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Item ID Number	04037 ☐ **Not Scanned**
Author	
Corporate Author	
Report/Article Title	Typescript: Analysis of Archived Samples of Herbicide Orange, USAFAM/EK, 28 November 1979
Journal/Book Title	
Year	1979
Month/Day	November 28
Color	☐
Number of Images	19
Description Notes	Attachments from cited literature: Table 6 from Young, et al., The Toxicology, Environmental Fate and Human Risk of Herbicide Orange and Its Associated Dioxin; Table 1 and Figures 1-4 from Fee, et al., Analytical Methodology for Herbicide Orange. Vol. II. Determination of Origin of USAF Stocks; and Tables XVI and XVII from Hughes, et al., Analytical Methodology for Herbicide Orange. Vol. I. Determination of Chemical Composition

ANALYSES OF ARCHIVED SAMPLES OF HERBICIDE ORANGE
USAFSAM/EK, 28 Nov 79

In a special report, dated 28 August 1979, the USAF Scientific Advisory Board Ad Hoc Committee Evaluating the Proposed Study of the Potential Long-Term Health Effects of Herbicides Containing 2,4,5-T and Associated Dioxin (TCDD) recommended that:

1. The Air Force inventory all available Herbicide Orange Samples, and

2. These Herbicide Orange Samples be re-analyzed for all toxic trace contaminants.

The objective of the present report is to document the status of the Air Force response to these two recommendations.

I. Herbicide Orange Sample Inventory

The Air Force currently has 243 50 ml samples of Herbicide Orange collected from 243 different 55-gallon drums that had been stored at the Naval Construction Battalion Center (NCBC), Gulfport, MS from 1969-1977. These samples are maintained in 60 ml glass bottles with aluminum-lined caps. Individual sample numbers are etched in the glass. The samples are currently maintained at the Herbicide Research Laboratory, Department of Chemistry and Biological Sciences, USAF Academy CO 80840. In addition, one 300-ml sample of Orange from the Johnston Island Inventory and one-100 ml sample of Orange II from the NCBC are available. These last two

samples are maintained at the USAF Occupational and Environmental Health Laboratory, Brooks AFB, TX.

II. Analyses of Herbicide Orange Samples

From 1972 to 1976, the Air Force sampled and analyzed the contents of at least 492 drums of Herbicide Orange from the surplus inventories stored at the NCBC, Gulfport, MS and Johnston Island (JI), Pacific Ocean (See Reference 3). Approximately 280 of 15,400 drums were sampled at NCBC and 210 of 26,600 drums were sampled from Johnston Island. All of the samples were analyzed for tetrachlorodibenzo-p-dioxin (TCDD). Selected samples were analyzed for all major components. A summary of the results of the tetrachlorodibenzo-p-dioxin analysis was published by Young et al.(3) and is provided as Attachment 1. The results of analyses for all major components in selected samples of Orange (including TCDD) were published by Fee et al. (1) and Hughes et al. (2). These data are provided in Attachments 2 and 3, respectively.

Most of the samples analyzed by Fee et al. (1) and Hughes et al. (2) are no longer available. However, within the archived set of 243 samples, some samples are subsamples of those analyzed. The archived set represents only two manufacturers (Hercules Company and Diamond Company). In the report by Fee et al. (1), ~~the~~ provided chromatograms (See Atch 2) of Analysis Sequence Group 8 (Drums 2,7,11B and 99) Group 14 (Drums 17, 27, 39, 42, 50 and 59). Group 18 (Drums 72 and 110) and Group 11 (Drums 139, 186, and 217). Hughes et al. (2) provided a detailed compositional analyses

(see Atch 3) of Analysis Sequence Group 8 (Drums 2,7, and 11B) and Analysis Sequence Group 14 (Drums 17, 27, 39, 42, 50 and 59). Sub-samples from all of these drums are available for re-analyses.

III. Recommendation for Re-Analyses at the American Chemical Society Meetings, Washington DC

In September 1979, H.R. Busser (National Laboratories, Switzerland) presented a paper on dibenzodioxins and dibenzofurans found in 2,4,5-T formulations. He specifically mentioned that Heribicide Orange contained the following dioxins:

2,3,7,8-TCDD
1,3,7,8-TCDD
1,3,7,9-TCDD
1,3,6,8-TCDD
2,3,7-Tri-CDD
1,3,7-Tri-CDD
2,7-DCDD
2,8-DCDD

He stated that dibenzofurans were presented but as yet unidentified isomerically.

The most toxic dioxin and furan is the 2,3,7,8-tetrachlorodibenzo isomer. The penta- and hexachloro isomers of both dioxin and furan are also toxic although less toxic than the 2,3,7,8-isomers.

A re-analyses of Herbicide Orange formulations should focus on the toxic isomers of dibenzodioxins and dibenzofurans. The analyses of herbicide formulations for these isomers is currently a developing technology. There are only four laboratories in the United States capable of elucidating

some of the these isomers. These laboratories include the Dow Chemical Laboratory, Midland, MI; Brehm Laboratory, Wright State University, Dayton, OH; the FDA Laboratory, Washington, DC; and the Gulf South Laboratories, New Orleans, LA. The cost of these analyses will necessarily be high. It is estimated that a single sample analyses will be at least $1,500.

It is recommended that the Gulf South Research Institute, Post Office Box 26518, New Orleans, LA 70186 be contracted for this effort on a sole source basis. The justification for this recommendation is as follows:

1. The Gulf South Research Institute is currently analyzing NIOSH Industrial Hygiene samples for isomeric identification of dioxins and furans. Thus, they are "on-line" with the instrumentation (High Resolution Gas Chromatography and Mass Spectrometry).

2. The principal investigator for these analyses at Gulf South is Dr. B. M. Hughes, a chemist who has intimate knowledge of Herbicide Orange. He developed the early techniques for the compositional analyses of Herbicide Orange while assigned at the Aerospace Research Laboratories WPAFB, OH (1974) and the Brehm Laboratory