relatively large amounts of the pesticide and its intermediate products being entrained in/or on the fly ash particles which are effectively removed by the scrubber.

5. There seems to be no significant differences noted between the several options for the pesticide feed — either as solution feed on the third hearth or as solid feed on the first hearth. In spite of the observed fact that the destruction ratio is the same for solid powder as for liquid preparation feed, there are practical considerations which strongly suggest the latter as the most useful and least complicated feed method. This topic will be discussed in some detail below.

6.2 Applicability of MHF Coincineration to Other Refractory Organic Compounds

Although the detailed chemistry of the processes that evidently occur in the furnace is by no means clear, it seems evident that the high efficiency of destruction for DDT and for 2,4,5-T by this method allows the cautious extrapolation that the method should be equally applicable to a wide variety of compounds having similar structure to the test compounds. Thus, it would appear that similar destruction ratios should be available for such compounds as:

a. The chlorinated (halogenated) biphenyls and related compounds, which would include:

DDT	Orthotian
DDD	Tedion
DDE	Tetradiphon
TDE	DFDT (fluorine analog of DDT)
DFDT	chlorobenside
Perthane	chlorobenzilate
Rhothane	Dilan
Mitox	DCPC
Methoxychlor	DMC
Ovotian	Kelthane
Ovotox	
Prolan	
Balan	

b. Chlorinated cyclopentadienes, which would include:

Chlordane

Heptachlor

Aldrin

Dieldrin

Endrin

Endosulfor

Heptachlor epoxide

Lindane

c. Phenoxy and benzoic acid derivatives:

2,4,5-T

Amiben

2,4-D

4-(2,4-DB)

MCPA

Methoxone

Agrosone

Methoxone B

MCPP

polychlorobenzoic acid

Silvex

trichlorobenzoic acid

In the absence of a detailed understanding of the chemical processes involved in multiple hearth furnace coincineration of refractory organic compounds, of course, it would be absolutely necessary to conduct tests quite similar to those reported here in order to apply these conclusions to compounds other than those actually studied. We can only say that a good probability appears to exist for effective destruction of the above materials.

Unfortunately, the studies reported herein allow no reasonable extrapolation as to the probability of a safe and effective destruction of the phosphorus and the carbamate pesticides. Only appropriate studies similar to those reported herein would allow such an extrapolation.

6.3   Availability of Multiple Hearth Sewage Sludge Incineration

There are at present a large number of operating multiple hearth furnaces widely distributed throughout the United States as is shown in Appendix D, which is a partial listing of such installations.

6.4   Feed Arrangements for Large Scale Destruction of Toxic Compounds

As has been pointed out above (Section 5.2) considerable physical and mechanical difficulty was experienced in feeding the powder preparation directly into the sludge at the top hearth. It appears that the final centrifugal dewatering is most conveniently accomplished in very close proximity of the actual sludge feed line to the upper hearth so that the only available site for powder injection would seem to be following the centrifuge. Necessity for control of the finer particulates of the preparation, coupled with the inconvenience of the process of transferring a solid preparation from its container to an appropriate feed system, suggest that solid preparation injection is less practical than a liquid feed method.

On the other hand, the use of a solvent increases disposal costs and probably would require petroleum products. However, the accessibility of the scum feed line and the ease with which provisions can be made for liquid (solution) injection into the scum line suggests that this method of injection of hazardous compounds is certainly the most reasonable from an operational viewpoint. For those materials not already in solution, it would be necessary to prepare a slurry or, if possible, a solution prior to their being injected into the furnace. Control of the rate of injection should be reasonably simple for such solution or slurries.

6.5   Safety Precautions

The required safety precautions for coincineration of hazardous materials involve the protection of operating personnel, the protection of the facility itself and finally the control and monitoring of the various effluent streams to be assured that the emissions are well within regulations.

Personnel protection can best be accomplished by utilizing an essentially closed system. The incoming containers of hazardous materials would be handled by normal industrial procedures for such materials as they are opened and connected to the feed pump/metering system whereby the material is pumped into the scum line.

Protection of the facility is best accomplished by the procedures of handling the incoming material and by careful control of the operating conditions within the furnace and its associated equipment. Even though HCl is produced by the combustion of chlorinated organic compounds, the rate of production is sufficiently low, for the feed ratios studied herein, that no significant corrosion problem should be encountered.

As has been demonstrated by this work, the feed ratios and the furnace conditions reported result in emission of toxic or hazardous compounds below acceptable levels. On the other hand, there is no absolute guarantee that the furnace operations will always be controlled within the limits set by these experiments. Under these conditions it would seem desirable to provide for at least periodic sampling of the emergent streams from the furnace (especially the stack gases) to be assured that the emissions are in fact within the required limits.

The essential difficulty with the analysis of stack gases for trace quantities of such compounds as the chlorinated pesticides or their possible decomposition products lies in the fact that rather elaborate measures must be taken in order to unambiguously determine the levels of such compounds. In view of this requirement there seems to be no reasonable method of obtaining real time control of the pesticide feed using the effluent level as input data.

As an alternative, we suggest that a feedback control system using the hearth temperature of the upper four (4) hearths, the O_2 content of the stack gas and perhaps the afterburner temperature could be used to control pesticide feed. In such a system, if any of the measured variables were to fall outside of predetermined limits, the system would automatically shut down the pesticide feed. In order to implement such a system it would be necessary to conduct a study of the effect of extreme excursions in hearth temperature and excess air in order to determine the critical levels of such parameters. Although it was the original intention of this study to carry out such an experiment, it was decided that the dangers inherent in such an experiment were such as to require a great deal more information prior to attempting such a parametric variation.

The previously mentioned increase in DDE production which correlates to a dramatic downward excursion in third hearth temperature at Palo Alto, suggests that DDE production might offer a safe and meaningful label for a study of extreme conditions.

87

7.0 DISCUSSION AND RECOMMENDATIONS

The experimental results reported here seem to bear out the original premise that the presence of burning sludge containing significant quantities of metallic ions (iron) in an atmosphere containing excess oxygen should cause the destruction of refractory organic compounds at temperatures considerably lower than those required for simple burning of the organic compound in oxygen. Further, the procedure can be implemented for the routine destruction of large quantities of such pesticides as DDT with only minimal modifications being required in the typical municipal plant. The state of the pesticide (solid or solution) appears to make little difference in the effectiveness of multiple hearth coincineration. A number of incidental observations suggest, however, that the solution feed is more practical than the solid feed.

In order to feed a dry (solid) preparation into the furnace the preparation must be pre-mixed into the sludge — a requirement which introduces a number of practical problems. Sludge feed is ordinarily accomplished at the top hearth of the furnace through a screw or belt feed which carries the dewatered sludge from the centrifugal separators. Mixing the pesticide powder would probably have to be accomplished in the physical space between the centrifuge and the furnace input. This requires that the container be lifted to the furnace top and the contents transferred to a suitable metering device in the somewhat restricted area at the furnace top. This procedure was followed during the Palo Alto experiments with results that were less than satisfactory, primarily because of the physical properties of the DDT powder preparation. There seemed no reasonable way to open the containers and transfer their contents to the metering device without the escape of at least some of the finer dust.

Although DDT is not acutely toxic on inhalation, the exposure to DDT dust over a period of some ten hours seemed to produce an irritation resembling an upper respiratory infection — the irritation lasted some 24 to 36 hours. This problem could, of course, be handled by providing the operational personnel with suitable dust protection equipment, but such an approach can only

88

aggravate the emotional problems of the operating personnel associated with handling "dangerous materials". In this context, the reaction at Palo Alto of the regular operating personnel is probably typical. It was necessary to spend a considerable amount of time explaining the nature of the experiment and in a candid and quite detailed discussion of the potential hazards involved in handling the DDT. In spite of what appeared to be an entirely satisfactory response to this briefing, the presence of an inevitable white film in the furnace top area due to the escaping dust caused considerable alarm. Thus for a variety of reasons, both practical and psychological, it seems that the best results will be obtained by using solution feed in the coincineration of pesticides.

Apparently it is quite routine for multiple hearth sewage sludge incineration to be equipped with a scum injection system feeding the second or third hearth. It is a simple matter to arrange to pump the solution to be destructed from the furnace floor into the scum line to effect injection of the pesticide. In this way, the handling of the material, the control of contamination and the metering of the feed rate should be easily controlled and greatly simplified.

8.0 CONCLUSIONS AND OBSERVATIONS

As a result of the experimental study on both prototype and full scale multiple hearth sewage sludge furnaces, several results have been obtained.

1. Solid DDT mixed with sludge and subsequently fed on the top hearth (normal sludge feed) shows destruction efficiencies in excess of 99 per cent in the absence of an afterburner. This result appears to be independent of feed ratio up to 5 per cent of DDT preparation per dry weight of sludge.

2. Solid DDT mixed with sludge and subsequently fed on the top hearth shows destruction efficiencies in excess of 99.9 per cent, essentially independent of the afterburner temperature provided the latter is at least 760 C (1400 F) (these results obtained with afterburner residence hold times on the order of 1 to 4 milliseconds) and independent of feed ratio up to 5 per cent of preparation per dry weight of sludge.

3. DDT solutions mixed with sludge and subsequently fed on the third hearth through the scum feed line show destruction efficiencies in excess of 99.9 per cent independent of feed ratio up to 5 per cent of the preparation in sludge (dry) and independent of the afterburner temperature or afterburner holding time.

4. 2,4,5-T solutions mixed with sludge and subsequently fed on the third hearth through the scum feed line show destruction efficiencies in excess of 99.99 per cent independent of the feed ratio up to 5 per cent of the preparation in sludge (dry) and independent of the afterburner holding time and temperature.

5. The results quoted above are found to be conservative since the destruction efficiencies have been found to be an order of magnitude better in the full scale experiments than was the case for the prototype scale experiments. This fact may well be attributed to the artifacts introduced by the use of a partially recycled scrubber water system in the prototype experiments.

6. The observation that a significant fraction of the pesticide
   (and its immediate derivatives in the case of DDT), appears in the
   scrubber water (which, in practice, is returned to the plant
   for recycling), indicates that the destruction efficiencies
   reported here are quite conservative.

7. In general, the results obtained in the prototype experiments
   at Brisbane adequately predicted the results obtained in the
   full scale experiments at the Palo Alto municipal incinerator.

8. There is some evidence (tests 3 and 4 at Palo Alto) that it is
   important to maintain the internal hearth temperatures in
   excess of 550-600 C (1000-1100 F) in order to minimize the
   release of such products as DDE.

9. The results of this study indicate that under the proper
   conditions DDT and 2,4,5-T can be safely destroyed by coincineration
   with sewage sludge in a multiple hearth incinerator.

APPENDIX A

DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

(From Standards of Performance for New Stationary
Sources, Federal Register vol. 36, no. 247)

1. PRINCIPLE AND APPLICABILITY.

1.1 Principle. Particulate matter is with-drawn isokinetically from the source and its weight is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary souces only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. APPARATUS.

2.1 Sampling train. The design specifications of the particulate sampling train used by EPA are described in APTD-0581. Commercial models of this train are available.

2.1.1. Nozzle - Stainless steel with sharp, tapered leading edge.

2.1.2 Probe - Pyrex glass with a heating system capable of maintaining a minimum gas temperature of 250°F. at the exit end during sampling to prevent condensation from occuring. When length limitations (greater than about 8 ft.) are encountered at temperatures less than 600°F., Incoloy 825, or equivalent, may be used. Probes for sampling gas streams at temperatures in excess of 600°F, must have been approved by the Administrator.

2.1.3 Pitot tube - Type S, or equivalent, attached to probe to monitor stack gas velocity.

2.1.4 Filter Holder - Pyrex glass with heating system capable of maintaining minimum temperature of 225°F.

2.1.5 Impingers/Condenser - Four impingers connected in series

with glass ball joint fittings. The first, third, and fourth impingers are of the Greenburg-Smith design, modified by replacing the tip with a .1/2 inch ID glass tube extending to one-half inch from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip. A condenser may be used in place of the impingers provided that the moisture content of the stack gas can still be determined.

2.1.6 Metering system - Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within $5^{\circ}F.$, dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer - To measure atmospheric pressure to $\pm$ 0.1 inches Hg.

2.2 Sample recovery.

2.2.1 Probe brush - At least as long as probe.

2.2.2 Glass wash bottles - Two.

2.2.3 Glass sample storage containers.

2.2.4 Graduated cylinder - 250 ml.

2.3 Analysis

2.3.1 Glass weighing dishes.

2.3.2 Desiccator.

2.3.3 Analytical balance - To measure to $\pm$ 0.1 mg.

2.3.4 Trip balance - 300 g. capacity to measure to $\pm$ 0.05 g.

3. REAGENTS

3.1 Sampling.

3.1.1 Filters - Glass fiber or equivalent, numbered for identification and preweighed.

96

3.1.2 Silica gel - Indicating type, 6-16 mesh, dried at 175°C. (350°F) for 2 hours.

3.1.3 Water.

3.1.4 Crushed ice.

3.2 Sample recovery.

3.2.1 Acetone - Reagent grade.

3.3. Analysis.

3.3.1 Water.

3.3.2 Desiccant - Drierite indicating.

4. PROCEDURE

4.1. Sampling.

4.1.1 After selecting the sampling site and the minimum number of sampling points, determine the stack pressure, temperature, moisture, and range of velocity head.

4.1.2 Preparation of collection train. Weigh to the nearest gram approximately 200 g. of silica gel. Label a filter of proper diameter, disiccate for at least 24 hours and weigh to the nearest 0.5 mg. in a room where the relative humidity is less than 50%. Place 100 ml. of water in each of the first two impingers, leave the third impinger empty, and place approximately 200 g. of preweighed silica gel in the fourth impinger. Set up the train without the probe. Leak check the sampling train at the sampling site by plugging up the inlet to the filter holder and pulling a 15 in. Hg vacuum. A leakage rate not in excess of 0.02 c.f.m. at vacuum of 15 in. Hg is acceptable. Attach the probe and adjust the heater to provide a gas temperature of about 250°F. at the probe outlet. Turn on the filter heating system. Place crushed ice around the impingers, add more ice during the run to keep the temperature of the gases leaving the last impinger as low as possible and preferably at 70°F., or less. Temperatures above 70°F. may result in damage to the dry gas meter from either moisture condensation or excessive heat.

4.1.3 Particulate train operation. For each run, record the data required on the example sheet shown in Figure 5-2. Take readings

97

at each sampling point, at least every 5 minutes, and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 minutes at .each traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without computations. APTD-0576 details the procedure for using these nomographs. Turn off the pump at the conclusion of each run and record the final readings. Remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in section 4.2

4.2 Sample recovery. Exercise care in moving the collection train from the test site to the sample recovery area to minimize the loss of collected sample or the gain of extraneous particulate matter. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. Measure the volume of water from the first three impingers,then discard. Place the samples in containers as follows:

Container No. 1. Remove the filter from its holder, place in this container, and seal.

Container No. 2. Place loose particulate matter and acetone washings from all sample-exposed surfaces prior to the filter in this container and seal. Use a razor blade, brush, or rubber policeman to lose adhering particles.

Container No. 3. Transfer the silica gel from the fourth impinger to the original container and seal. Use a rubber policeman as an aid in removing silica gel from the impinger.

4.3 Analysis. Record the data required on the example sheet shown

in Figure 5-3. Handle each sample container as follows:

Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a tared glass weighing dish, desiccate,and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 2. Transfer the acetone washings to a tared beaker and evaporate to dryness at ambient temperature and pressure. Desiccate and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 3. Weigh the spent silica gel and report to the nearest gram.

5. CALIBRATION

Use methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter and probe heater. Recalibrate after each test series.

6. CALCULATIONS

6.1 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.2 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70°F. 29.92 inches Hg) by using Equation 5-1

$$Vm_{std} = V_m \left(\frac{T_{std}}{T_m} \right) \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right) =$$

$$\left(17.71 \ \frac{°R}{In. \ Hg} \right) V_m \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{Tm} \right)$$

equation 5-1

99

PLANT_____

LOCATION_____

OPERATOR_____

DATE_____

RUN NO._____

SAMPLE BOX NO._____

METER BOX NO._____

METER $\triangle$ H@_____

C FACTOR_____

AMBIENT TEMPERATURE_____

BAROMETRIC PRESSURE_____

ASSUMED MOISTURE, %_____

HEATER BOX SETTING_____

PROBE LENGTH, m._____

NOZZLE DIAMETER, in._____

PROBE HEATER SETTING_____

SCHEMATIC OF STACK CROSS SECTION

TRAVERSE POINT NUMBER	SAMPLING TIME (e) min.	STATIC PRESSURE (P_s) inHg	STACK TEMP. (T_s)°F	VELOCITY HEAD $(\triangle P_s)$	ORIFICE PRESSURE DIFFERENTIAL $(_\triangle H)$ In. H_2O	GAS SAMPLE VOLUME (Vm)ft.^{3}	GAS SAMPLE TEMPERATURE AT DRY GAS METER		SAMPLE BOX TEMPERATURE °F	TEMPERATURE OF GAS LEAVING LAST IMPINGER °F
							INLET (Tm_{in})°F	OUTLET (Tm_{out})°F		
TOTAL							avg.	avg.		
AVERAGE							avg.			

Figure 5.2   Particular field data.

where:

Vm_{std} = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, $530°R$.

T_m = Average dry gas meter temperature, $°R$.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

H = Average pressure drop across the orifice meter, inches H_2O.

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.3 Volume of water vapor.

$$V_{w_{std}} = V_{l_c} \left(\frac{pH_2O}{M_{H_2O}} \quad \frac{RT_{std}}{P_{std}} \right) = \left(0.0474 \frac{cu. \ ft.}{ml.} \right) V_{l_c}$$

equation 5-2

where:

$V_{w_{std}}$ = Volume of water vapor in the gas sample (standard conditions), cu. ft.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

pH_2O = Density of water, 1 g./ml.

M_{H_2O} = Molecular weight of water, 18 lb./lb. - mole.

R = Ideal gas constant, 21.83 inches Hg - cu.ft./lb. mole-$°R$.

T_{std} = Absolute temperature at standard conditions, $530°R$.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

101

6.4 Moisture content.

$$B_{wo} = \frac{V_{w_{std}}}{V_{m_{std}} + V_{w_{std}}}$$

equation 5-3

where:

B_{wo} = Proportion by volume of water vapor in the gas stream, dimensionless.

$V_{w_{std}}$ = Volume of water in the gas sample (standard conditions), cu. ft.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

6.5 Total particulate weight. Determine the total particulate catch from the sum of the weights on the analysis data sheet (Figure 5-3)

6.6 Concentration.

6.6.1 Concentration in gr./s.c.f.

$$c'_s = \left(0.0154 \frac{gr.}{mg.}\right) \left(\frac{M_n}{V_{m_{std}}}\right)$$

equation 5-4

where:

c'_s = Concentration of particulate matter in stack gas, gr./s.c.f., dry basis.

M_a = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

102

6.6.2 Concentration in lb/.cu.ft.

$$c_s = \frac{\left(\frac{1}{453,600}\ \frac{lb}{mg}\right)M_n}{V_{m_{std}}} = 2.205 \times 10^{-6}\frac{M_n}{V_{m_{std}}}$$

equation 5-5

where:

c_s = Concentration of particulate matter in stack gas, lb./s.c.f., dry basis

$453,600$ = Mg/lb.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

6.7 Isokinetic variation.

$$I = \frac{T_s\left[\frac{V_{l_c}\ (pH_2O)R}{M_{H_2O}} + \frac{V_m}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{\theta V_s P_s A_n} \times 100$$

$$= \frac{T_s\left(1.667\ \frac{min.}{sec.}\right)\left[\left(0.00267\ \frac{in.\ Hg-cu.ft.}{ml.-\ ^\circ R}\right)V_{l_c} + \frac{V_m}{T_m}\left(P_{bar} + \frac{\Delta H}{13.6}\right)\right]}{\theta\ V_s P_s A_n}$$

Equation 5-6

where:

I = Percent of isokinetic sampling.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (See Fig. 5-3), ml.

pH_2O = Density of water, 1 g./ml.

R = Ideal gas constant, 21.83 inches Hg-cu.ft./lb. mole-$^\circ$R

M_{H_2O} = Molecular weight of water, 18 lb./lb-mole.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_m = Absolute average dry gas meter temperature (see Figure 5-2), $^{\circ}R$.

P_{bar} = Barometric pressure at sampling site, inches Hg.

ΔH = Average pressure drop across the orifice (see Figure 5-2), inches H_2O.

T_s = Absolute average stack gas temperature (see Figure 5-2), $^{\circ}R$.

θ = Total sampling time, min.

V_s = Stack gas velocity calculated by Method 2, Equation 2-2, ft./sec.

P_s = Absolute stack gas pressure, inches Hg.

A_n = Cross-sectional area of nozzle, sq. ft.

6.8 Acceptable results. The follwing range sets the limit on acceptable isokinetic sampling results:

If $90\% \leq I \leq 110\%$, the results are acceptable; otherwise, reject the results and repeat the test.

7. OPERATING NOMOGRAPH FOR ISOKINETIC SAMPLING

The correction factor nomograph and the operating nomograph have been designed for use with the sampling train as aids for rapid isokinetic sampling rate adjustments and for selection of a convenient nozzle size. To determine the correction factor, C, on the nomograph, the following information is first required:

1. Percent moisture, $(\% \ H_2O.)$ This may be determined from a previous test or presurvey, or before the sample run.

2. Orifice calibration factor, $\Delta H@$. This is determined from the calibration sheet. Use the $\Delta H@$ corresponding to 2". If a "C" value cannot be obtained, use a higher or lower $\Delta H@$ corresponding to higher or lower manometer reading from the calibration sheet until "C" is obtained.

3. Meter temperature, T_m. Temperature at the meter rises above ambient temperature because of the pump and can easily be estimated with experience. An estimate within $10^{\circ}F$ (approximately $\pm$ 1 percent error) is all that is necessary (an initial estimate of about $25^{\circ}F$ above ambient temperature has been used).

4. Stack pressure, P_s. This is measured before the sample run; or if the sampling site is near the exit of the stack, atmospheric pressure is used.

5. Meter pressure, P_m. Same as atmospheric pressure.

To obtain correction factor, C

1. Draw line from $\Delta H@$ to T_m to obtain point "A" on reference line 1 (REF 1).

2. Draw line from point "A" to $\% \ H_2O$ to obtain point "B" on reference line 2 (REF 2).

3. Draw line from point "B" to the calculated value P_s/P_m to obtain correction factor, C.

105

To select the nozzle size and to set the K-factor on the oper-
ating nomograph, the following information is first required:

1. C factor. This is obtained from the correction-factor
   nomograph (Figure 9).

2. Stack temperature, T_s. This is determined in $^\circ F$ by a
   rough temperature traverse to within $\pm$ 25$^\circ F$ before the
   sample run.

3. Average velocity pressure, ΔP. This is determined by a
   rough preliminary pitot traverse, using the average of
   minimum and maxiumu ΔP's in inches of water.

4. Available nozzle sizes, D.

To select the nozzle size and to set the K-factor pivot point,
use the following procedure (Figure 8):

1. Set correction factor, C, on sliding scale to the refer-
   ence mark, "A".

2. Align T_s with average ΔP, note probe tip diameter on D
   scale, and select exact nozzle closest to it.

3. Align T_s with exact nozzle size selected and obtain a $.45$
   value on the ΔP scale.

4. Align the P value with reference mark, "B" on ΔH Scale,
   and set the K-factor pivot point.

To obtain the orifice meter setting, ΔH, for isokinetic con-
ditions after the K-factor pivot point has been set, use the follow-
ing procedure (Figure 8):

1. Position the pitobe nozzle at the sampling point.

2. Read the pitot tube ΔP.

3. Align the ΔP through the K-factor pivot point.

4. Obtain ΔH and adjust metering valves.

The nomograph assumes the following once the K-factor pivot is set:

1. T_s does not change more than 25° for $T_s < 1000^\circ F$ or 50° for $T_s > 1000^\circ F$.

2. D is not changed during the test.

3. T_m was estimated correctly and does not vary more than 10°.

4. Percent H_2O remains constant, within $\pm 1.0\%$.

5. P_s and P_m remain constant, within $\pm 1.0\%$.

Operating nomograph.

108
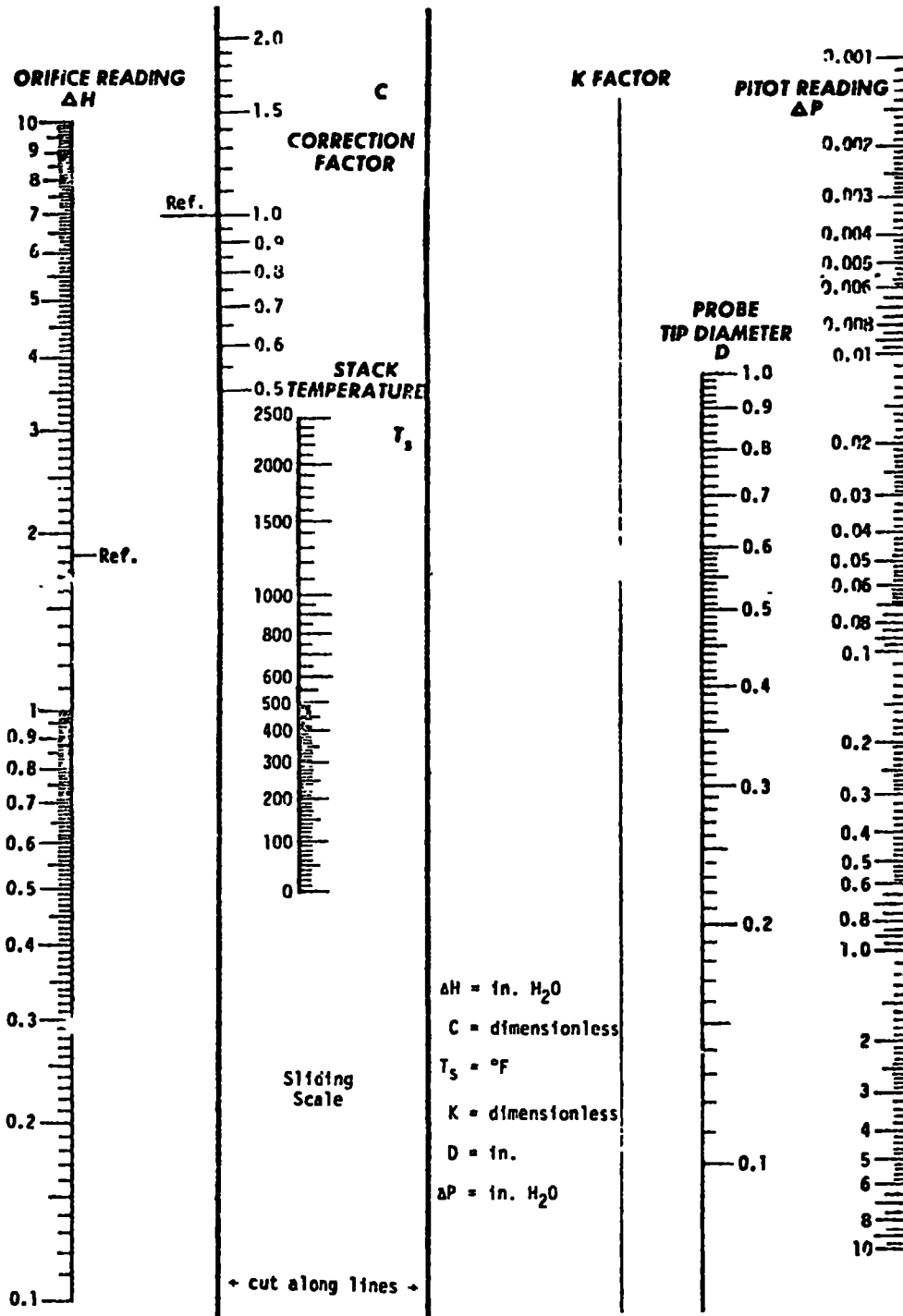
APPENDIX B

METHOD FOR ORGANOCHLORINE PESTICIDES IN INDUSTRIAL EFFLUENTS

(from National Pollutant Discharge Elimination
System, Appendix A, Federal Register vol. 38, no. 75, pt. II)

1. Scope and Application

1.1 This method covers the determination of various organochlorine pesticides, including some pesticidal degradation products and related compounds in industrial effluents. Such compounds are composed of carbon, hydrogen, and chlorine, but may also contain oxygen, sulfur, phosphorus, nitrogen or other halogens.

1.2 The following compounds may be determined individually by this method with a sensitivity of 1 μg/liter: BHC, lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, Captan, DDE, DDD, DDT, methoxychlor, endosulfan, dichloran, mirex, pentachloronitrobenzene and trifluralin. Under favorable circumstances, Strobane, toxaphene, chlordane (tech.) and others may also be determined. The usefulness of the method for other specific pesticides must be demonstrated by the analyst before any attempt is made to apply it to sample analysis.

1.3 When organochlorine pesticides exist as complex mixtures, the individual compounds may be difficult to distinguish. High, low, or otherwise unreliable results may be obtained through misidentification and/or one compound obscuring another of lesser concentration. Provisions incorporated in this method are intended to minimize the occurrence of such interferences.

2. Summary

2.1 The method offers several analytical alternatives, dependent on the analyst's assessment of the nature and extent of interferences and/or the complexity of the pesticide mixtures found. Specifically, the procedure describes the use of an effective co-solvent for efficient sample extraction; provides, through use of column chromatography

and liquid-liquid partition, methods for elimination of non-pesticide interferences and the pre-separation of pesticide mixtures. Identification is made by selective gas chromatographic separations and may be corroborated through the use of two or more unlike columns. Detection and measurement is accomplished by electron capture, micro-coulometric or electrolytic conductivity gas chromatography. Results are reported in micrograms per liter.

2.2 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Part I, Sections 1.4 and 1.5, (1).

3.2 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurement of organochlorine pesticides. Sample clean-up procedures are generally required and may result in the loss of certain organo-chlorine pesticides. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for over-coming all of the interferences that may be encountered in industrial effluents.

3.3 Polychlorinated Biphenyls (PCB's) - Special attention is called to industrial plasticizers and hydraulic fluids such as the PCB's which are a potential source of interference in pesticide analysis. The presence of PCB's is indicated by a large number of partially resolved or unresolved peaks which may occur throughout the entire chromatogram. Particularly severe PCB interference will require special separation procedures (2,3).

3.4 Phthalate Esters - These compounds, widely used as plasticizers, respond to the electron capture detector and are a source of interference in the determination of organochlorine pesticides using this detector. Water leaches these materials from plastics, such as polyethylene bottles and tygon tubing. The presence of phthalate esters is implicated in samples that respond to electron capture but not to the microcoulometric or electrolytic conductivity halogen detectors or to the flame photometric detector.

3.5 Organophosphorus Pesticides - A number of organophosphorus pesticides, such as those containing a nitro group, eg, parathion, also respond to the electron capture detector and may interfere with the determination of the organochlorine pesticides. Such compounds can be identified by their response to the flame photometric detector (4).

4. Apparatus and Materials

4.1 Gas Chromatograph - Equipped with glass lined injection port.

4.2 Detector Options:

4.2.1 Electron Capture - Radioactive (tritium or nickel 63)

4.2.2 Microcoulometric Titration

4.2.3 Electrolytic Conductivity

113

4 3   Recorder - Potentiometric strip chart (10 in.) compatible with the detector.

4.4   Gas Chromatographic Column Materials:

    4.4.1   Tubing - Pyrex (180 cm long x 4 mm ID)

    4.4.2   Glass Wool - Silanized

    4.4.3   Solid Support - Gas-Chrom Q (100-120 mesh)

    4.4.4   Liquid Phases - Expressed as weight percent coated on solid support.

        4.4.4.1   OV-1, 3%

        4.4.4.2   OV-210, 5%

        4.4.4.3   OV-17, 1.5% plus QF-1, 1.95%

        4.4.4.4   QF-1, 6% plus SE-30, 4%

4.5   Kuderna-Danish (K-D) Glassware (Kontes)

    4.5.1   Snyder Column - three ball (macro) and two ball (micro)

    4.5.2   Evaporative Flasks - 500 ml

    4.5.3   Receiver Ampuls - 10 ml, graduated

    4.5.4   Ampul Stoppers

4.6   Chromatographic Column - Chromaflex (400 mm long x 19 mm ID) with coarse fritted plate on bottom and Teflon stopcock; 250 ml reservoir bulb at top of column with flared out funnel shape at top of bulb - a special order (Kontes K-420540-9011).

4.7   Chromatographic Column - pyrex (approximately 400 mm long x 20 mm ID) with coarse fritted plate on bottom.

4 8   Micro Syringes - 10, 25, 50 and 100 µl

4.9   Separatory Funnels - 125 ml, 1000 ml and 2000 ml with Teflon stopcock.

4.10 Blender - High speed, glass or stainless steel cup.

4.11 Graduated cylinders - 100, 250 and 1000 ml.

4.12 Florisil - PR Grade (60-100 mesh); purchase activated at 1250 F
and store in the dark in glass containers with glass stoppers or
foil-lined screw caps. Before use, activate each batch overnight
at 130 C in foil-covered glass container. Determine lauric-acid
value (See Appendix I).

5. Reagents, Solvents, and Standards

5.1 Ferrous Sulfate - (ACS) 30% solution in distilled water.

5.2 Potassium Iodide - (ACS) 10% solution in distilled water.

5.3 Sodium Chloride - (ACS) Saturated solution in distilled water
(pre-rinse NaCl with hexane).

5.4 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.5 Sodium Sulfate - (ACS) Granular, anhydrous(conditioned @ 400 C for 4 hrs).

5.6 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with
distilled water.

5.7 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

　　5.7.1 Must contain 2% alcohol and be free of peroxides by
following test: To 10 ml of ether in glass-stoppered
cylinder previously rinsed with ether, add one ml of
freshly prepared 10% KI solution. Shake and let stand
one minute. No yellow color should be observed in either layer.

　　5.7.2 Decompose ether peroxides by adding 40 g of 30% ferrous sulfate
solution to each liter of solvent. CAUTION: Reaction may be
vigorous if the solvent contains a high concentration of
peroxides.

　　5.7.3 Distill deperoxidized ether in glass and add 2% ethanol.

115

5.8 Acetonitrile, Hexane, Methanol, Methylene Chloride, Petroleum
Ether (boiling range 30-60 C) - nanograde, redistill in glass
if necessary

5.9 Pesticide Standards - Reference grade.

6. Calibration

6.1 Gas chromatographic operating conditions are considered acceptable
if the response to dicapthon is at least 50% of full scale when
$\leq$ 0.06 ng is injected for electron capture detection and $\leq$ 100 ng is
injected for microcoulometric or electrolytic conductivity detection.
For all quantitative measurements, the detector must be operated
within its linear response range and the detector noise level should
be less than 2% of full scale.

6.2 Standards are injected frequently as a check on the stability of
operating conditions. Gas chromatograms of several standard
pesticides are shown in Figures 1, 2, 3 and 4 and provide reference
operating conditions for the four recommended columns.

6.3 The elution order and retention ratios of various organochlorine
pesticides are provided in Table 1, as a guide.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control
checks. When the routine occurrence of a pesticide is being observed,
the use of quality control charts is recommended (5).

7.2 Each time a set of samples is extracted, a method blank is determined
on a volume of distilled water equivalent to that used to dilute the
sample.

116

8. **Sample Preparation**

    8.1 Blend the sample if suspended matter is present and adjust pH to near neutral (pH 6.5-7.5) with 50% sulfuric acid or 10 N sodium hydroxide.

    8.2 For a sensitivity requirement of 1 µg/l, when using microcoulometric or electrolytic conductivity methods for detection, 100 ml or more of sample will be required for analysis. If interferences pose no problem, the sensitivity of the electron capture detector should permit as little as 50 ml of sample to be used. Background information on the extent and nature of interferences will assist the analyst in choosing the required sample size and preferred detector.

    8.3 Quantitatively transfer the proper aliquot into a two-liter separatory funnel and dilute to one liter.

9. **Extraction**

    9.1 Add 60 ml of 15% methylene chloride in hexane (v:v) to the sample in the separatory funnel and shake vigorously for two minutes.

    9.2 Allow the mixed solvent to separate from the sample, then draw the water into a one-liter Erlenmeyer flask. Pour the organic layer into a 100 ml beaker and then pass it through a column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K-D flask equipped with a 10 ml ampul. Return the water phase to the separatory funnel. Rinse the Erlenmeyer flask with a second 60 ml volume of solvent; add the solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

    9.3 Concentrate the extract in the K-D evaporator on a hot water bath.

9.4 Analyze by gas chromatography unless a need for cleanup is indicated. (See Section 10).

10. Clean-up and Separation Procedures

10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate whether clean-up is required. When these interfere with measurement of the pesticides, or affect column life or detector sensitivity, proceed as directed below.

10.2 Acetonitrile Partition - This procedure is used to isolate fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for specific pesticides. Of the pesticides listed in Scope (1.2) only mirex is not efficiently recovered.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125 ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 30 ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for 30-45 seconds. Extract with two 100 ml portions of

hexane by vigorously shaking about 15 seconds.

10.2.3   Combine the hexane extracts in a one-liter separatory funnel
and wash with two 100 ml portions of distilled water. Dis-
card the water layer and pour the hexane layer through a
3-4 inch anhydrous sodium sulfate column into a 500 ml K-D
flask equipped with a 10 ml ampul. Rinse the separatory
funnel and column with three 10 ml portions of hexane.

10.2.4   Concentrate the extracts to 6-10 ml in the K-D evaporator
in a hot water bath.

10.2.5   Analyze by gas chromatography unless a need for further
cleanup is indicated.

10.3   Florisil Column Adsorption Chromatography

10.3.1   Adjust the sample extract volume to 10 ml.

10.3.2   Place a charge of activated Florisil (weight determined by
lauric-acid value, see Appendix I) in a Chromaflex column.
After settling the Florisil by tapping the column, add about
one-half inch layer of anhydrous granular sodium sulfate to
the top.

10.3.3   Pre-elute the column, after cooling, with 50-60 ml of
petroleum ether. Discard the eluate and just prior to
exposure of the sulfate layer to air, quantitatively transfer
the sample extract into the column by decantation and subse-
quent petroleum ether washings. Adjust the elution rate to
about 5 ml per minute and, separately, collect up to three
eluates in 500 ml K-D flasks equipped with 10 ml ampuls.
(See Eluate Composition 10.4).

119

Perform the first elution with 200 ml of 6% ethyl ether in

petroleum ether, and the second elution with 200 ml of 15%

ethyl ether in petroleum ether. Perform the third elution

with 200 ml of 50% ethyl ether - petroleum ether and the

fourth elution with 200 ml of 100% ethyl ether.

10.3.4 Concentrate the eluates to 6-10 ml in the K-D evaporator

in a hot water bath.

10.3.5 Analyze by gas chromatography.

10.4 Eluate Composition - By using an equivalent quantity of any batch of

Florisil as determined by its lauric acid value, the pesticides will

be separated into the eluates indicated below:

6% Eluate

Aldrin	DDT	Pentachloro-
BHC	Heptachlor	nitrobenzene
Chlordane	Heptachlor Epoxide	Strobane
DDD	Lindane	Toxaphene
DDE	Methoxychlor	Trifluralin
	Mirex	PCB's

15% Eluate	50% Eluate
Endosulfan I	Endosulfan II
Endrin	Captan
Dieldrin	
Dichloran	
Phthalate esters	

Certain thiophosphate pesticides will occur in each of the above

fractions as well as the 100% fraction. For additional information

regarding eluate composition, refer to the FDA Pesticide Analytical

Manual (6).

11. Calculation of Results

11.1 Determine the pesticide concentration by using the absolute calibration procedure described below or the relative calibration procedure described in Part I, Section 3.4.2. (1).

(1) $\text{Micrograms/liter} = \dfrac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$

$A = \dfrac{\text{ng standard}}{\text{Standard area}}$

B = Sample aliquot area

V_i = Volume of extract injected (μl)

V_t = Volume of total extract (μl)

V_s = Volume of water extracted (ml)

12. Reporting Results

12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

REFERENCES

1. "Method for Organic Pesticides in Water and Wastewater," Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio 45268, 1971.

2. Monsanto Methodology for Aroclors - Analysis of Environmental Materials for Biphenyls, Analytical Chemistry Method 71-35, Monsanto Company, St. Louis, Missouri 63166, 1970.

3. "Method for Polychlorinated Biphenyls in Industrial Effluents," Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio 45268, 1973.

4. "Method for Organophosphorus Pesticides in Industrial Effluents," Environmental Protection Agency, National Environmental Research Center, Cincinnati Ohio 45268, 1973.

5. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," Chapter 6, Section 6.4, U.S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio 45268, 1973.

6. "Pesticide Analytical Manual," U.S. Dept. of Health, Education and Welfare, Food and Drug Administration, Washington, D.C.

7. "Analysis of Pesticide Residues in Human and Environmental Samples," U.S. Environmental Protection Agency, Perrine Primate Research Laboratories, Perrine, Florida 33157, 1971.

8. Mills, P.A., "Variation of Florisil Activity: Simple Method for Measuring Adsorbent Capacity and its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29 (1968).

9. Goerlitz, D.F. and Brown, E., "Methods for Analysis of Organic Substances in Water," Techniques of Water Resources Investigations of the United States Geological Survey, Book 5, Chapter A3, U.S. Department of the Interior, Geological Survey, Washington, D.C. 20402, 1972, pp. 24-40.

10. Steere, N.V., editor, "Handbook of Laboratory Safety," Chemical Rubber Company, 18901 Cranwood Parkway, Cleveland, Ohio 44128, 1971, pp. 250-254.

13. Standardization of Florisil Column by Weight Adjustment Based on Adsorption of Lauric Acid.

13.1 A rapid method for determining adsorptive capacity of Florisil is based on adsorption of lauric acid from hexane solution (6) (8). An excess of lauric acid is used and amount not adsorbed is measured by alkali titration. Weight of lauric acid adsorbed is used to calculate, by simple proportion, equivalent quantities of Florisil for batches having different adsorptive capacities.

13.2 Apparatus

    13.2.1 Buret. -- 25 ml with 1/10 ml graduations.

    13.2.2 Erlenmeyer flasks. -- 125 ml narrow mouth and 25 ml, glass stoppered.

    13.2.3 Pipet. -- 10 and 20 ml transfer.

    13.2.4 Volumetric flasks. -- 500 ml.

13.3 Reagents and Solvents

    13.3.1 Alcohol, ethyl. -- USP or absolute, neutralized to phenolphthalein.

    13.3.2 Hexane. -- Distilled from all glass apparatus.

    13.3.3 Lauric acid. --Purified, CP.

    13.3.4 Lauric acid solution. -- Transfer 10.000 g lauric acid to 500 ml volumetric flask, dissolve in hexane, and dilute to 500 ml (1 ml = 20 mg).

    13.3.5 Phenolphthalein Indicator. -- Dissolve 1 g in alcohol and dilute to 100 ml.

13.3.6 Sodium hydroxide. -- Dissolve 20 g NaOH (pellets, reagent

grade) in water and dilute to 500 ml (1N). Dilute 25 ml

1N NaOH to 500 ml with water (0.05N). Standardize as follows:

Weigh 100-200 mg lauric acid into 125 ml Erlenmeyer flask.

Add 50 ml neutralized ethyl alcohol and 3 drops phenol-

phthalein indicator; titrate to permanent end point. Calculate

mg lauric acid/ml 0.05 N NaOH (about 10 mg/ml).

13.4 Procedure

13.4.1 Transfer 2.000 g Florisil to 25 ml glass stoppered Erlenmeyer

flasks. Cover loosely with aluminum foil and heat overnight

at 130°C. Stopper, cool to room temperature, add 20.0 ml

lauric acid solution (400 mg), stopper, and shake occasionally

for 15 min. Let adsorbent settle and pipet 10.0 ml of

supernatant into 125 ml Erlenmeyer flask. Avoid inclusion

of any Florisil.

13.4.2 Add 50 ml neutral alcohol and 3 drops indicator solution;

titrate with 0.05N to a permanent end point.

13.5 Calculation of Lauric Acid Value and Adjustment of Column Weight

13.5.1 Calculate amount of lauric acid adsorbed on Florisil as

follows:

Lauric Acid value = mg lauric acid/g Florisil = 200 - (ml

required for titration X mg lauric acid/ml 0.05N NaOH).

13.5.2 To obtain an equivalent quantity of any batch of Florisil,

divide 110 by lauric acid value for that batch and multiply

by 20 g. Verify proper elution of pesticides by 13.6.

15.6 Test for Proper Elution Pattern and Recovery of Pesticides.
Prepare a test mixture containing aldrin, heptachlor epoxide,
p,p'-DDE, dieldrin, Parathion and malathion. Dieldrin and
Parathion should elute in the 15% eluate; all but a trace of
malathion in the 50% eluate and the others in the 6% eluate

DDT

(15 gm) **SOLID**	(100 mls) **LIQUID (WATER)**	(ALL RECEIVED) **LIQUID SOLVENT**

SAMPLES.

ASH
AIR STREAM
    PARTICULATES
SCRUBBER WATER
    PARTICULATES
SEWAGE SLUDGE

SAMPLE:
FILTERED SCRUBBER WATER

SAMPLE
FILTERED AIR

**NEUTRALIZE
pH 6.5-7.5**

**EXTRACT c̄ HEXANE
24 HOURS**

SOLVENT EXTRACT

DRY

EVAPORATE

● FOR ASH, AIR STREAM PARTICULATE,
SCRUBBER WATER PARTICULATE,
SEWAGE SLUDGE, SCRUBBER WATER
FILTRATE, AND SOLVENT EXTRACTED
AIR STREAM SAMPLES.

FLORISIL CLEANUP

LG CONCENTRATION

**CONCENTRATION
IN 10 ML TO 4-6 ml**

**REMOVE 1 ML
FOR G.C.**

GLC

SEWAGE SLUDGE TREATED AS A SOLID, OVEN DRIED

FIGURE B-I
ANALYTICAL FLOW SCHEME
FOR DDT AND ITS DEGRADATION PRODUCTS●

The handwritten annotations on the chromatogram read:

SAMPLE NO. 2-437-3H (X10)
AMT. INJECTED : 3.2 μl
ATTENUATION : 128
DATE OF GC ANALYSIS:
9/17/74

PEAK HEIGHTS:

OP' DDE : 184.6 mm
OP' DDT : 1.2 mm
PP' DDT : 2.0 mm

Peak labels: OP'DDE, PP'DDE, OP'DDD, OP'DDT, PP'DDD, PP'DDT
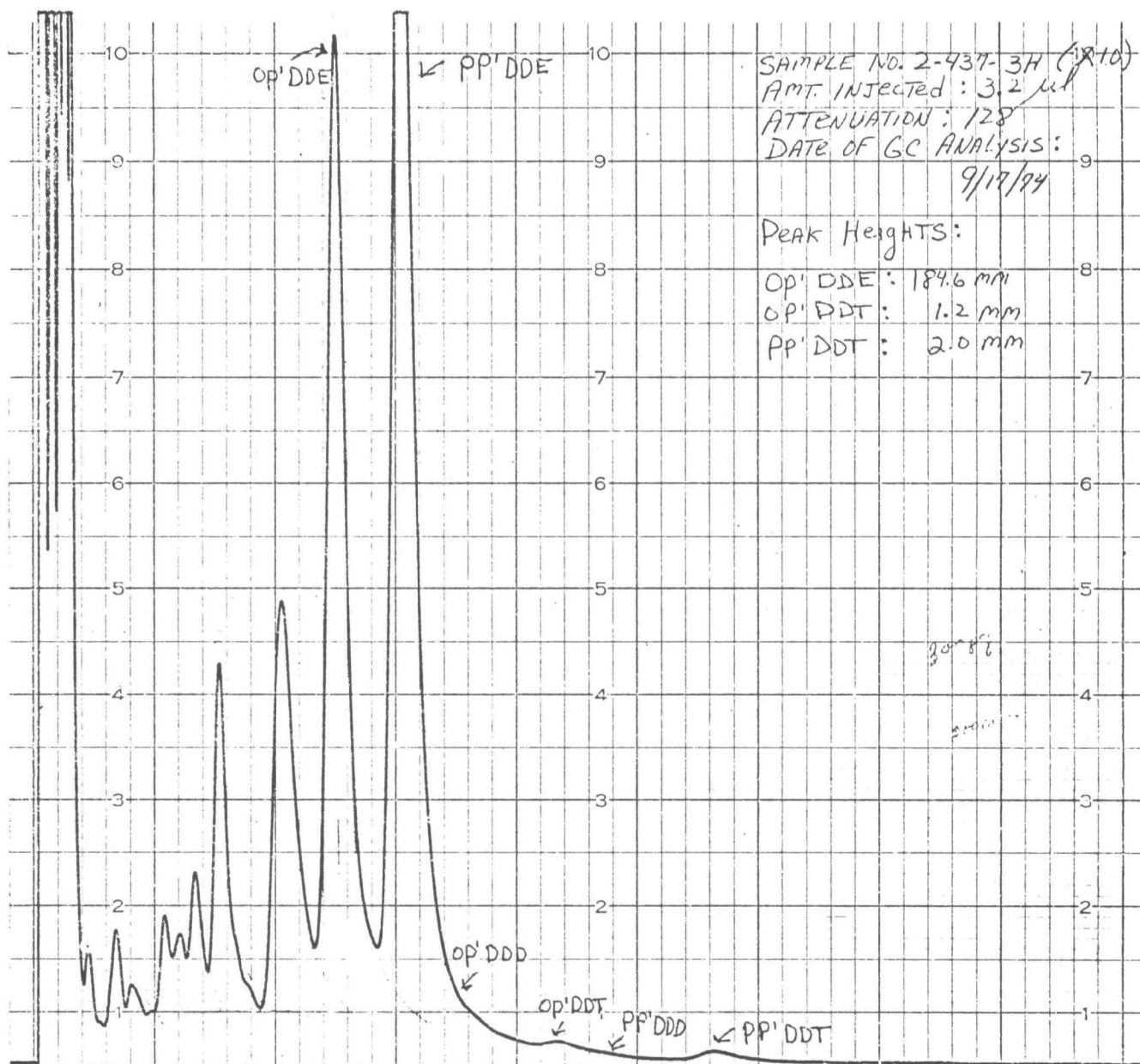
Figure B-2. Chromatogram of Typical Non-Particulate Stack Gas Sample
(Full scale DDT burn)

Note: Figures B-2 through B-7 show that o-p' - DDE and p-p' -
DDE were the prominent degradation products of the full
scale DDT burn.

127
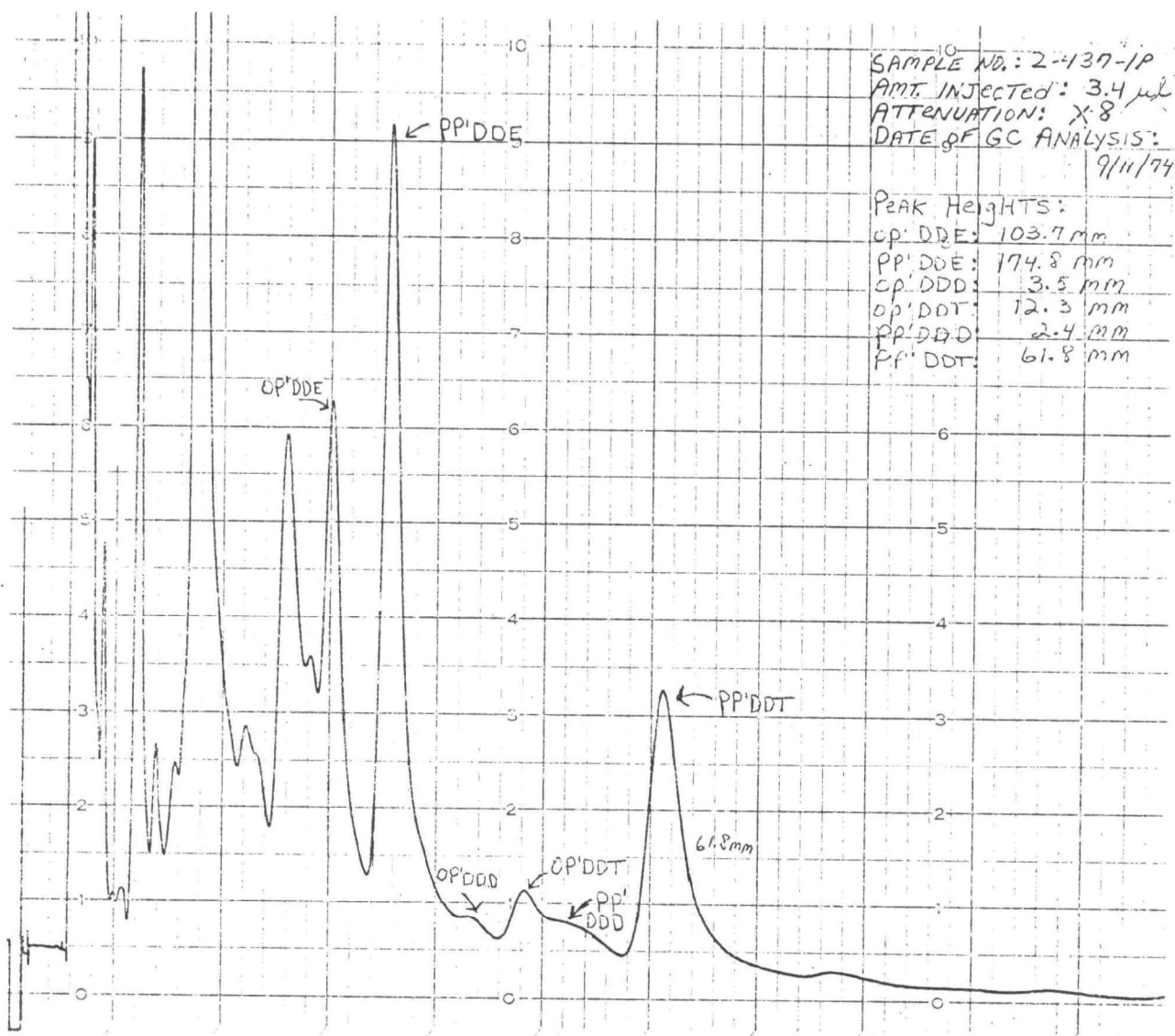
Figure B-3.   Chromatogram of Typical Stack Gas Particulate Sample
(Full scale DDT burn)
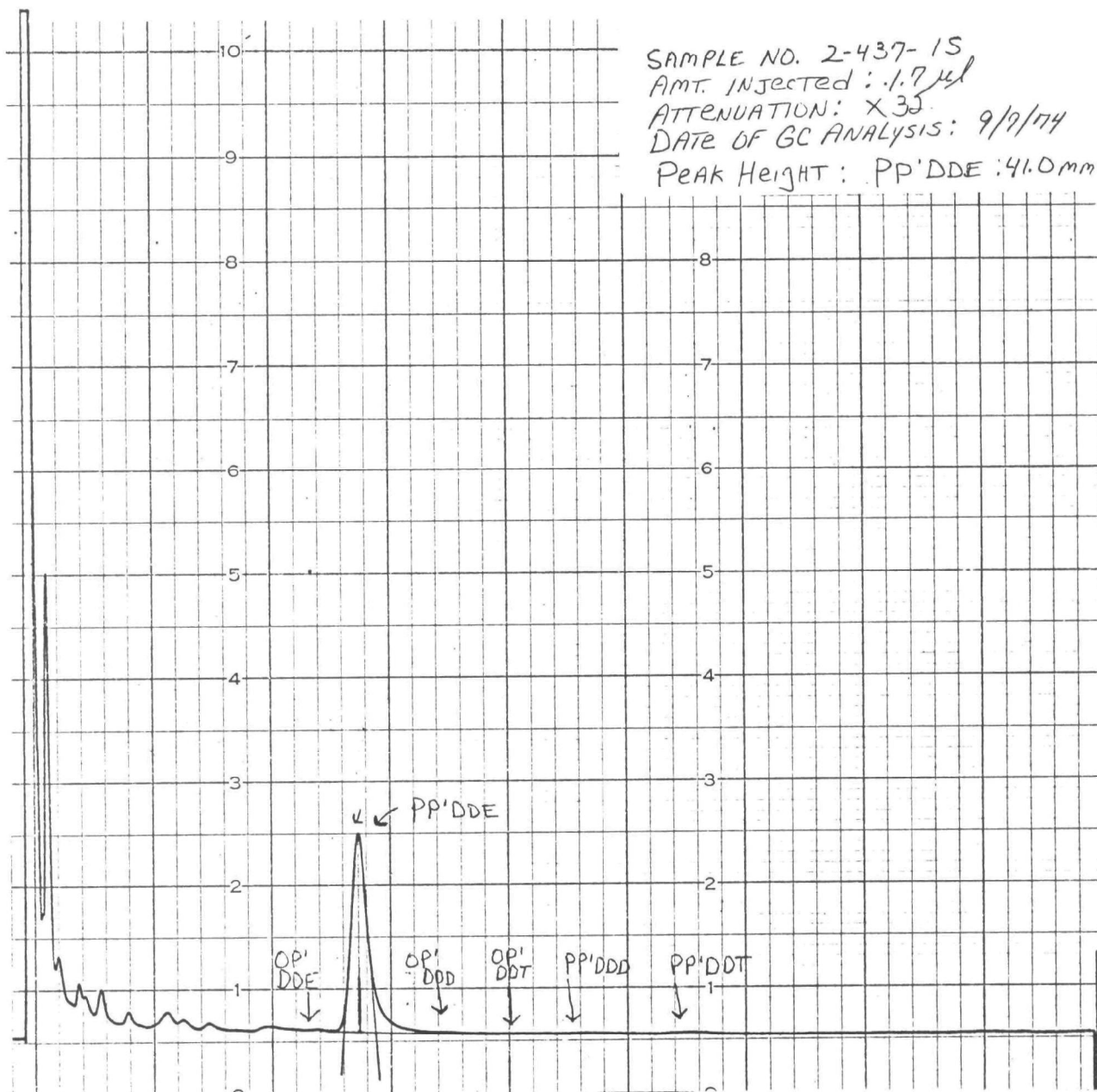
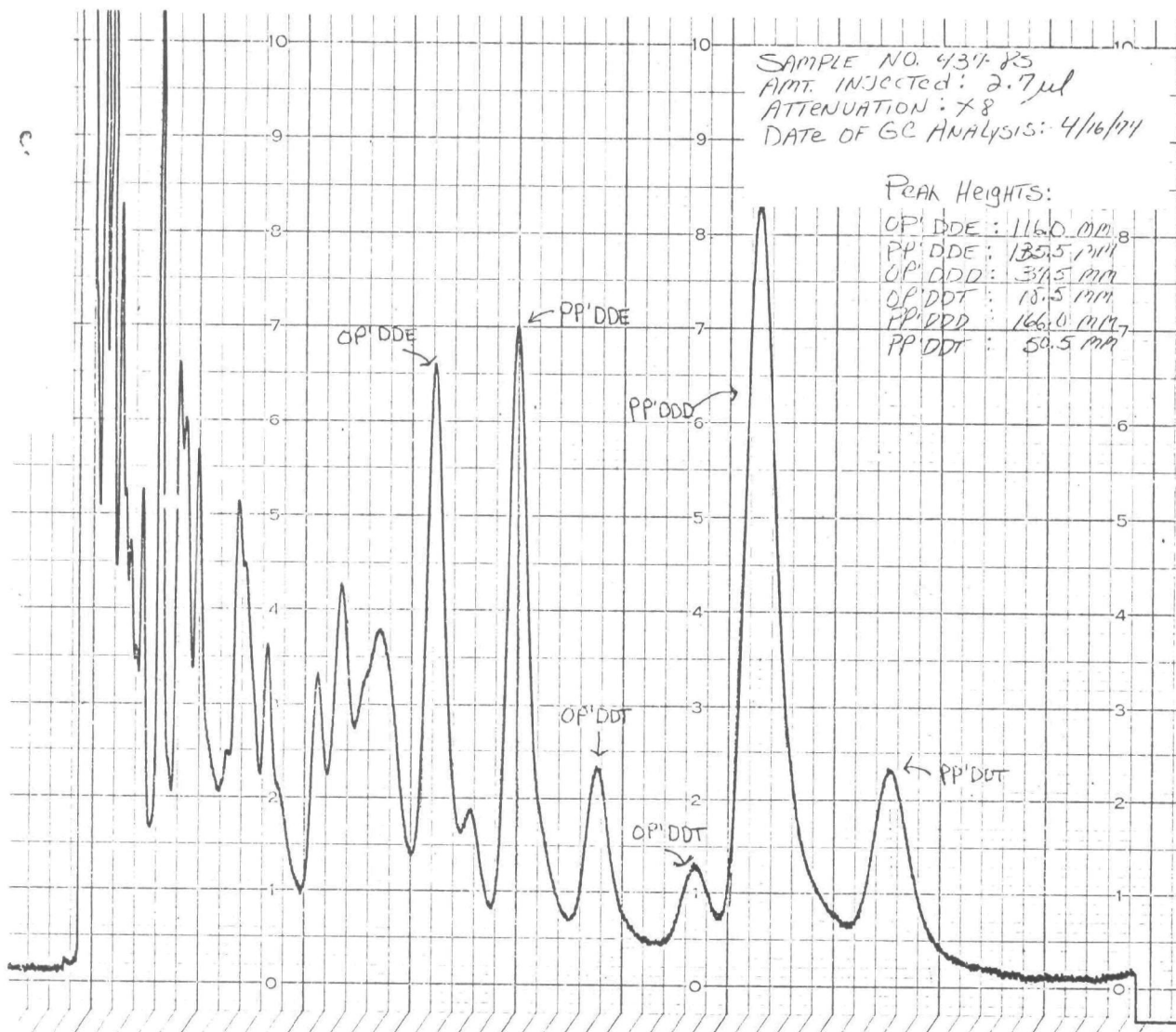Figure B-4. Chromatogram of Typical Scrubber Water Filtrate Sample
(Full scale DDT burn)

129

SAMPLE NO. 2-437-15P
AMT INJECTED: 2.0 µl
ATTENUATION: X128
DATE OF GC ANALYSIS: 9/17/74
PP'DDE PEAK HEIGHT: 115.8 mm

← PP'DDE

OP'DDE

OP'DDD OP'DDT PP'DDD PP'DDT
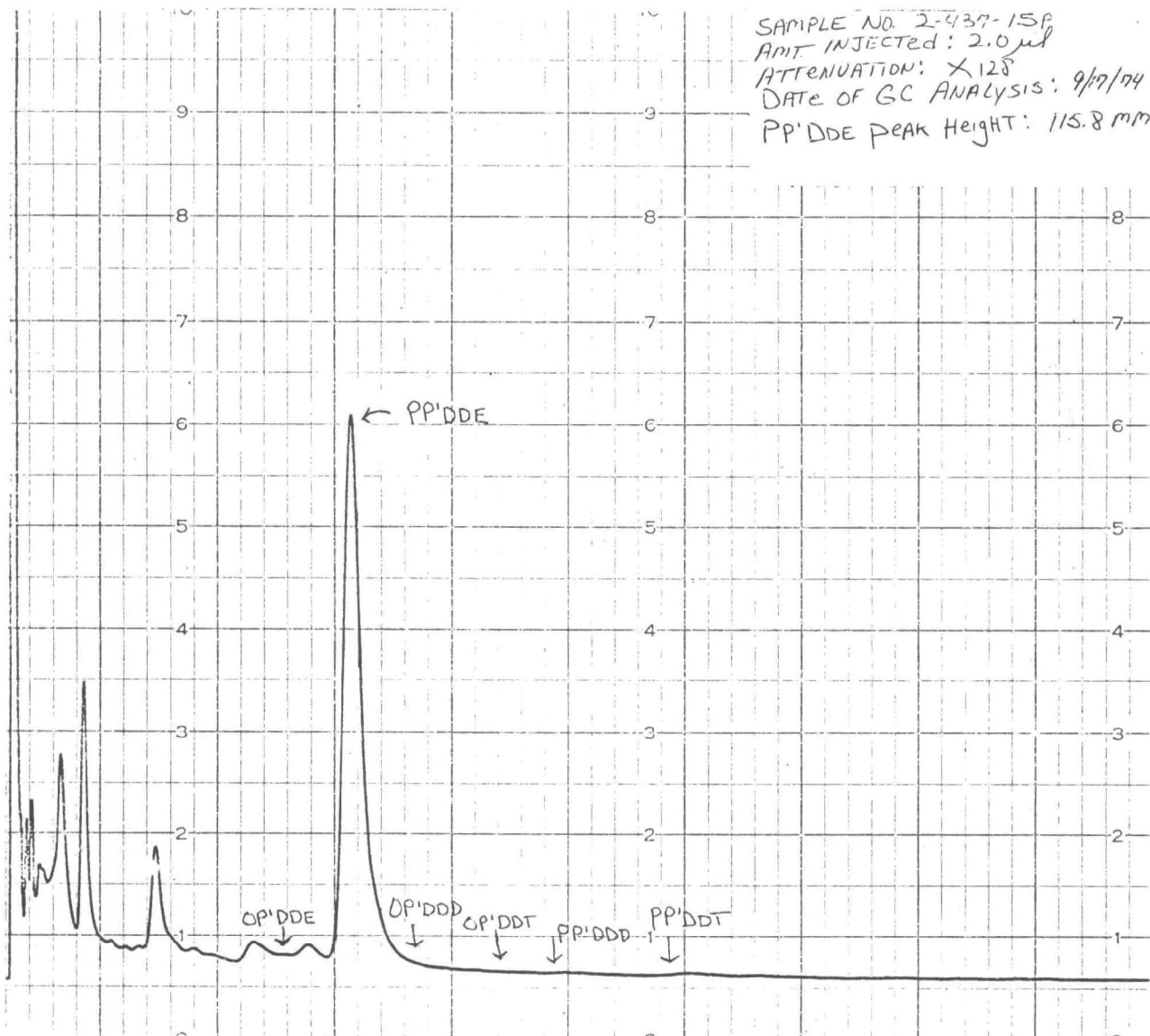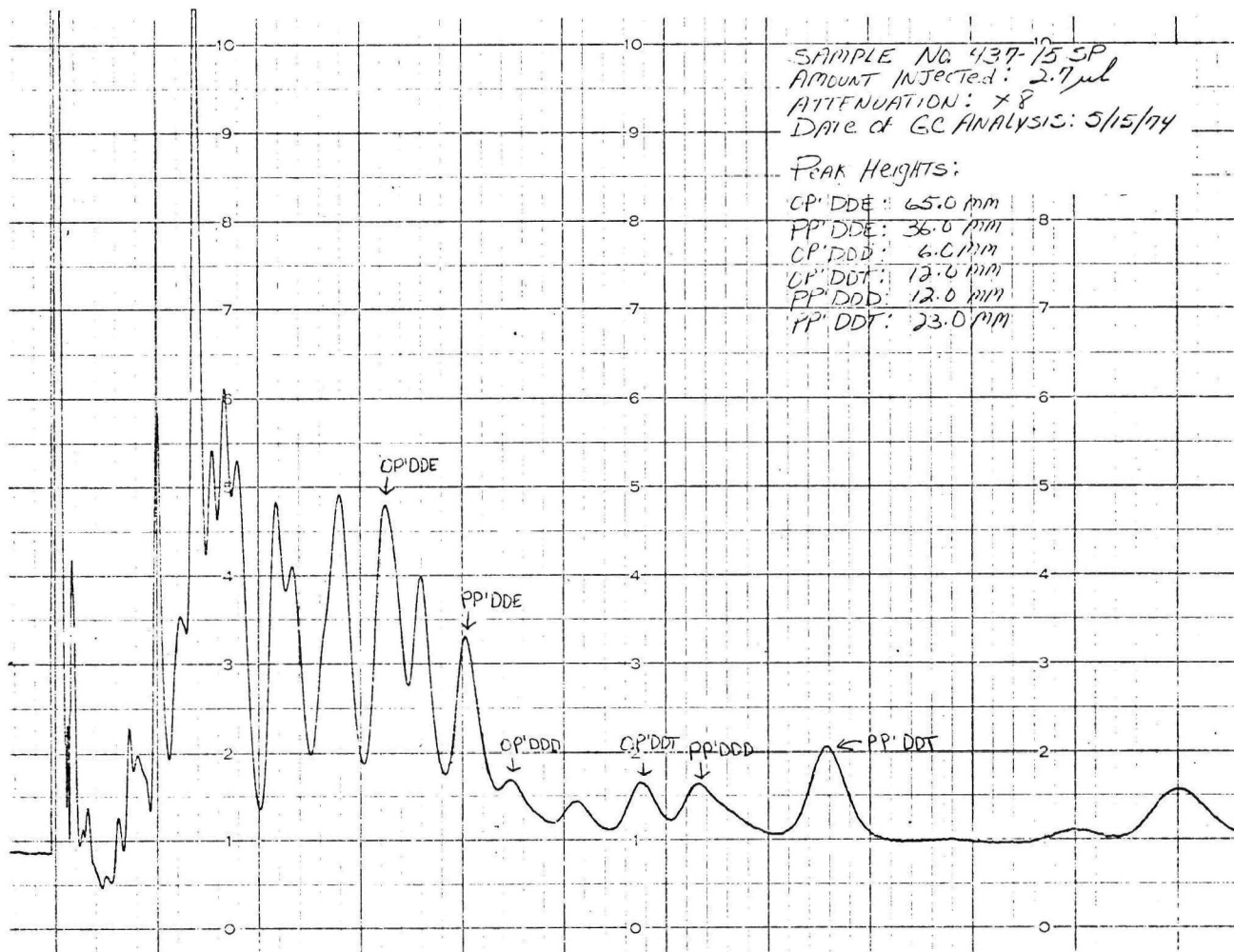
Figure B-5. Chromatogram of Typical Scrubber Water Particulate Sample
(Full scale DDT burn)

130
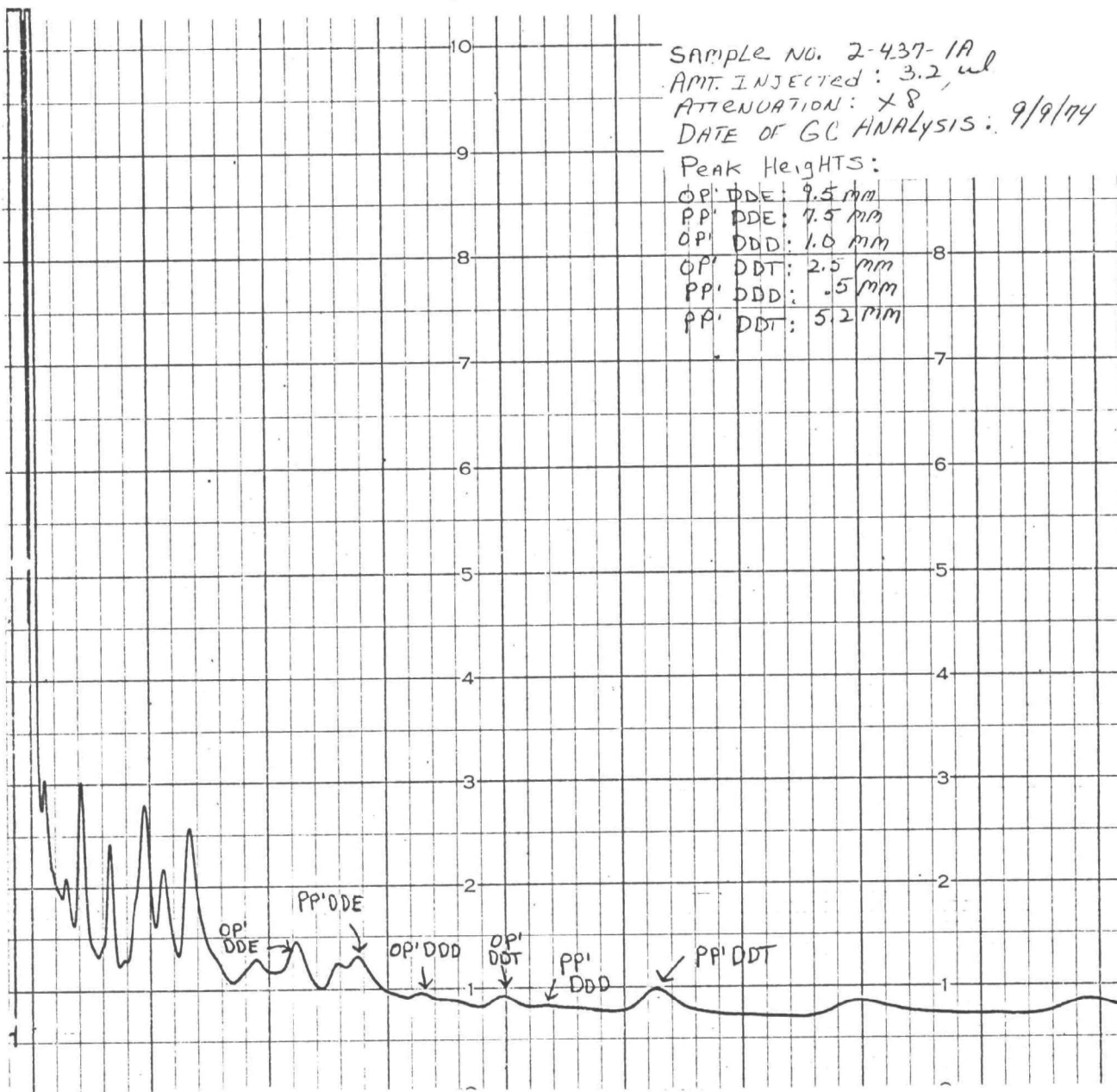
Figure B-6. Chromatogram of Typical Product Sample
(Full scale DDT burn)
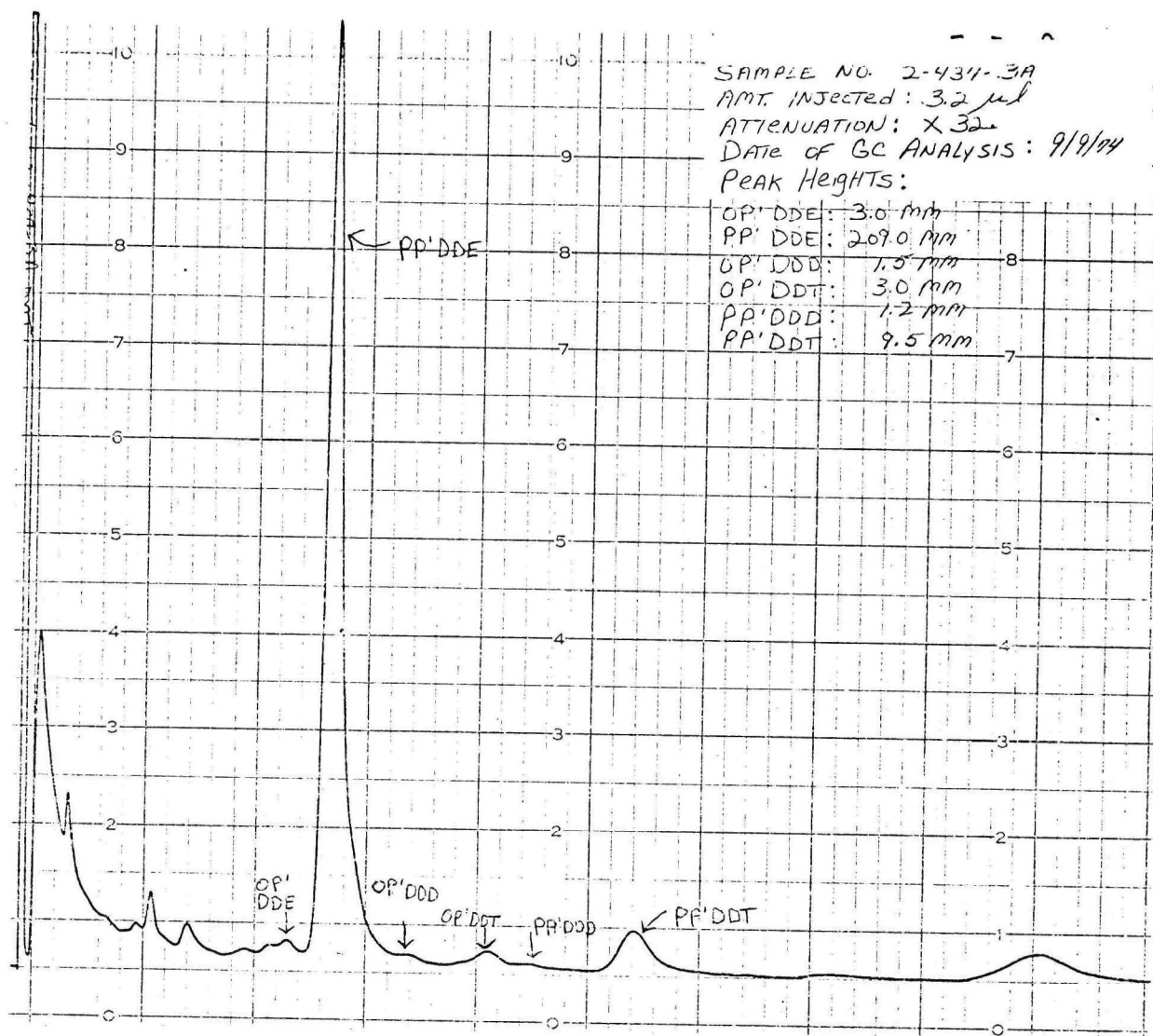
Figure B-7. Chromatogram of Product Sample
(Full Scale DDT Burn)

In comparison to Figure B-6, this tracing
illustrates some of the degradation pro-
duct variation encountered.

132
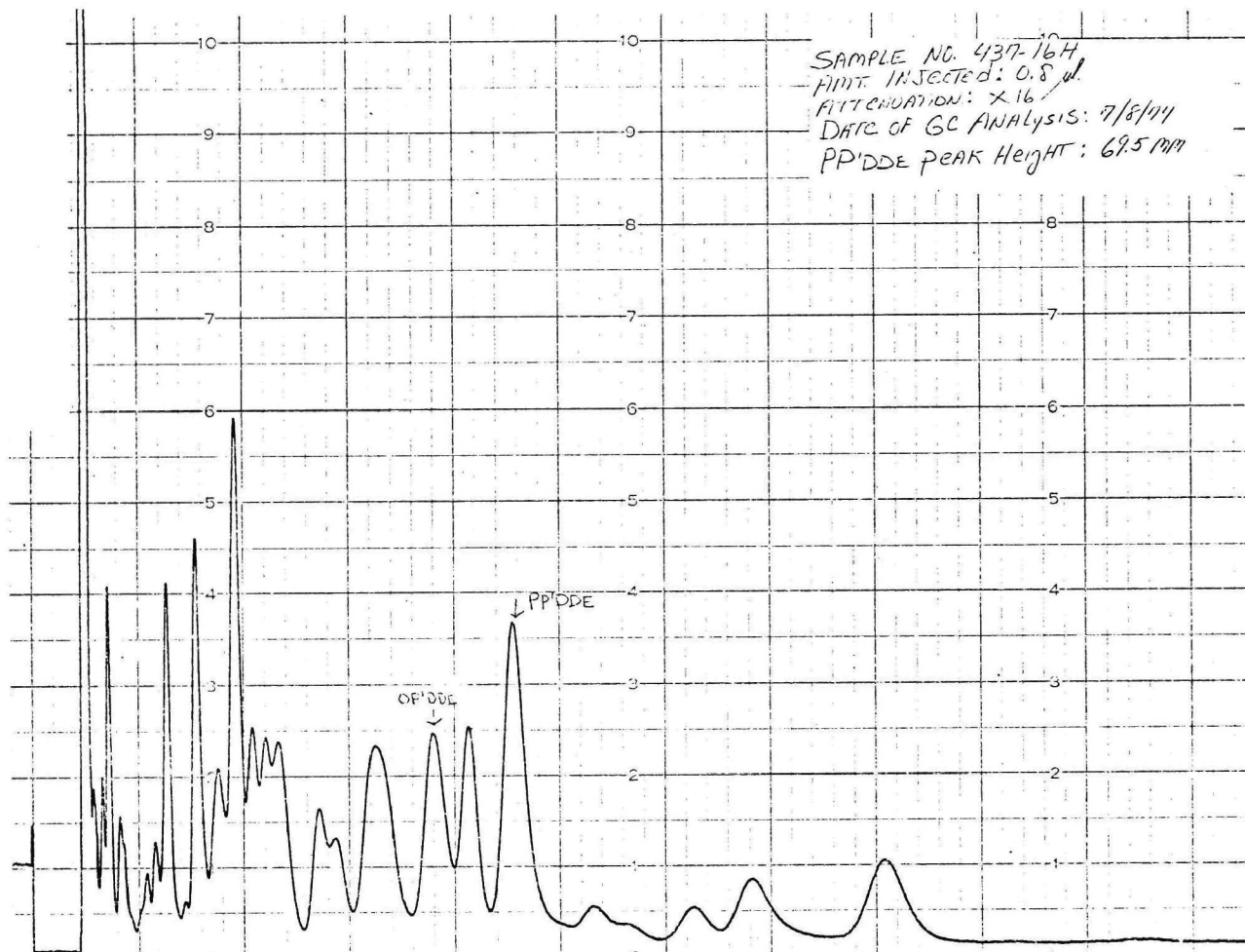
Figure B-8. Chromatogram of Typical Non-Particulate Stack Gas Sample
(Pilot scale DDT burn)

Note: Figures B-8 through B-16 show that o-p' and p-p' -
DDE were not consistently the major combustion pro-
ducts of the pilot scale test burn, p-p' - DDT was
equally prominent.
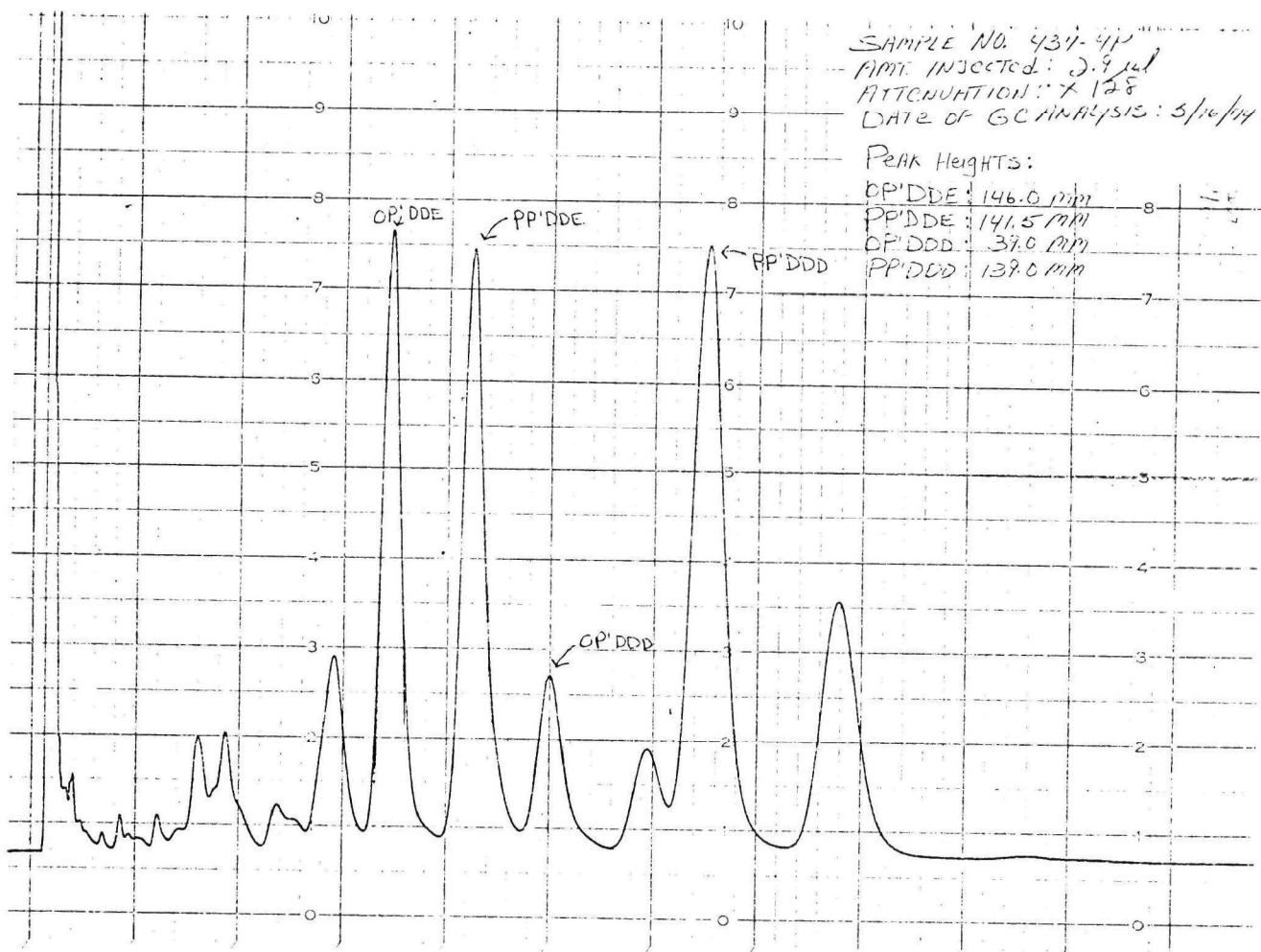
Figure B-9. Chromatogram of Typical Stack Gas Particulate Sample
(Pilot scale DDT burn)
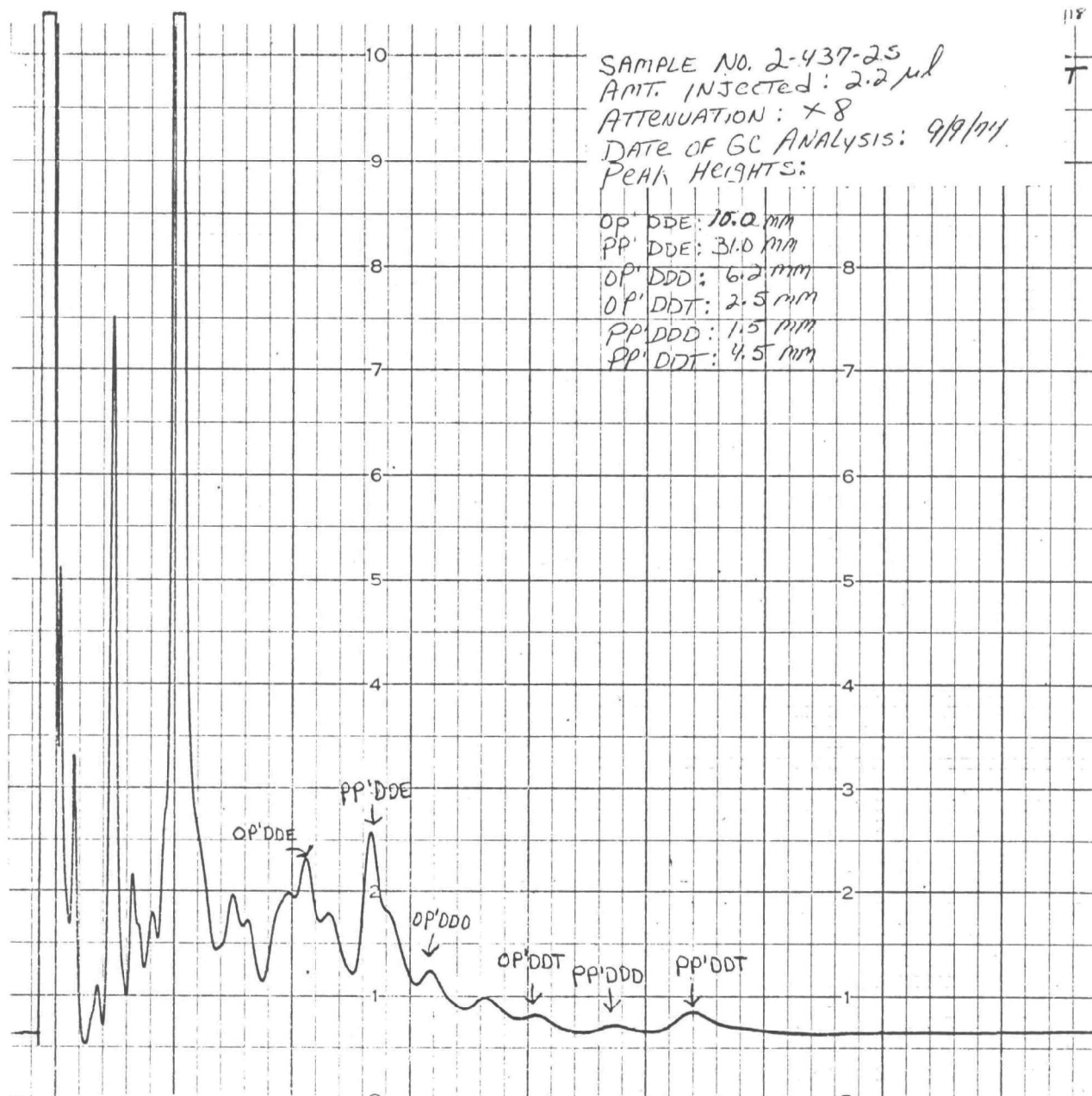
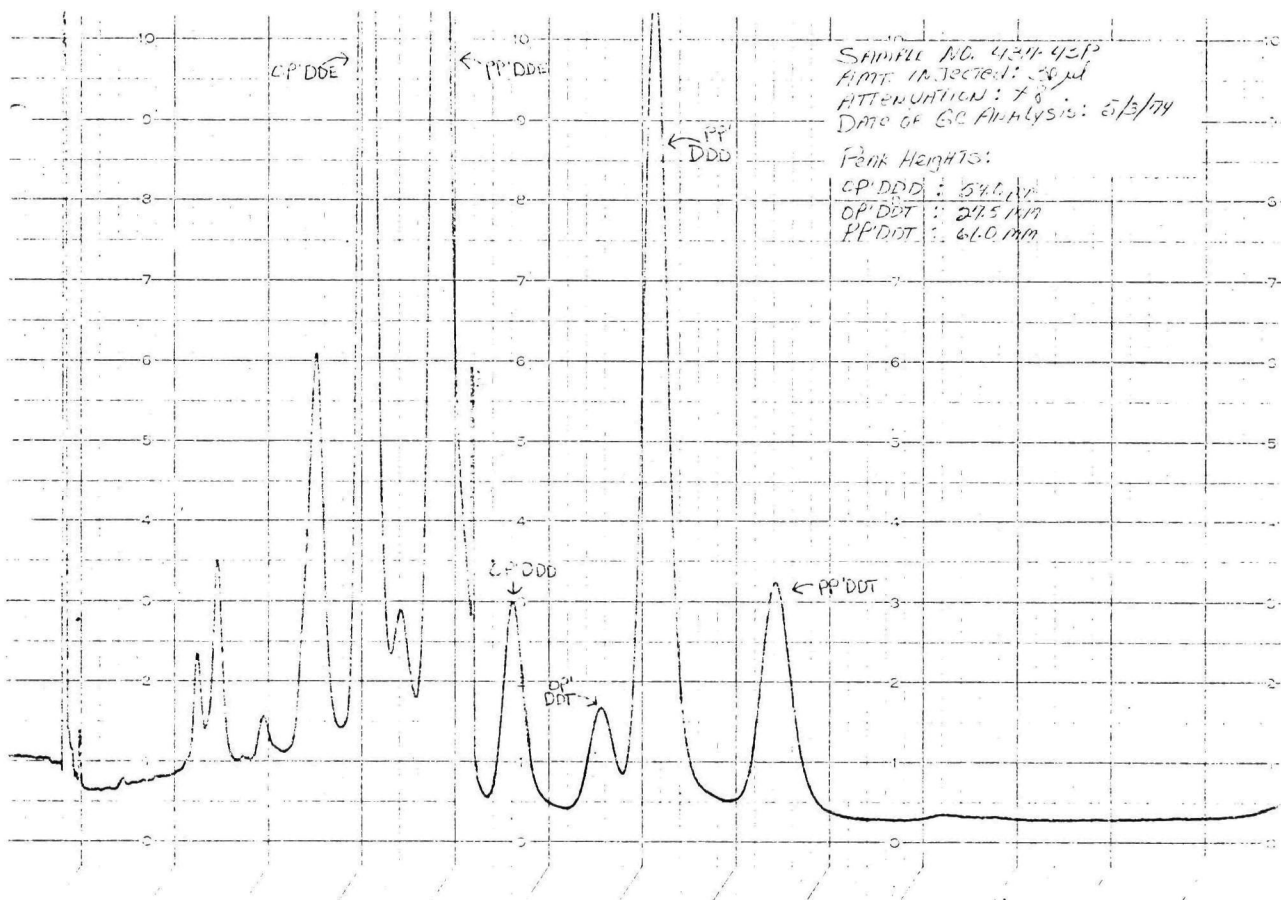Figure B-10. Chromatogram of Typical Scrubber Water Filtrate Sample
(Pilot scale DDT burn)

135

Figure B-11. Chromatogram of Scrubber Water Filtrate Sample
(Pilot scale DDT burn)

136

Figure B-12. Chromatogram of Typical Scrubber Water Particulate Sample
(Pilot scale DDT burn)

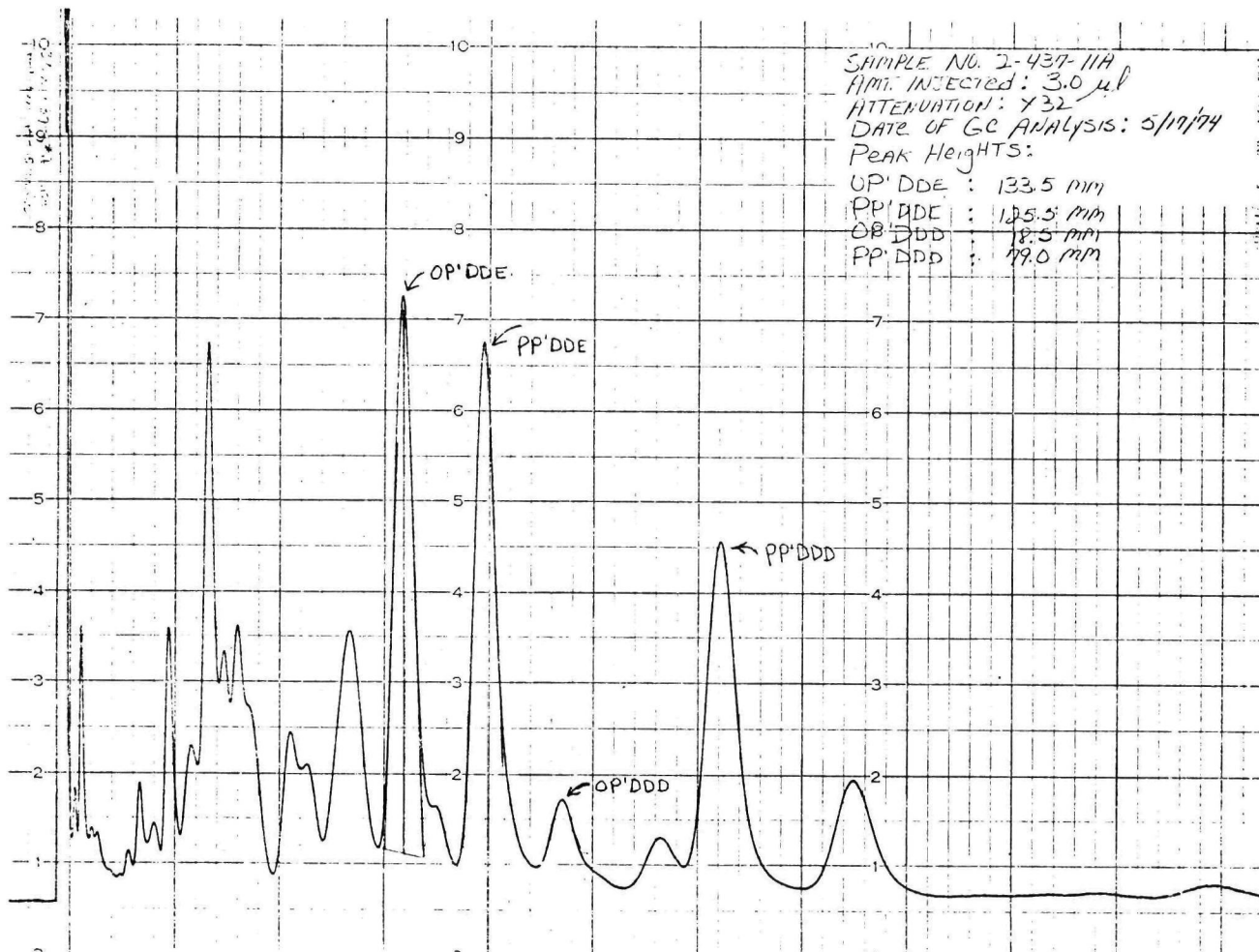Figure B-13. Chromatogram of Scrubber Water Particulate Sample
(Pilot scale DDT burn)

Figure B-14. Chromatogram of Typical Product Sample
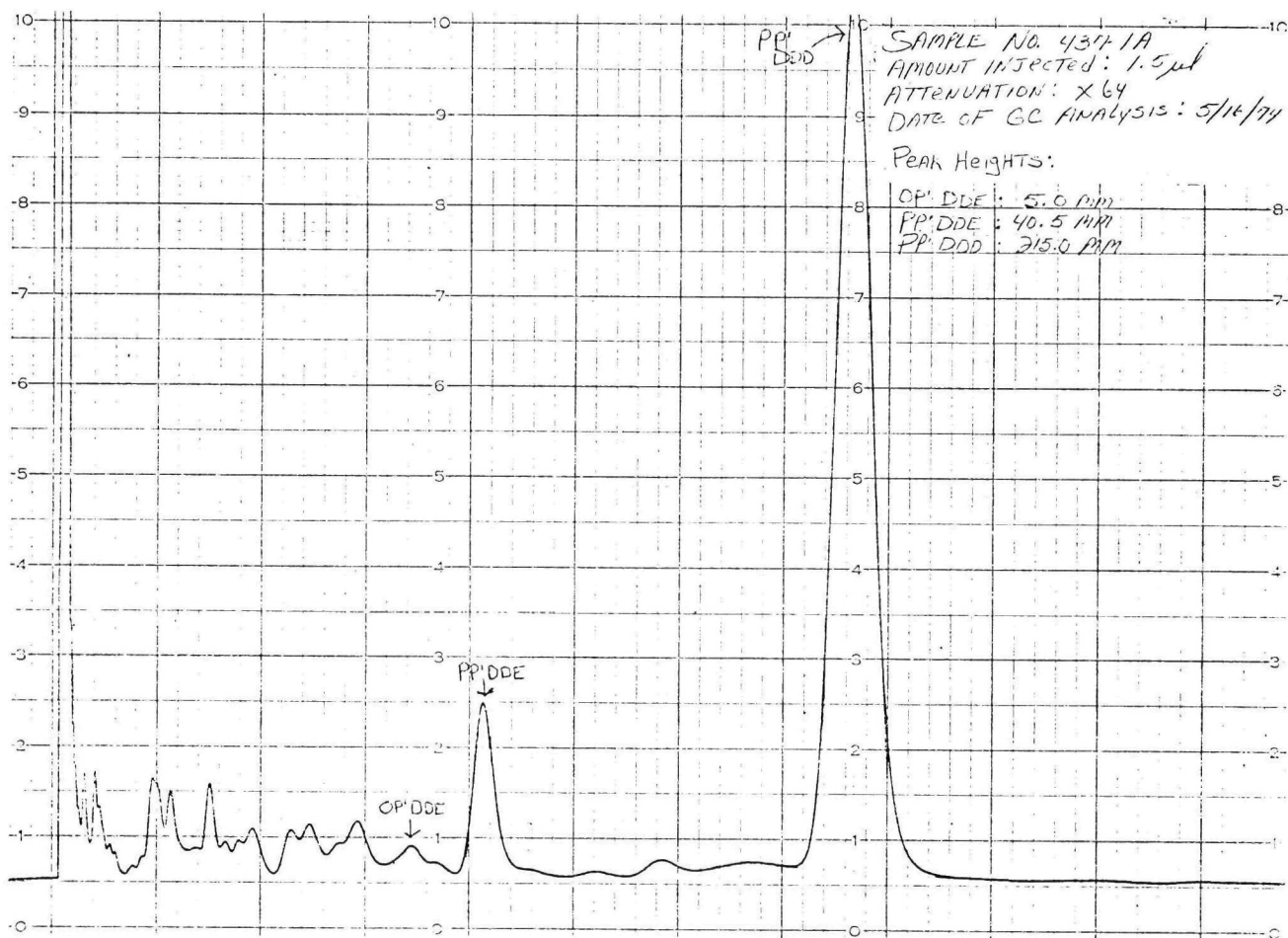(Pilot scale DDT burn)

Figure B-15.   Chromatogram of Product Sample
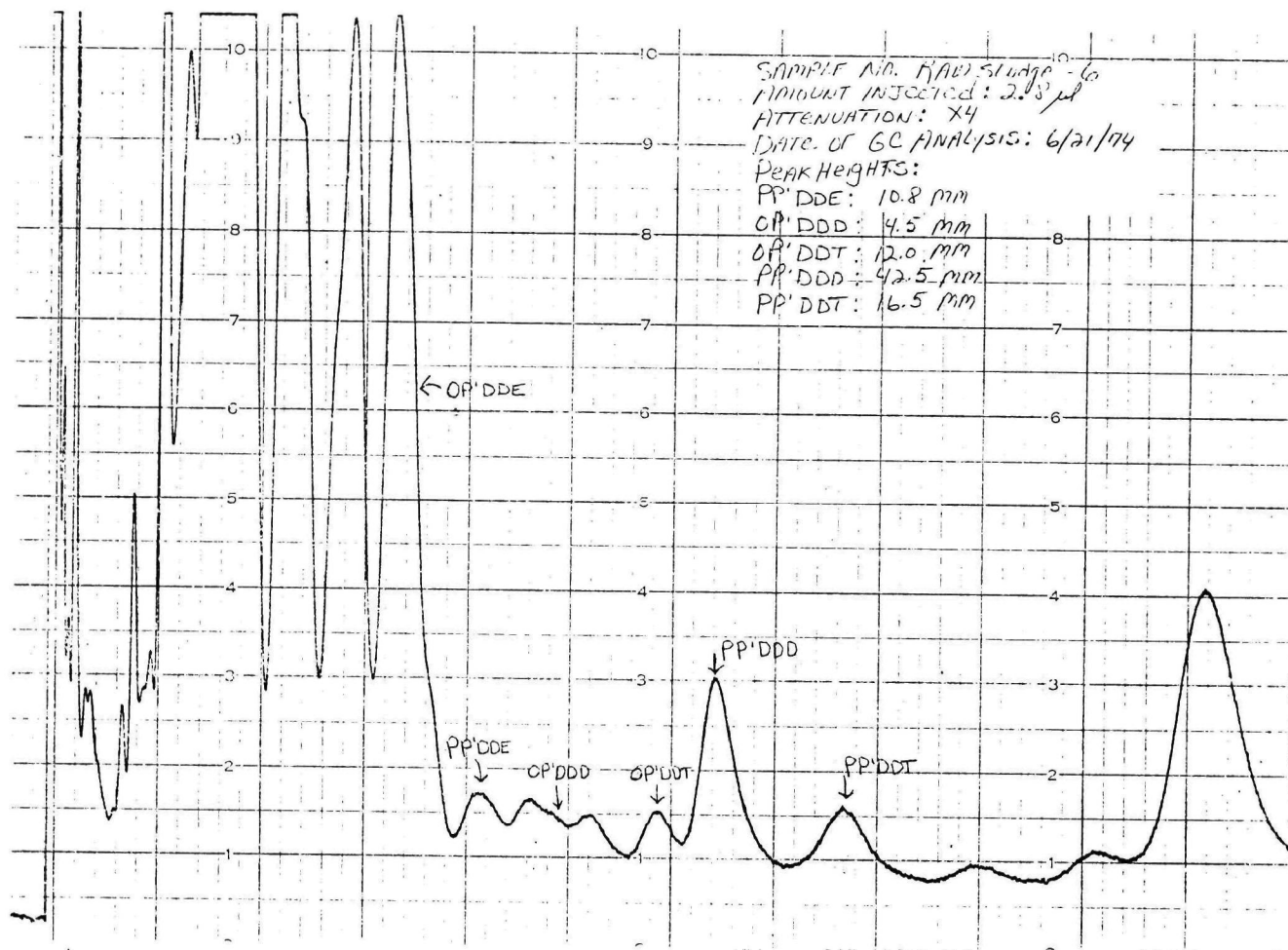
(Pilot scale DDT burn)

140

The handwritten annotations on the chromatogram read:

SAMPLE NO. RAW SLUDGE - 6
AMOUNT INJECTED: 2.8 μℓ
ATTENUATION: X4
DATE OF GC ANALYSIS: 6/21/74
PEAK HEIGHTS:
PP'DDE: 10.8 mm
OP'DDD: 4.5 mm
OP'DDT: 12.0 mm
PP'DDD: 42.5 mm
PP'DDT: 16.5 mm

Figure B-16.   Typical Chromatogram of Sewage Sludge Sample
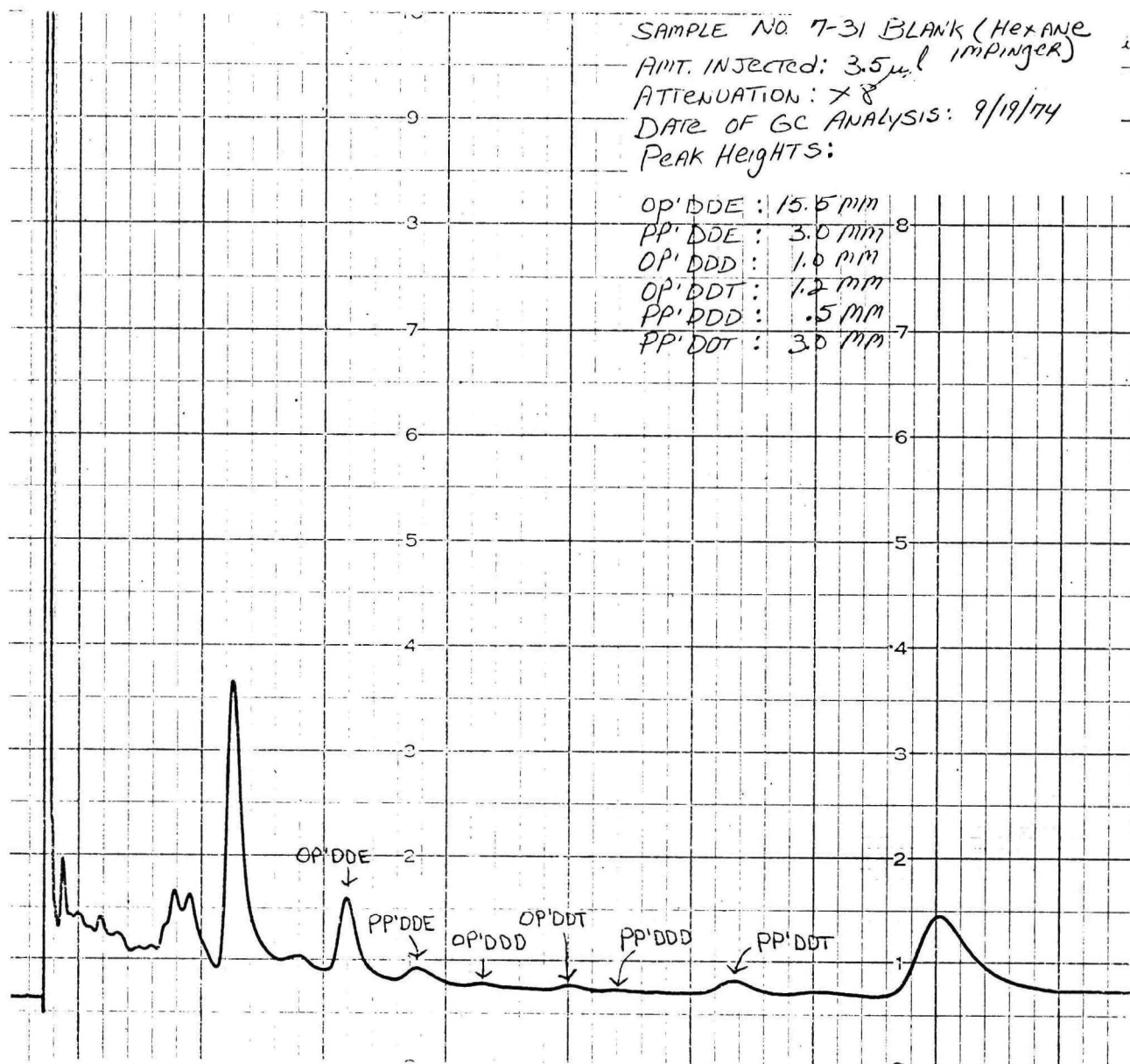(Pilot scale DDT burn)

141

Figure B-17. Typical Chromatogram of Laboratory Blank

Note: A laboratory blank was analyzed with every four
samples processed. The raw data was then
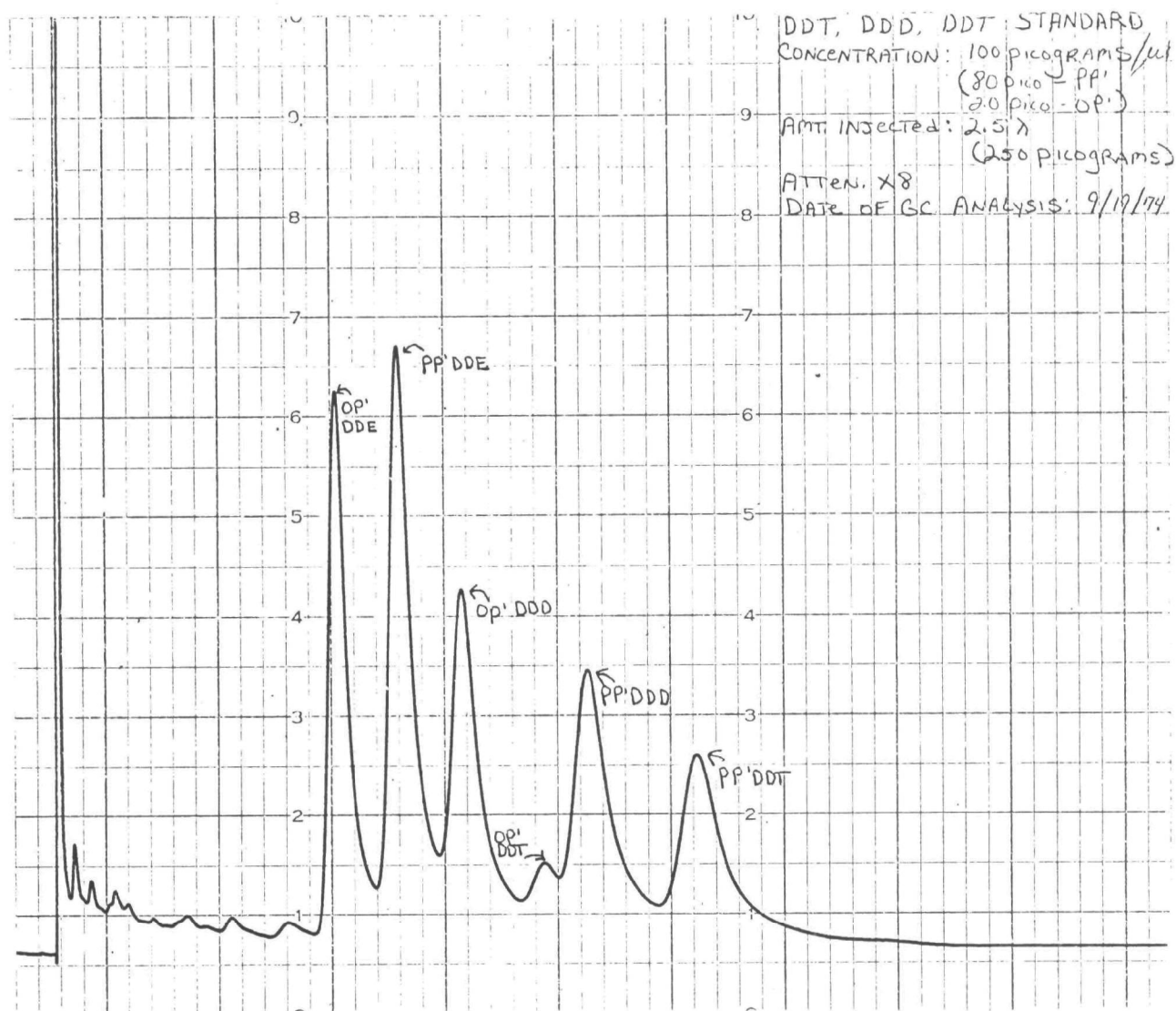corrected for these residual levels.

142

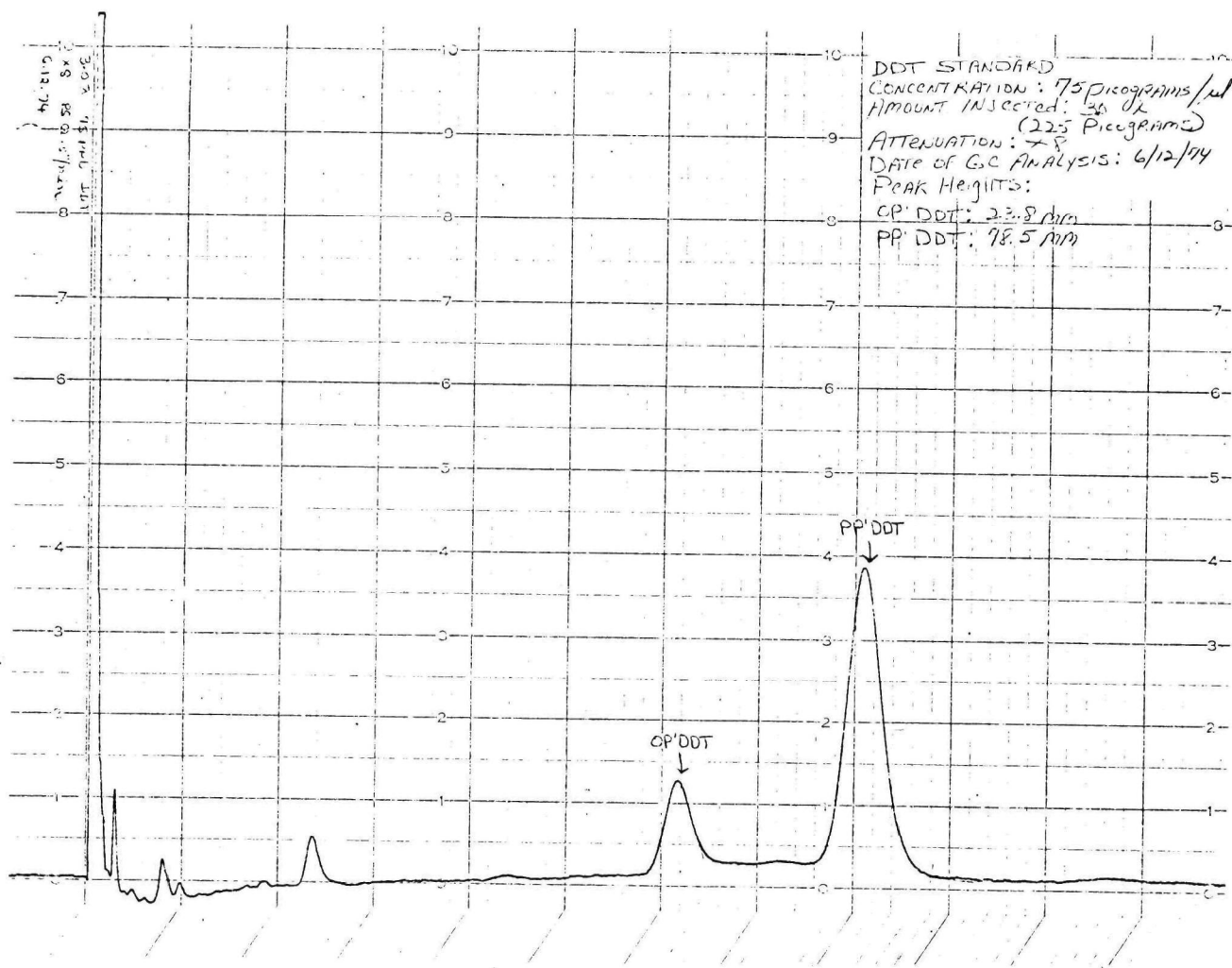Figure B-18. Chromatogram of Typical Pesticide Composite Standard

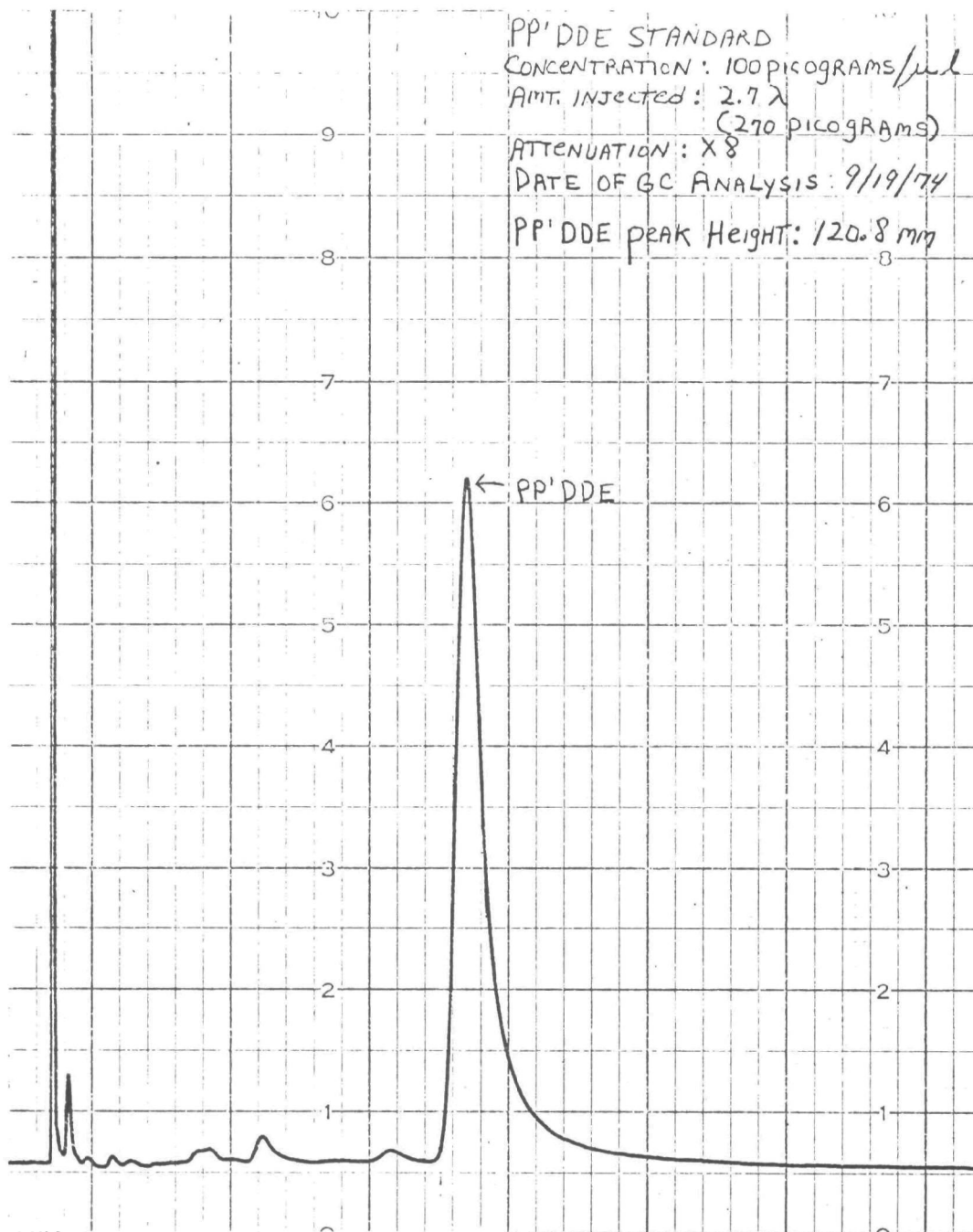Figure B-19. Chromatogram of DDT Standard

144

Figure B-20.   Chromatogram of p-p' - DDE Standard
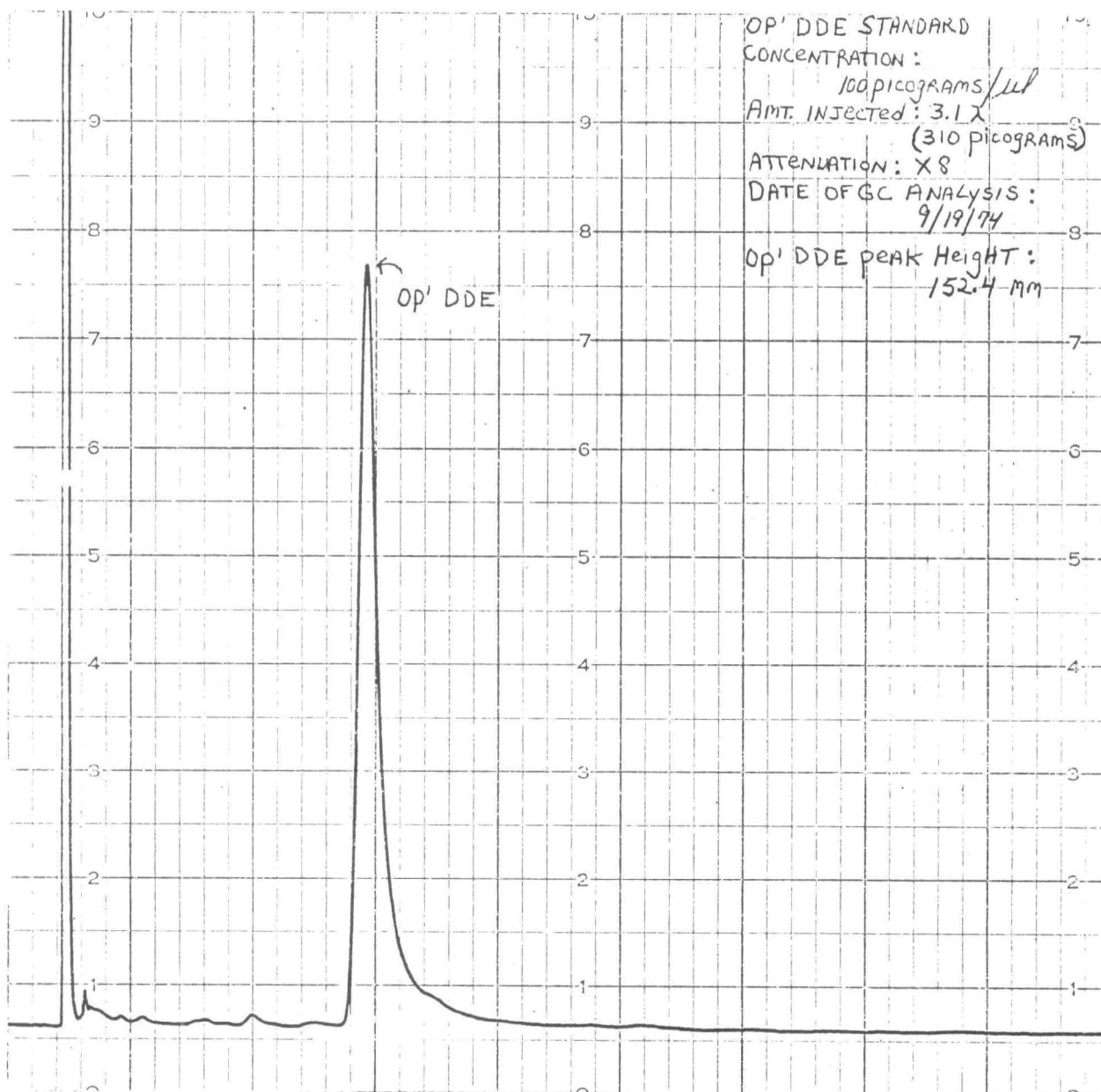
Figure B-21. Chromatogram of o-p' - DDE Standard

OP' DDE STANDARD
CONCENTRATION:
     100 picograms/μl
AMT. INJECTED: 3.1 λ
     (310 picograms)
ATTENUATION: X8
DATE OF GC ANALYSIS:
     9/19/74
OP' DDE PEAK HEIGHT:
     152.4 mm
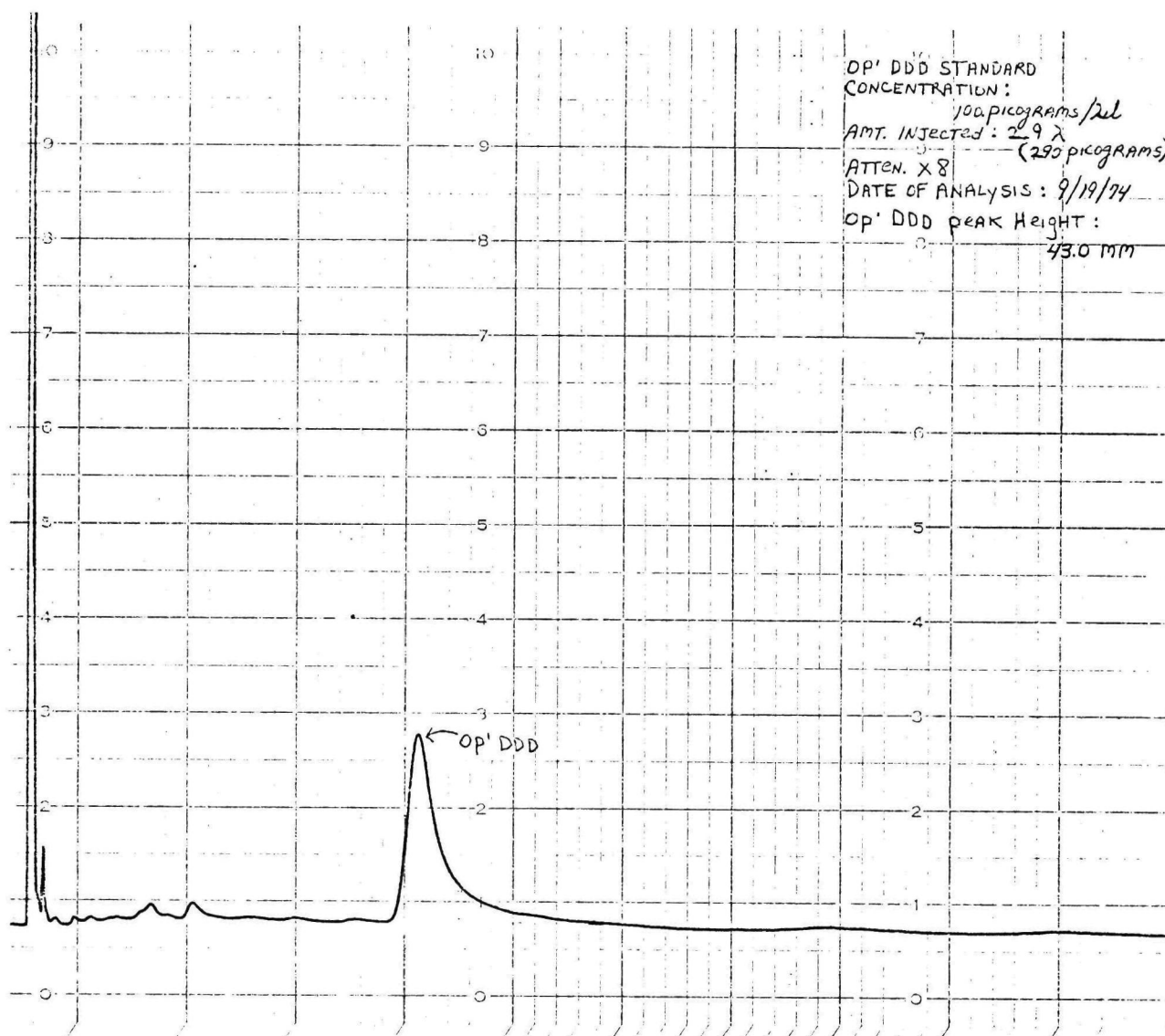
OP' DDE

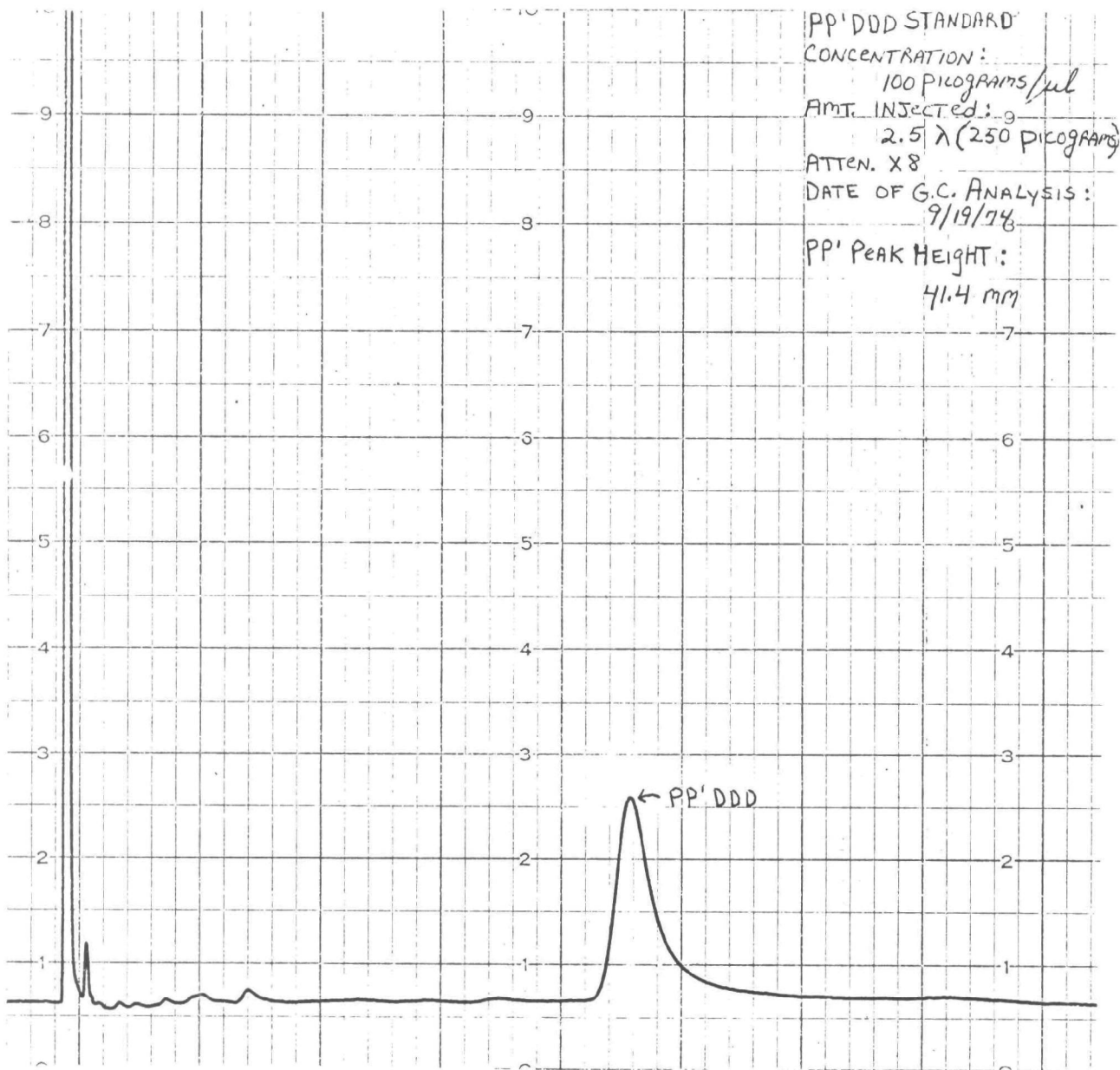Figure B-22.   Chromatogram of o-p' - DDD Standard

147

Figure B-23. Chromatogram of p-p' - DDD Standard

148

APPENDIX C

METHOD FOR CHLORINATED PHENOXY ACID HERBICIDES IN
INDUSTRIAL EFFLUENTS

(from National Pollutant Discharge Elimination
System, Appendix A, Federal Register vol. 38, no. 75, pt. II)

1. Scope and Application

   1.1 This method covers the determination of chlorinated phenoxy acid
   herbicides in industrial effluents. The compounds 2,4-dichloro-
   phenoxyacetic acid (2,4-D), 2-(2,4,5-trichlorophenoxy) propionic
   acid (silvex), 2,3-dichloro-o-anisic acid (dicamba) and 2,4,5-
   trichlorophenoxyacetic acid (2,4,5-T) may be determined by this
   procedure.

   1.2 Since these compounds may occur in water in various forms (i.e., acid,
   salt, ester, etc.) a hydrolysis step is included to permit the deter-
   mination of the active part of the herbicide. The method may be
   applied to additional phenoxy acids and certain phenols. However,
   the analyst must demonstrate the usefulness of the method for each
   specific compound before applying it to sample analysis.

2. Summary

   2.1 Chlorinated phenoxy acids and their esters are extracted from the
   acidified water sample with ethyl ether. The esters are hydrolyzed
   to acids and extraneous organic material is removed by a solvent wash.
   The acids are converted to methyl esters which are extracted from
   the aqueous phase. The extract is cleaned up by passing it through
   a micro-adsorption column. Identification of the esters is made by
   selective gas chromatographic separations and may be corroborated
   through the use of two or more unlike columns. Detection and measure-
   ment is accomplished by electron capture, microcoulometric or
   electrolytic conductivity gas chromatography (1). Results are
   reported in micrograms per liter.

   2.2 This method is recommended for use only by experienced pesticide
   analysts or under the close supervision of such qualified persons.

151

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware
may yield discrete artifacts and/or elevated baselines causing
misinterpretation of gas chromatograms. All of these materials must
be demonstrated to be free from interference under the conditions of
the analysis. Specific selection of reagents and purification of
solvents by distillation in all-glass systems may be required.
Refer to Part 1, Sections 1.4 and 1.5, (2).

3.2 The interferences in industrial effluents are high and varied and
often pose great difficulty in obtaining accurate and precise
measurement of chlorinated phenoxy acid herbicides. Sample clean-up
procedures are generally required and may result in loss of certain
of these herbicides. It is not possible to describe procedures for
overcoming all of the interferences that may be encountered in
industrial effluents.

3.3 Organic acids, especially chlorinated acids, cause the most direct
interference with the determination. Phenols including chlorophenols
will also interfere with this procedure.

3.4 Alkaline hydrolysis and subsequent extraction eliminates many of
the predominant chlorinated insecticides which might otherwise
interfere with the test.

3.5 The herbicides, being strong organic acids, react readily with
alkaline substances and may be lost during analysis. Glassware and
glass wool should be acid-rinsed and sodium sulfate should be acidi-
fied with sulfuric acid to avoid this possibility.

4. <u>Apparatus and Materials</u>

   4.1 Gas Chromatograph - Equipped with glass lined injection port.

   4.2 Detector Options:

       4.2.1 Electron Capture - Radioactive (tritium or nickel-63)

       4.2.2 Microcoulometric Titration

       4.2.3 Electrolytic Conductivity

   4.3 Recorder - Potentiometric strip chart (10 in.) compatible with the detector.

   4.4 Gas Chromatographic Column Materials:

       4.4.1 Tubing - Pyrex (180 cm long X 4 mm ID)

       4.4.2 Glass Wool - Silanized

       4.4.3 Solid Support - Gas-Chrom-Q (100-120 mesh)

       4.4.4 Liquid Phases - Expressed as weight percent coated on solid support.

           4.4.4.1 OV-210, 5%

           4.4.4.2 OV-17, 1.5% plus QF-1, 1.95%

   4.5 Kuderna-Danish (K-D) Glassware (Kontes)

       4.5.1 Snyder Column - three ball (macro) and two ball (micro)

       4.5.2 Evaporative Flasks - 250 ml

       4.5.3 Receiver Ampuls - 10 ml, graduated

       4.5.4 Ampul Stoppers

   4.6 Blender - High speed, glass or stainless steel cup.

   4.7 Graduated cylinders - 100 and 250 ml.

   4.8 Erlenmeyer flasks - 125 ml, 250 ml ground glass Ꝩ 24/40

   4.9 Microsyringes - 10, 25, 50 and 100 μl.

   4.10 Pipets - Pasteur, glass disposable (140 mm long X 5 mm ID).

   4.11 Separatory Funnels - 60 ...ı and 2000 ml with Teflon stopcock.

4.12 Glass wool - Filtering grade, acid washed.

4.13 Diazald Kit - recommended for the generation of diazomethane (available from Aldrich Chemical Co., Cat. #210,025-2)

4.14 Florisil - PR grade (60-100 mesh) purchased activated at 1250F and stored at 130 C

5. Reagents, Solvents and Standards

5.1 Boron Trifluoride-Methanol-esterification-reagent, 14 percent boron trifluoride by weight.

5.2 N-methyl-N-nitroso-p-toluenesulfonamide (Diazald) - High purity, melting point range 60-62 C   Precursor for the generation of diazomethane (see Appendix I).

5.3 Ferrous Sulfate - (ACS) 30% solution in distilled water.

5.4 Potassium Hydroxide Solution - A 37 percent aqueous solution prepared from reagent grade potassium hydroxide pellets and reagent water.

5.5 Potassium Iodide - (ACS) 10% solution in distilled water.

5.6 Sodium Chloride - (ACS) Saturated solution (pre-rinse NaCl with hexane) in distilled water.

5.7 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.8 Sodium Sulfate, Acidified. -- (ACS) granular sodium sulfate, treated as follows. Add 0.1 ml of conc. sulfuric acid to 100 g of sodium sulfate slurried with enough ethyl ether to just cover the solid. Remove the ether with the vacuum. Mix 1 g of the resulting solid with 5 ml of reagent water and ensure the mixture to have a pH below .   Store at 130 C

5 9 Sulfuric acid -- (ACS) concentrated, Sp. Gr. 1.84.

5.9.a. Carbitol (diethylene glycol monoethyl ether).

5.10 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

    5.10.1 Must contain 2% alcohol and be free of peroxides by following test: To 10 ml of ether in glass-stoppered cylinder previously rinsed with ether, add one ml of freshly prepared 10% KI solution. Shake and let stand one minute. No yellow color should be observed in either layer.

    5.10.2 Decompose ether peroxides by adding 40 g of 30% ferrous sulfate solution to each liter of solvent. <u>CAUTION</u>: Reaction may be vigorous if the solvent contains a high concentration of peroxides.

    5 10.3 Distill deperoxidized ether in glass and add 2% ethanol.

5.11 Benzene Hexane - Nanograde, redistilled in glass, if necessary.

5.12 Pesticide Standards - Acids and Methyl Esters, reference grade.

    5.12.1 Stock standard solutions - Dissolve 100 mg of each herbicide in 60 ml ethyl ether, then make to 100 ml with redistilled hexane. Solution contains 1 mg/ml.

    5.12.2 Working standard - Pipet 1.0 ml of each stock soln into a single 100 ml volumetric flask. Make to volume with a mixture of ethyl ether and hexane (1:1). Solution contains 10 µg/ml of each standard.

    5.12.3 Standard for Chromatography - (Diazomethane Procedure) Pipet 1.0 ml of the working standard into a glass stoppered test tube and evaporate off the solvent using steam bath. Add 2 ml diazomethane to the residue. Let stand 10 minutes with occasional shaking, then allow the solvent to evaporate spontaneously. Dissolve the residue in 200 µl of hexane for gas chromatography.

5.12.4 Standard for Chromatography -(Boron Trifluoride Procedure)

Pipet 1.0 ml of the working standard into a glass stoppered

test tube. Add 0.5 ml of Benzene and evaporate to 0.4 ml

using a two-ball Snyder microcolumn and a steam bath.

Proceed as in 11.3.1. Esters are then ready for gas

chromatography.

6. Calibration

6.1 Gas chromatographic operating conditions are considered acceptable

if the response to dicapthon is at least 50% of full scale when $\leq$ 0.06

ng is injected for electron capture detection and $\leq$ 100 ng is injected

for microcoulometric or electrolytic conductivity detection. For all

quantitative measurements, the detector must be operated within its

linear response range and the detector noise level should be less

than 2% of full scale.

6.2 Standards, prepared from methyl esters of phenoxy acid herbicides

calculated as the acid equivalent, are injected frequently as a check

on the stability of operating conditions.

6.3 The elution order and retention ratios of methyl esters of chlorinated

phenoxy acid herbicides are provided in Table 1, as a guide.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control

checks. When the routine occurrence of a pesticide is being observed

the use of quality control charts is recommended (3).

7.2 Each time a set of samples is extracted, a method blank is determined

on a volume of distilled water equivalent to that used to dilute the

sample.

8. Sample Preparation

   8.1 Blend the sample, if suspended matter is present.

   8.2 For a sensitivity requirement of 1 µg/1, when using electron
   capture for detection, take 100 ml of sample for analysis.
   For microcoulometric or electrolytic conductivity detection, take
   1-liter of sample. Background information on the extent and nature
   of interferences will assist the analyst in selecting the proper
   sample size and detector.

   8.3 Quantitatively transfer the proper aliquot of sample into a two-liter
   separatory funnel, dilute to one liter and acidify to approximately
   pH 2 with concentrated sulfuric acid. Check pH with indicator paper.

9. Extraction

   9.1 Add 150 ml of ether to the sample in the separatory funnel and shake
   vigorously for one minute.

   9.2 Allow the contents to separate for at least ten minutes. After the
   layers have separated, drain the water phase into a one-liter
   Erlenmeyer flask. Then collect the extract in a 250 ml ground-glass
   Erlenmeyer flask containing 2 ml of 37 percent aqueous potassium
   hydroxide.

   9.3 Extract the sample two more times using 50 ml of ether each time, and
   combine the extracts in the Erlenmeyer flask. (Rinse the one-liter
   flask with each additional aliquot of extracting solvent.)

10. Hydrolysis

   10.1 Add 15 ml of distilled water and a small boiling stone to the flask
   containing the ether extract, and fit the flask with a 3-ball Snyder
   column. Evaporate the ether on a steam bath and continue heating
   for a total of 60 minutes.

10.2 Transfer the concentrate to a 60 ml separatory funnel. Extract the basic solution two times with 20 ml of ether and discard the ether layers. The herbicides remain in the aqueous phase.

10.3 Acidify the contents of the separatory funnel by adding 2 ml of cold (4 C) 25 percent sulfuric acid (5.9). Extract the herbicides once with 20 ml of ether and twice with 10 ml of ether. Collect the extracts in a 125 ml Erlenmeyer flask containing about 0.5 g of acidified anhydrous sodium sulfate (5.8). Allow the extract to remain in contact with the sodium sulfate for approximately two hours.

11. Esterification (4,5)

11.1 Transfer the ether extract, through a funnel plugged with glass wool, into a Kuderna-Danish flask equipped with a 10 ml graduated ampul. Use liberal washings of ether. Using a glass rod, crush any caked sodium sulfate during the transfer.

11.1.1 If esterification is to be done with diazomethane, evaporate to approximately 4 ml on a steam bath (do not immerse the ampul in water) and proceed as directed in Section 11.2.

11.1.2 If esterification is to be done with boron trifluoride, add 0.5 ml benzene and evaporate to about 5 ml on a steam bath. Remove the ampul from the flask and further concentrate the extract to 0.4 ml using a two-ball Snyder microcolumn and proceed as in 11.3.

11.2 Diazomethane Esterification

11.2.1 Disconnect the ampul from the K-D flask and place in a hood away from steam bath. Adjust volume to 4 ml with ether, add 2 ml diazomethane, and let stand 10 minutes with occasional swirling.

158

11.2.2 Rinse inside wall of ampul with several hundred microliters of ethyl ether. Take sample to approximately 2 ml to remove excess diazomethane by allowing solvent to evaporate spontaneously (room temperature).

11.2.3 Dissolve residue in 5 ml of hexane. Analyze by gas chromatography.

11.2.4 If further clean-up of the sample is required, proceed as in 11.3.4 substituting hexane for benzene.

11.3 Boron Trifluoride Esterification

11.3.1 After the benzene solution in the ampul has cooled, add 0.5 ml of borontrifluoride-methanol reagent. Use the two-ball Snyder micro column as an air-cooled condenser and hold the contents of the ampul at 50 C for 30 minutes on the steam bath.

11.3.2 Cool and add about 4.5 ml of a neutral 5 percent aqueous sodium sulfate solution so that the benzene-water interface is in the neck of the Kuderna-Danish ampul. Seal the flask with a ground glass stopper and shake vigorously for about one minute. Allow to stand for three minutes for phase separation.

11.3.4 Pipet the solvent layer from the ampul to the top of a small column prepared by plugging a disposable Pasteur pipet with glass wool and packing with 2.0 cm of sodium sulfate over 1.5 cm of Florisil adsorbent. Collect the eluate in a graduated ampul. Complete the transfer by repeatedly rinsing the ampul with small quantities of benzene and passing the rinses through the column until a final volume of 5.0 ml of eluate is obtained. Analyze by gas chromatography.

12 Calculation of Results

12.1 Determine the methyl ester concentration by using the absolute

calibration procedure described below or the relative calibration

procedure described in Part I, Section 3.4.2 (2).

(1) Micrograms/liter = $\dfrac{(A)\quad(B)\quad(V_t)}{(V_1)\quad(V_s)}$

A = $\dfrac{\text{ng standard}}{\text{Standard area}}$

B = Sample aliquot area

V_1 = Volume of extract injected (μl)

V_t = Volume of total extract (μl)

V_s = Volume of water extracted (ml)

12.2 Molecular weights for the calculation of the methyl esters as the

acid equivalents.

2,4-D	222.0	Dicamba	221.0
2,4-D Methyl ester	236.0	Dicamba methyl ester	236.1
Silvex	269.5	2,4,5-T	255.5
Silvex methyl ester	283.5	2,4,5-T methyl ester	269 5

13. Reporting Results

13.1 Report results in micrograms per liter as the acid equivalent without

correction for recovery data. When duplicate and spiked samples are

analyzed all data obtained should be reported.

REFERENCES

(1) Goerlitz, D. G., and Lamar, W. L., "Determination of Phenoxy and Herbicides in Water by Electron-Capture and Microcoulometric Gas Chromatography", U. S. Geol. Survey Water-Supply Paper 1817-C (1967).

(2) "Methods for Organic Pesticides in Water and Wastewater", (1971) U. S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio.

(3) "Handbook for Analytical Quality Control in Water and Wastewater Laboratories" (1972), U. S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio 45268.

(4) Metcalf, L. D., and Schmitz, A. A., "The Rapid Preparation of Fatty Acid Esters for Gas Chromatographic Analysis", _Analytical Chemistry_, _33_, 363 (1961).

(5) Schlenk, H. and Gellerman, J. L., "Esterification of Fatty Acids with Diazomethane on a Small Scale", _Analytical Chemistry_, _32_, 1412 (1960).

(6) "Pesticide Analytical Manual", U. S. Department of Health, Education, and Welfare, Food and Drug Administration, Washington, D.C.

(7) Steere, N. V., editor, "Handbook of Laboratory Safety," Chemical Rubber Company, 18901 Cranwood Parkway, Cleveland, Ohio 44128, 1971, pp. 250-254.

APPENDIX I

Diazomethane in ether (6).

1. CAUTIONS. Diazomethane is very toxic. It can explode under certain

conditions. The following precautions should be observed.

Avoid breathing vapors.

Use only in well-ventilated hood.

Use safety screen.

Do not pipette solution of diazomethane by mouth.

For pouring solutions of diazomethane, use of gloves is optional.

Do not heat solutions to 100 C (EXPLOSIONS).

Store solutions of gas at low temperatures (Freezer compartment of explosion

proof refrigerators).

Avoid ground glass apparatus, glass stirrers and sleeve bearings where

grinding may occur (EXPLOSIONS).

Keep solutions away from alkali metals (EXPLOSIONS).

Solutions of diazomethane decompose rapidly in presence of solid material

such as copper powder, calcium chloride, boiling stones, etc. These solid

materials cause solid polymethylene and nitrogen gas to form.

2. PREPARATION.

Use a well-ventilated hood and cork stoppers for all connections.

Fit a 125 ml long-neck distilling flask with a dropping funnel and an

efficient condenser set downward for distillation. Connect the condenser

to two receiving flasks in series - a 500 ml Erlenmeyer followed by a

125 ml Erlenmeyer containing 30 ml ether. The inlet to the 125 ml Erlenmeyer

should dip below the ether. Cool both receivers to 0 C.

As water bath for the distilling flask, set up a 2-liter beaker on a

stirplate (hot plate and stirrer), maintaining temperature at 70 C.

Dissolve 6 g KOH in 10 ml water in the distilling flask (no heat).
Add 35 ml Carbitol (diethylene glycol monoethyl ether), stirring bar, and
another 10 ml ether. Connect the distilling flask to the condenser and
immerse distilling flask in water bath. By means of the dropping funnel,
add a solution of 21.5 g Diazald in 140 ml ether over a period of 20 minutes.
After distillation is apparently complete, add another 20 ml ether and
continue distilling until distillate is colorless. Combine the contents of
the two receivers in a glass bottle (WITHOUT ground glass neck), stopper
with cork, and freeze overnight. Decant the diazomethane from the ice
crystals into a glass bottle, stopper with cork, and store in freezer until
ready for use. The final solution may be stored up to six months without
marked deterioration.

The 21.5 g of Diazald reacted in this manner produce about 3 g of
Diazomethane.

SAIS

Figure C-1

SLUDGE
3.0 grams
  Sample
    + 100 ml MeOH
    + 10 ml 5N KOH
    + stirring rod
Stir 1 hour
    + 100 ml hexane
    + 200 ml dist. H_2O
Stir 1 hour
  Millipore
    discard filters
Transfer fillerate into
  separate funnel

Scrubber H_2O
  Sample
    + 100 ml MeOH
    + 10 ml 5N KOH
    in a sep. funnel
Stand 20 min.
    + 200 ml dist. H_2O
    + 100 ml hexane
    shake
Extract

separate hexane layer
  save hexane

Extract
  aqueous layer $\bar{c}$ 100 ml hexane
  discard aqueous layer

Combine hexane layers
  wash with
  2X 100 ml in NaOH
  2X 100 ml in HCl
  2X 100 ml dist. H_2O

Separatory funnel
  shake $\bar{c}$ H_2SO_4 till acid is
    clear after standing 10 mins.

Wash extract $\bar{c}$ 2 x 100 ml dist. H_2O
  discard aqueous layer

Dry extract over Na_2SO_4

Boil down to 10 mls

Pass through Na_2SO_4 - $NaHCO_3$ column

Pass hexane through prerinsed
  15 gm Al_2O_3 column
    elute with
    (1) 100 ml pet ether
    (2) 50 ml of 5% diethyl ether
        in pet ether
    discard

Pass 100 ml of 50% diethylether in pet ether
  through column
  & collect

Boil down to about 5 ml

Evaporate to dryness

Adjust volume to 1 ml with hexane
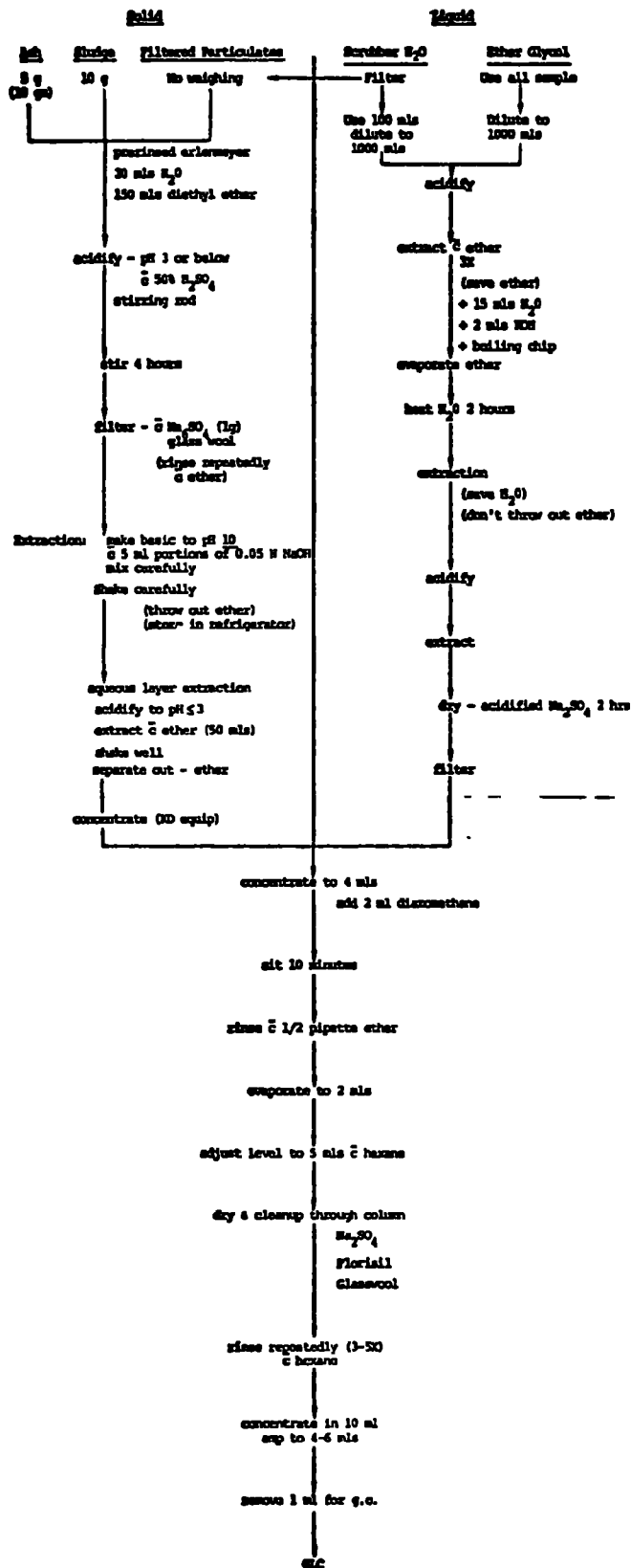
GLC

Figure C-2

165

Figure C-3. Chromatogram of Typical Non-Particulate Stack Gas Sample
(Full scale 2,4,5-T burn)

Full scale tracings are also typical of pilot scale
tracings.
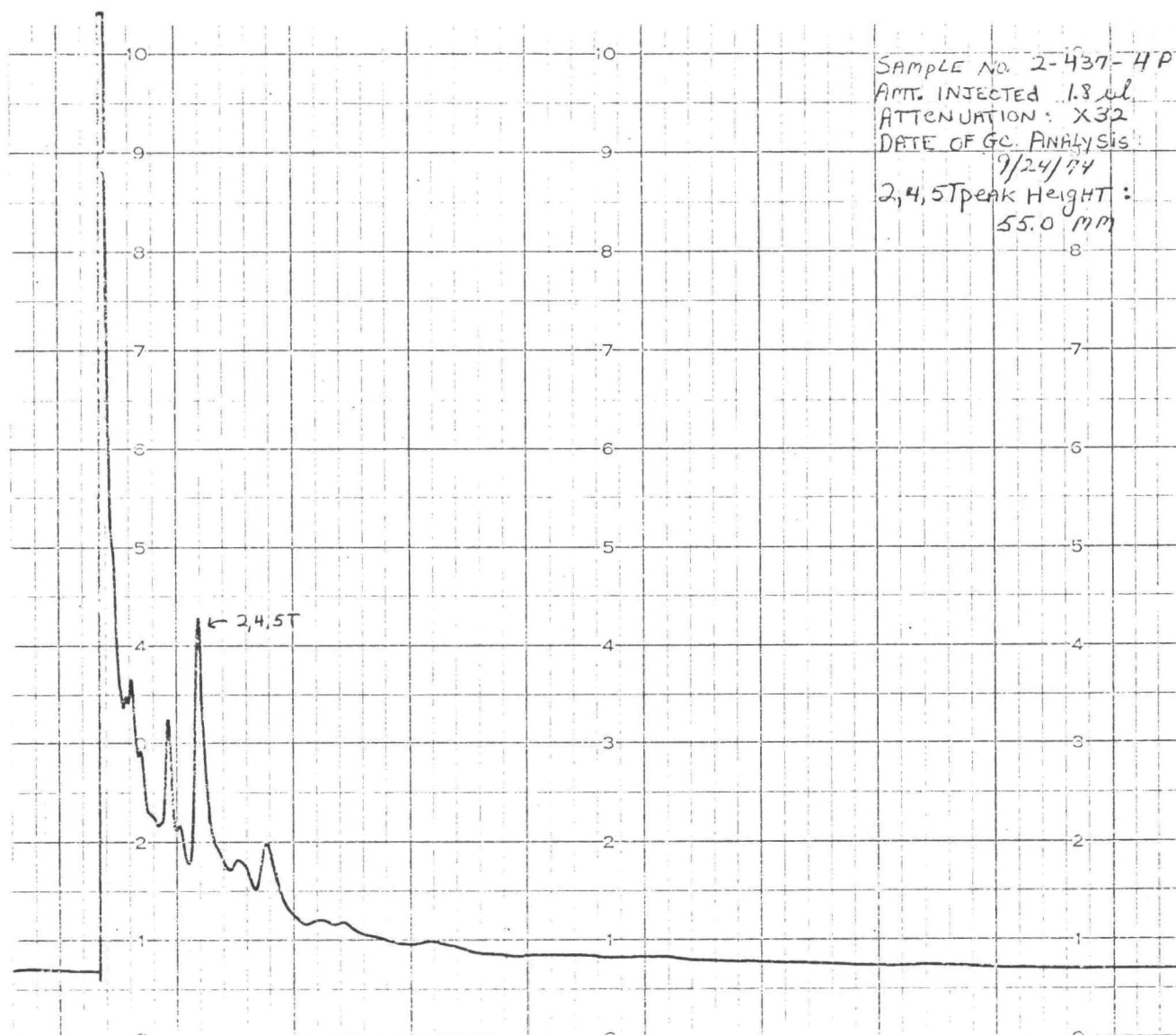
Figure C-4. Chromatogram of Typical Stack Gas Particulate Sample
(Full scale 2,4,5-T burn)
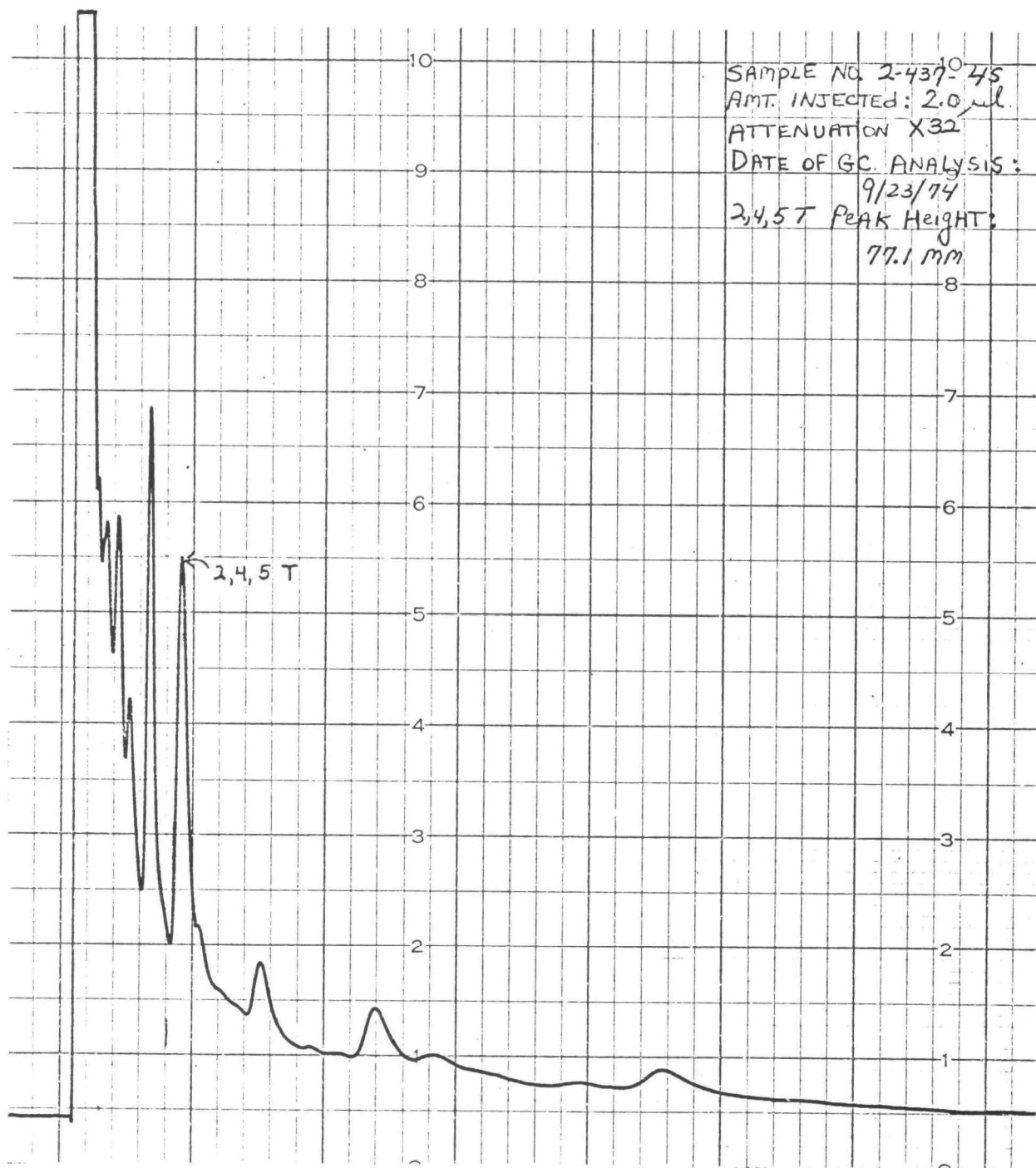
Figure C-5. Chromatogram of Typical Scrubber Water Filtrate Sample
(Full Scale 2,4,5-T burn)

168
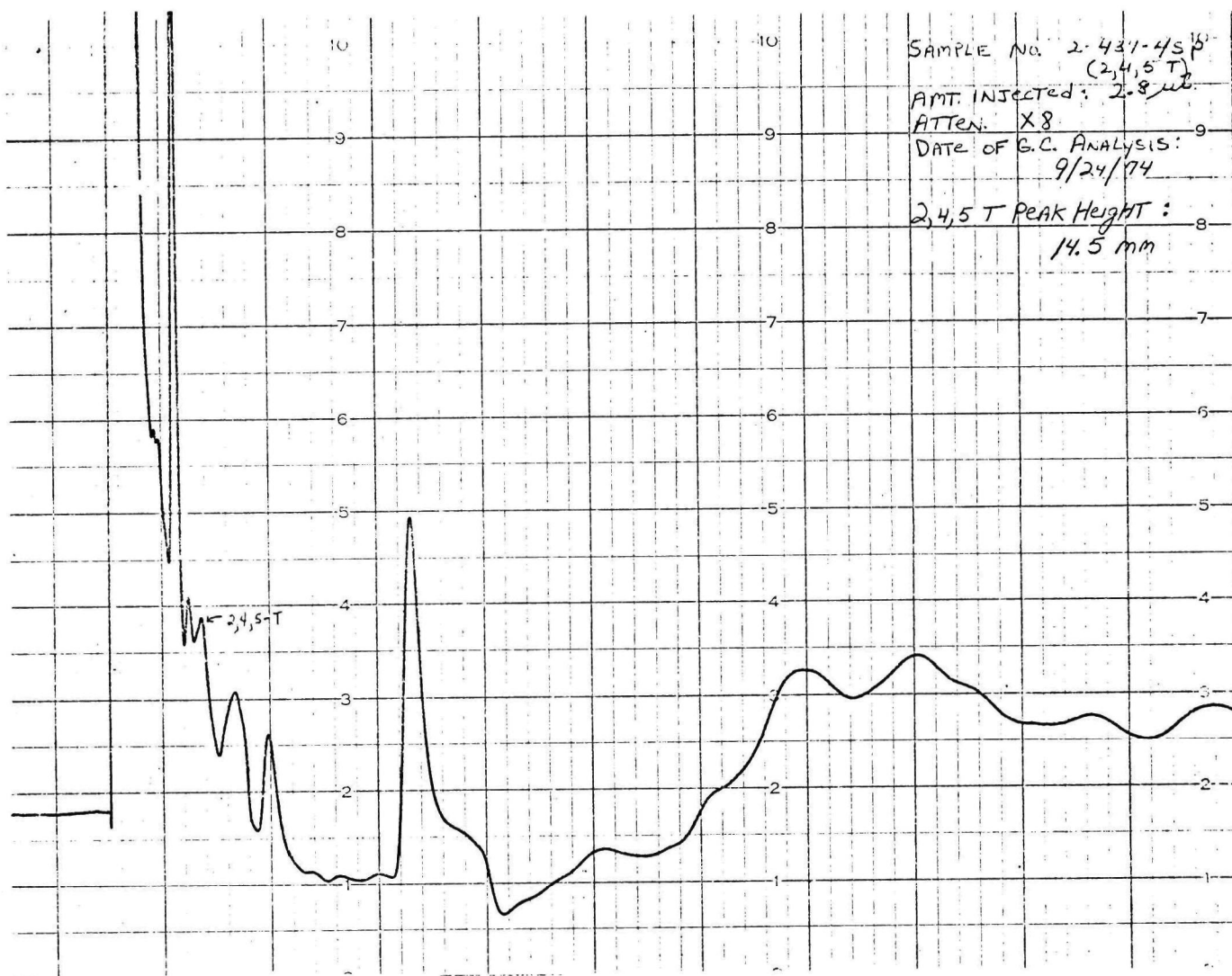
Figure C-6. Chromatogram of Typical Scrubber Water Particulate Samples
(Full scale 2,4,5-T burn)

169
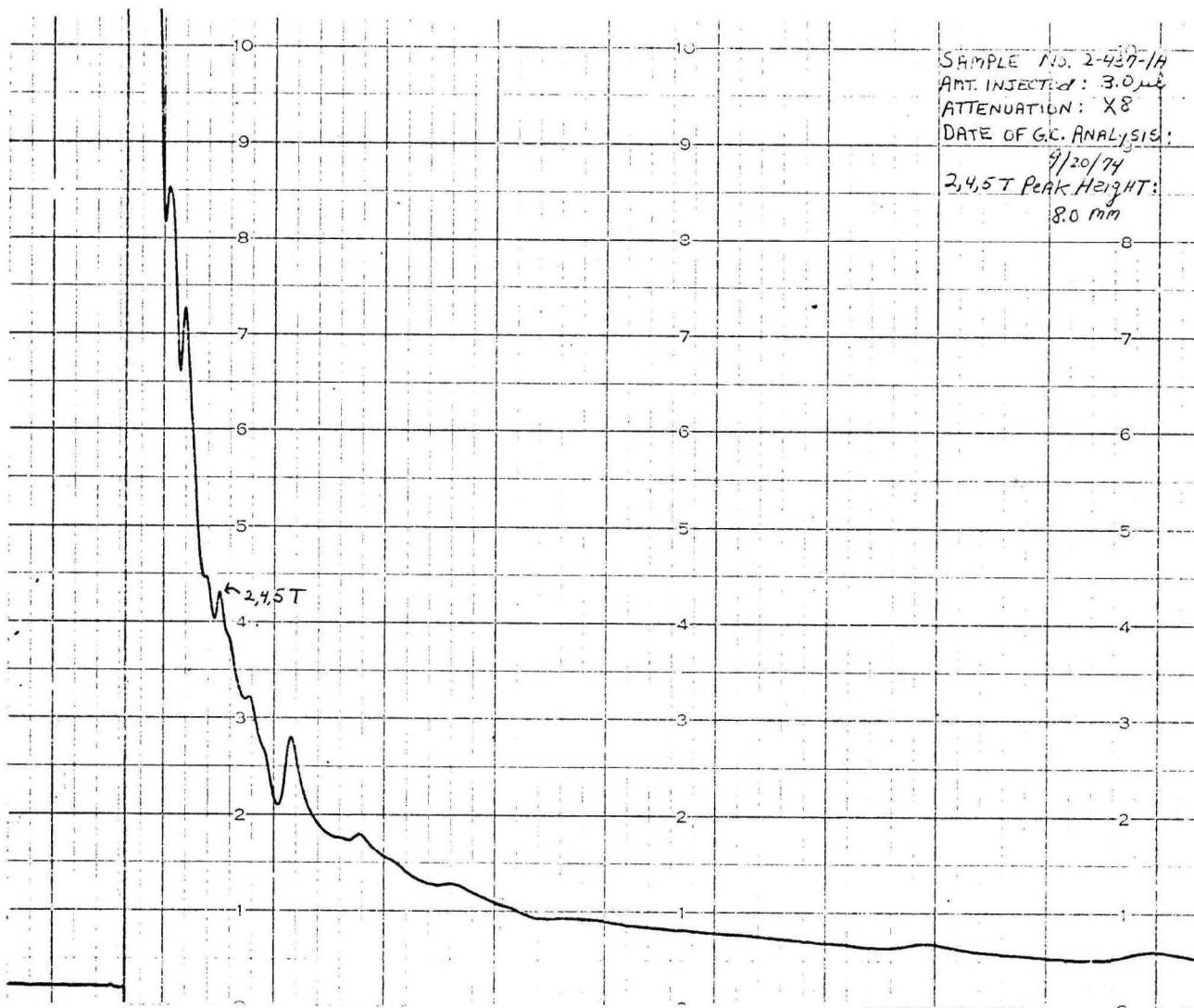
Figure C-7.   Chromatogram of Typical Product Sample
(Full scale 2,4,5-T burn)

170
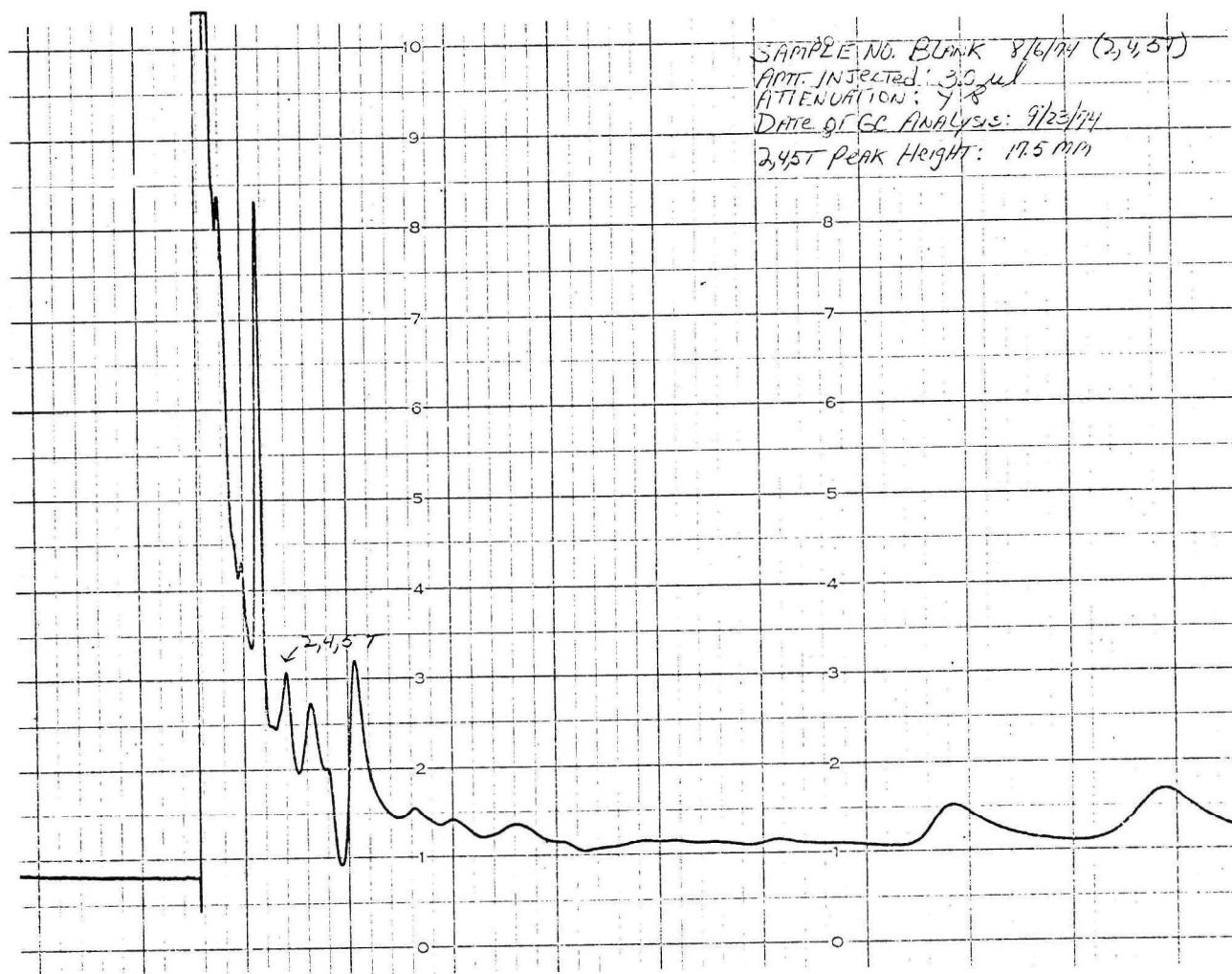
Figure C-8. Laboratory Blank - 2,4,5-T

Note: A laboratory blank was analyzed with every four samples processed. The raw data was then corrected for these residual levels.

171

2,4,5 T STANDARD
CONCENTRATION: 50 pico-
grams/μl
AMT. INJECTED: 3.1 λ
(155 picograms)
ATTENUATION: X8
DATE OF ANALYSIS: 9/25/74
2,4,5 T PEAK HEIGHT:
193.5 mm
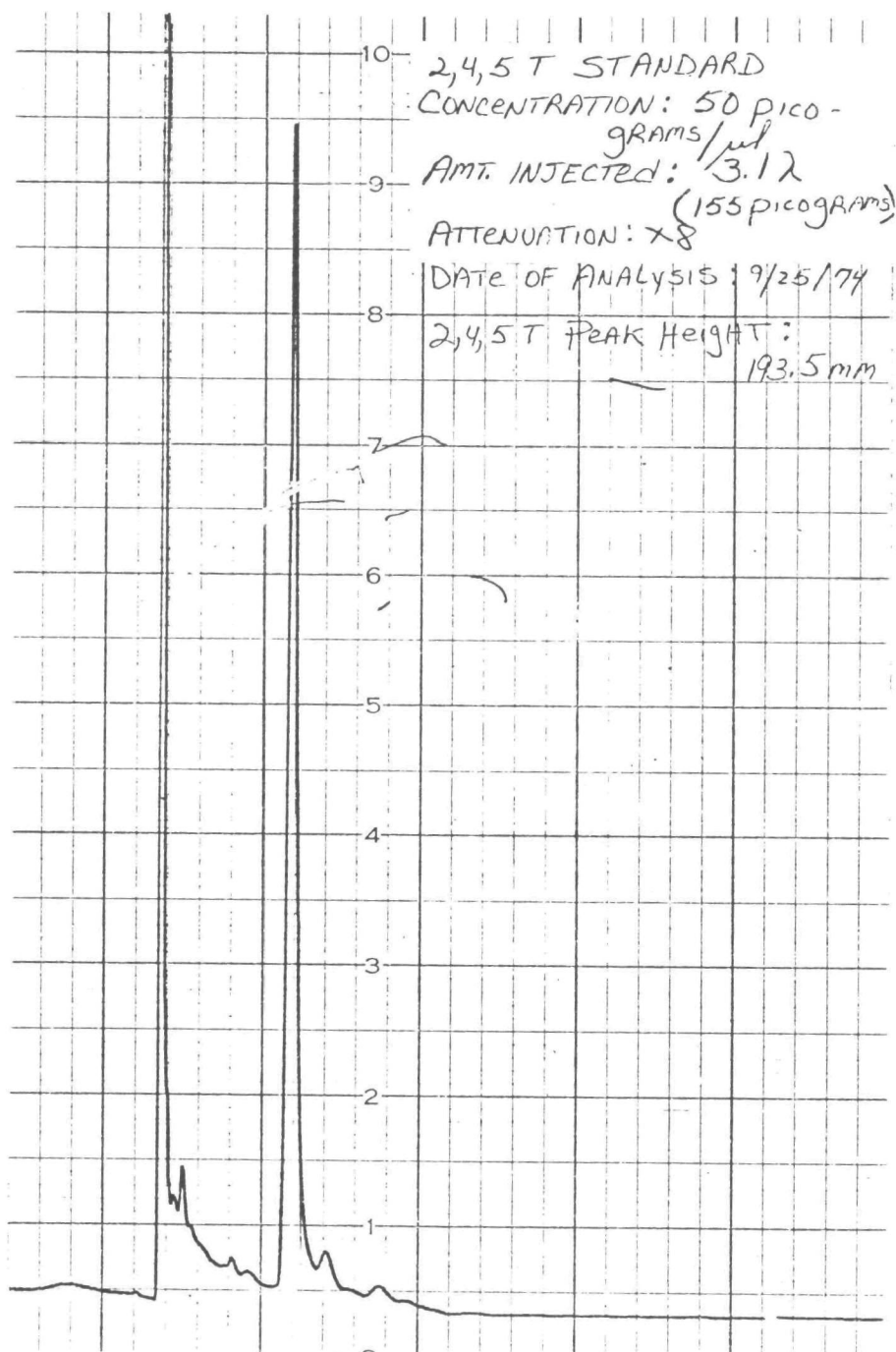
Figure C-9. Chromatogram of 2,4,5-T Standard

172

APPENDIX D

PARTIAL LIST OF OPERATING MUNICIPAL INCINERATORS
IN THE CONTINENTAL UNITED STATES

NOTE: In general, all of the following facilities have
       installed scrubber systems which allow them to
       comply with current emission standards. Most fa-
       cilities constructed previous to 1972 have im-
       pingement type scrubbers. High energy venturi
       scrubbers have normally been installed in the fa-
       cilities constructed after 1972.

173

BSP DIVISION, ENVIROTECH SYSTEMS
MUNICIPAL WASTE SLUDGE DISPOSAL INSTALLATIONS SINCE 1963

Year Sold	Location	Furnace Dia.	Design Dry Solids (lbs/hr) Each	Design Solids Content	Sludge Source
1963	Cleveland, Ohio	22'3" O.D.- 9H	5400	20-28%	Dig.P./Act.
1963	East Rochester, N.Y.	10'9" O.D.- 5H	600	25%	Pri./Humus
1963	Oakland, California	10'9" O.D.- 6H	900	25-60%	Grease Skimmings
1964	New Orleans, La.	18'9" O.D.- 9H	3600	30%	Pri./Grit/Scum/Screening
1964	Holyoke, Mass.	7'0" x 40' lg.	2030	30%	Primary
1964	Ann Arbor, Michigan	16'9" O.D.- 6H	1700	20-22%	Pri./Act.
1964	East Lansing, Mich.	16'9" O.D.- 6H	1700	19-22%	Pri./Act.
1965	Cinnaminson, N.J.	10'9" O.D.- 6H	500	20-22%	Pri./Act.
1965	Minn.-St. Paul, Minn.	22'3" O.D.-11H	6600	23-25%	Pri./Act.
1966	Battle Creek, Mich.	18'9" O.D.- 6H	2200	23-25%	Pri./Humus/Act.
1966	Mattabasset, Conn.	22'3" O.D.- 7H	4000	25-30%	Pri./Chem. Precip.
1966	Washington, D.C.	39" I.D.- 6H	25	20-30%	Pri./Act./Lime Sludge
1966	Orangetown, N.Y.	16'9" O.D.- 6H	1750	20-22%	Pri./Humus
1967	So. Tahoe, Ca.	14'3" O.D.- 6H	900	20%	Pri./Act.
1967	So. Tahoe, Ca.	14'3" O.D.- 6H	1500	40%	Lime Sludge
1967	Lake Charles, La.	14'3" O.D.- 6H	1500	22%	Dig. Act.
1967	San Lorenzo, Ca.	22'3" O.D.- 6H	3250	22%	Pri./Act./Dig.
1967	Middleburg Hts., O.	10'9" O.D.- 6H	450	20%	Dig. Act.
1967	Chicopee, Mass.	14'3" O.D.- 5H	1000	28%	Primary
1968	Johnston County, Kan.	18'9" O.D.- 5H	1800	22%	Pri./Act./Dig.
1968	San Mateo, Ca.	18'9" O.D.- 5H	2000	25%	Primary
1968	Colorado Springs, Col.	4500 GPH	2100	5.6%	Pri./Humus

Year Sold	Location	Furnace Dia.	Design Solids (lbs/hr) Each	Design Solids Content	Sludge Source
1969	Monterey, Calif.	14'3" O.D.- 6H	900	20%	Pri./Act.
1969	Atlanta, Ga.	22'3" O.D.-10H	5000	20-30%	Dig.Pri./Act.
1969	Lake Arrowhead, Ca.	10'9" O.D.- 5H	500	22%	Pri./Act.
1969	Sunset Valley, Ore.	1000 GPH	420	5%	Pri./Act.
1969	Concord, Calif.	16'9" O.D.- 6H	1200	20-25%	Pri./Humus
1969	San Clemente, Ca.	14'3" O.D.- 7H	1100	22-28%	Pri./Act.
1969	Palo Alto, Ca.	18'9" O.D.- 6H	1200	15%	Pri./Act.
1969	Trenton, Mich.	16'9" O.D.- 8H	1200	20%	Pri./Act.
1969	Colorado Springs, Col.	6'0" O.D.- 6H	250	60%	Lime Sludge
1969	Colorado Springs, Col.	4'0" O.D.- 6H	83	50%	Act. Carbon
1969	BEB, Minn.	22'3" O.D.- 7H	3300	22%	Pri./Act.
1970	Enfield, Conn.	22'3" O.D.- 6H	2400	20%	Pri./Act.
1970	Middletown, O.	18'9" O.D.- 6H	1900	25%	Pri./Act.
1970	Monroe County, N.Y.	22'3" O.D.- 6H	3600	40%	Lime Sludge
1970	Monroe County, N.Y.	22'3" O.D.- 6H	2000	20%	Pri/Act.
1970	Glastonbury, Conn.	16'9" O.D.- 6H	1200	22%	Pri./Act.
1971	New Bedford, Mass.	16'9" O.D.- 5H	1500	30%	Primary
1971	Stafford Springs, Conn.	10'9" O.D.- 6H	390	20%	Pri./Act.
1971	Cincinnati, O. (Muddy Creek Plant)	4000 GPH	1830	4-6 %	Pri./Act.
1971	Cincinnati, O. (Muddy Creek Plant)	16'9" O.D.- 6H	2300	35%	Pri.Act.
1971	Little Rock, Ark.	22'3" O.D.- 7H	2300	35%	Pri./Act.
1971	Muskogee, Okla.	3000 GPH	1375	5.5%	Pri./Humus
1971	Muskogee, Okla.	10'9" O.D.- 6H	1500	35%	Pri./Humus
1971	Stratford, Conn.	16'9" O.D.- 8H	1750	22%	Pri./Act.
1971	Bristol, Tenn.	18'9" O.D.- 6H	1350	20%	Pri./Act.
1971	Rutherford Heights (Swatara) Penn.	10'9" O.D.- 6H	390	20%	Pri./Act.
1971	Canton, Ohio	18'9" O.D.- 6H	2400	30%	Pri./Dig.
1971	Colorado Springs, Col.	5000 GPH	2330	5.6%	Pri./Humus/Dig. Act.
1971	Albany, N.Y.	22'3" O.D.-10H	5000	20%	Pri./Act.
1971	Anchorage, Alaska	14'3" O.D.- 6H	1100	25%	Primary

Year Sold	Location	Furnace Dia.	Design Solids (lbs/hr) Each	Design Solids Content	Sludge Source
1971	Auburn, N.Y.	22'3" O.D.- 6H	3000	22%	Pri./Act.
1971	Columbia, S.C.	16'9" O.D.- 7H	1695	50%	Pri./Act.
1971	San Jose, Ca.	22'3" O.D.- 4H	5000	40%	Grease/Grit/Screen
1971	Vancouver, Wash.	4000 GPH	1675	3-8 %	Pri./Act.
1971	Erie, Pa.	22'3" O.D.-10H	4500	20%	Pri./Act.
1972	Portland, Ore.	5000 GPH	1875	4.5%	Waste Activated
1972	Groton, Conn.	2000 GPH	835	5%	Pri./Act.
1972	Groton, Conn.	10'9" O.D.- 7H	1000	35%	Pri./Act.
1972	Savannah, Ga.	16'9" O.D.- 8H	5200	50%	Pri./Act.
1972	Grand Haven, Mich.	16'9" O.D.- 6H	1675	30%	Pri./Act.
1972	Camp-Hill, Lemyone, Pa.	10'9" O.D.- 7H	670	30-35%	Pri./Act.
1972	Wyoming, Mich.	18'9" O.D.- 6H	1950	18-26%	Pri./Act.
1972	East Lansing, Mich.	16'9" O.D.- 6H	1750	25-30%	Pri./Act.

NICHOLS ENGINEERING & RESEARCH CORPORATION
SEWAGE SLUDGE INSTALLATION LIST

City	Year Built	No. of Units	Size O.D.	Hearths	Capac. Tons/ 24 Hrs.	Type of Sludge
Dearborn	1934	1	16'9"	6	50	Raw primary
Auburn, N.Y.	1936	1	10'9"	6	28	Digested activated
New Britain, Conn.	1936	1	14'3"	6	48	Chem.-aerated
Cleveland-West	1937	2	14'3"	6	96	Digested
Minneapolis-St. Paul	1938	3	22'3"	8	540	Raw primary
Cleveland-South	1938	4	18'9"	8	400	Digested
Barberton, Ohio	1938	1	10'9"	6	24	Raw primary
Columbus, Ohio	1938	1	16'9"	6	60	Digested activated
Wayne County, Mich.	1939	1	16'9	8	75	Raw primary
Detroit, Mich.	1939	4	22'3"	11	1100	Raw primary
New Haven, Blvd.	1939	1	14'3"	6	40	Digested primary
New Haven, East	1939	1	14'3"	6	40	Raw primary
Dayton, Ohio	1939	1	14'3"	6	48	Digested
Cranston, R.I.	1941	1	14'3"	6	48	Digested
Dearborn, Mich.	1945	1	16'9"	7	75	Raw primary
Fall River, Mass.	1948	1	16'9"	6	65	Digested
Akron, Ohio	1949	4	18'9"	5	300	Digested
Ann Arbor, Mich.	1949	1	14'3"	6	45	Digested activated
Providence, R.I.	1949	1	22'3"	8	165	Raw primary
Bridgeport-West	1949	1	18'9"	5	90	Raw primary
Bridgeport-East	1949	1	18'9"	5	75	Raw primary
Cincinnati-Little Miami	1950	2	14'3"	5	90	Digested
Minneapolis-St. Paul	1950	1	22'3"	8	170	Raw primary

City	Year Built	No. of Units	Size O.D.	Hearths	Capac. Tons/ 24 Hrs.	Type of Sludge
Bay City, Mich.	1952	1	14'3"	6	45	Raw primary
Arlington, Va.	1952	1	18'9"	6	80	Digested
Campbell-Kenton, Ky.	1952	1	18'9"	5	55	Raw primary
West New York, N.J.	1952	1	12'10"	4	25	Raw primary
Milwaukee, Wis.	1952	1	16'9"	5	48	G & SC only
Williamsport, Pa. (West)	1953	1	14'3"	6	45	Raw primary
Williamsport, Pa. (Cent.)	1953	1	14'3"	6	45	Digested
Steubenville, Ohio	1954	1	12'10"	6	36	Digested
Marietta, Ohio	1954	1	9'3"	6	18	Digested
Columbus, Ohio	1954	1	22'3"	7	150	Digested activated
Indianapolis, Ind.	1955	4	22'3"	8	675	Raw primary
Cincinnati, Mill Creek	1955	4	22'3"	9	600	Digested
Columbus, Ohio	1956	1	22'3"	7	150	Digested activated
Nashville, Tenn.	1956	1	18'9"	7	108	Raw primary
Grand Rapids, Mich.	1956	1	16'9"	7	80	Digested
Rochester, N.Y.	1957	2	22'3"	5	288	Digested, G & SC
Euclid, Ohio	1958	1	14'3"	6	48	Digested
Bradford, Pa.	1958	1	16'9"	7	74	Liquid
Milwaukee, Wis.	1959	1	16'9"	5	48	G & SC only
Warren, Ohio	1959	2	16'9"	5	100	Raw primary
McKeesport, Pa.	1959	1	16'9"	7	70	Raw primary
Battle Creek, Mich.	1960	1	18'9"	5	78	Digested
Johnstown, Pa.	1960	1	14'3"	5	39	Raw primary
Cuyahoga Co., Ohio	1961	1	18'9"	5	75	Digested
Boston, Mass.	1961	1	12'10"	6	36	G & SC only
Pontiac, Mich.	1961	1	22'3"	7	144	Digested
Fairbanks, Alaska	1961	1	12'10"	5	27	Raw primary

City	Year Built	No. of Units	O.D.	Hearths	Capac. Tons/ 24 Hrs.	Type of Sludge
Detroit, Mich.	1962	1	22'3"	11	294	Raw primary, G & Sk
Flint, Mich.	1962	2	18'9"	6	209	Digested
Huntington, W. Va.	1962	1	18'9"	6	108	Raw primary, G, SC&GS
Wayne County, Mich.	1962	1	22'3"	6	135	Raw primary
Wyoming, Mich.	1962	1	16'9"	6	69	Digested
Youngstown, Ohio	1962	2	22'3"	7	319	Raw primary
Saginaw, Mich.	1963	1	16'9"	6	70	Raw primary
Rock Falls, Ill.	1963	1	10'9"	5	22	Raw primary
Detroit, Mich.	1963	1	22'3"	11	294	Raw primary, G & GS
Kansas City, Mo.	1963	3	22'3"	8	550	Raw primary & GS
Canajoharie, N.Y.	1963	1	14'3"	5	39	Raw primary
Providence, R.I.	1963	1	22'3"	9	240	Raw primary
Burlington Twsp., N.J.	1964	1	6'0"	6	5	Raw primary TF
Bridgeport, Pa.	1964	1	6'0"	6	8	Raw primary, TF
Jersey City, N.J.	1964	1	22'3"	10	246	Raw primary, SC & G
St. Charles, Mo.	1964	1	12'10"	5	34	Raw primary
New Haven, Conn.	1964	1	22'3"	9	246	Raw primary GS & S
St. Louis (Lemay Plant)	1965	3	22'3"	11	750	Raw primary & G
St. Louis (Bissell Point)	1965	5	22'3"	11	1,250	Raw primary, GS & G
Hatfield, Pa.	1965	1	10'9"	6	22	Raw primary & A
Nashville, Tenn.	1965	1	18'9"	7	104	Raw primary & A
Columbus, Ohio	1966	2	22'3"	8	360	Raw primary, digested & GS
Indianapolis, Ind.	1967	4	22'3"	8	672	Digested primary & A
Wyoming Valley, Pa.	1967	1	18'9"	8	159	Raw primary & A
Tonawanda, N.Y.	1967	1	22'3"	5	132	Raw primary, digested & G
Fairfax County, Va.	1968	2	18'9"	7	252	Raw primary & GS
Richmond, Calif.	1968	1	16'9"	7	84	Digested primary & A
Up. Moreland-Hatboro, Pa.	1968	1	16'9"	5	60	Raw primary & A
Plymouth, E. Norriton, Pa.	1968	1	18'9"	8	123	Raw primary & sec.

City	Year Built	No. of Units	Size O.D.	Hearths	Capac. Tons/ 24 Hrs.	Type of Sludge
Greensboro, N.C.	1969	1	18'9"	5	72	Raw primary, TF & A
Charleston, S.C.	1969	1	22'3"	5	132	Raw primary
Oswego, N.Y.	1969	2	16'9"	6	125	Raw primary
Hartford, Conn.	1969	3	22'3"	11	800	Raw primary, activated
Newark, Ohio	1969	1	18'9"	5	73	Digested primary & A
Upper Gwynedd, Pa.	1969	1	9'3"	5	13	Raw primary, TF
Kalamazoo, Mich.	1969	1	22'3"	7	187	Raw primary & A Low oxidation
Saginaw, Mich.	1970	1	22'3"	6	156	Raw primary & A
Minneapolis-St. Paul	1970	1	22'3"	11	300	Raw primary & A
Rochester, N.Y.	1970	1	22'3"	6	143	Raw primary & A
Rochester, N.Y.	1970	2	22'3"	11	537	Raw primary & A
Portage, Indiana	1970	1	10'9"	5	12	Raw primary & A
Delta Township, Mich.	1970	1	16'9"	5	58	Raw primary & A
Beacon, N.Y.	1970	1	14'3"	6	43	Raw primary & digested waste activated
Detroit, Mich.	1971	6	25'9"	12	2,622	Raw primary & A
Elizabethton, Tenn.	1971	1	12'10"	5	24	Raw primary & A
Warren, Mich.	1971	1	25'9"	10	326	Raw primary & A
Brookfield, Wisc.	1971	1	12'10"	5	32	Raw primary & A
Clarksburg, W. Va.	1971	1	14'3"	6	44	Raw primary & A
Paw Paw Lake, Mich.	1971	1	12'10"	5	31	Raw primary & TF
Passaic Valley, N.J.	1971	2	25'9"	6	125	G, SC & SK
Clark County, Nev.	1971	1	18'9"	7	104	Heat treated primary & TF
Waterbury, Conn.	1971	1	22'3"	7	136	Primary waste activated & SK
Oxnard, Calif.	1971	1	22'3"	6	35	Raw primary & SK
Naugatuck, Conn.	1971	2	22'3"	6	250	Primary & secondary & SK
Dunkirk, N.Y.	1972	2	18'9"	5	44	Primary, secondary
Carson City, Nev.	1972	1	10'9"	6	128	Raw primary, TF, scum
Nashville, Tenn.	1972	2	22'3"	11	480	Primary, waste activated scum

City	Year Built	No. of Units	Size O.D.	Hearths	Capac. Tons/ 24 Hrs.	Type of Sludge
Monroe Co., N.Y.	1972	1	18'9"	6	84	Primary digested
Monroe Co., N.Y.	1972	1	18'9"	8	72	Lime
Louisville, Ky.	1972	3	22'3"	8	1,200	Primary, scum waste activated
Orange Co., Calif.	1972	1	9'3"	6	12	Carbon
Orange Co., Calif.	1972	1	22'3"	6	106	Lime
St. Charles, Mo.	1972	1	9'3"	6	12	Carbon
St. Charles, Mo.	1972	1	16'9"	5	55	Primary, waste activated
New Orleans, La.	1972	1	16'9"	5	52	Primary, trickling filter
Utoy Creek, Ga.	1973	1	22'3"	6	114	Raw primary digested
Detroit, Mich.	1973	2	25'9"	12	437	Primary, secondary
Fitchburg, Mass.	1973	1	10'9"	6	108	S., G., waste activated
Lower Lackawanna, Penna.	1973	1	16'9"	7	68	Primary
Fairfax, Va.	1973	2	25'9"	6	356	Raw, primary & waste activated
Genesee Co., Michigan	1973	3	18'9"	7	306	Primary, secondary, scum
Fitchburg E., Mass.	1973	1	22'3"	9	14	Carbon
Middletown, Conn.	1973	1	12'10"	6	32	Raw primary, waste activated
Killingby, Conn.	1973	1	22'3"	7	168	Primary, secondary

Designed to also handle grit (G), screenings (SC), skimmings (SK), scum (S), grease (GS), and ground refuse (GR). Also trickling filter (TF), activated (A), and activated press cake (APC).

APPENDIX E

STACK SAMPLING PROCEDURES

STACK SAMPLING PROCEDURES

The following section has been included in this report to explain the stack sampling procedures used in this study. Standard EPA methods were followed to the degree practically feasible. However, the reader should be aware that the sampling procedures were modified slightly to accomodate the physical characteristics of the pilot and full-scale systems. Consequently the data may not be rigorously quantitative. However, the potential for error is minimal and the results are considered substantially accurate.

In neither furnace used in this study did there exist a point in the exhaust duct that was completely suitable for applying the standard techniques. There was no accessible point that was sufficiently removed from any flow obstruction to insure a uniform velocity distribution across the duct. The velocity profile measured across each of the two stacks deviated slightly from a fully established, uniform velocity profile in the specific sense that the maximum velocity was found to be slightly closer to one wall of the duct than to the center. Under these conditions, perfectly isokinetic sampling is difficult, but was approximated insofar as was possible. The procedures used are described below.

A single four-point traverse was used in the pilot-scale tests. The stack of the pilot-scale incinerator was only eight inches in diameter and had only one sampling port available at the best sampling position. Therefore, it was impossible to conduct perpendicular traverses without installing a second sampling port, which was beyond the means of the contract. On the basis of the small size of the stack, it was concluded that a four-point traverse would be adequate to collect a representative sample.

In the full-scale tests, a seven point single traverse was used. As in the pilot-scale test, only one sampling port was available at the best position. A perpendicular traverse would have required another sample port which the city would not provide and for which there was not available funding. The circular stack was 18 inches in diameter. Under these conditions, it was decided that a seven-point single traverse would be adequate to collect a representative sample.

Since the above procedures are not precisely standard, it cannot be guaranteed that the samples collected were perfectly representative. However, the potential for error is very small:

1. Only particulates ranging in size from 2 to 3 microns could have been misrepresented. Gases and particles less than 2 microns have uniform concentrations and can be sampled representatively at any point inside a stack. Furthermore, it is an established fact that high energy venturi scrubbers such as used in this project can remove particulates greater than 3 microns with 95 percent efficiency. Thus, the potential for error with this sampling methodology would apply only to a small fraction of the particulates.

2. Given the sampling conditions used, the maximum potential error can be illustrated in the following worst-case example:

> If the total amount of pesticide-bearing particulate matter that was not collected was of the same amount as that actually collected (an assumption that obviously greatly overestimates the actual situation since at least half of the collected pesticide was included with particulates that passed through a 0.45 micron filter) the effect on the results of the experiment would amount to a decrease of less than 0.01 percent in the destruction ratio. This point can best be demonstrated by considering the experimental data in Tables 23, 24, and 25. If one were to double the quantity of each of the pesticide residues in the columns headed "Particulates" on these three tables, sum all the contributions as is shown in Table 33, one would find, for the worst-case (Experiment 3), that the total emitted pesticide would be at the rate of 5.24 gm/hr rather than the figure of 3.78 quoted in Table 33. The destruction ratio would, under these conditions, be 99.968 rather than the quoted 99.977.

From the above it is clear that, under the special circumstances of the reported experiments, the error in the quoted results that could have been associated with the selection of the sampling point is below that associated with normal analytical errors. Thus, the emission data is considered substantially correct.

μσ1238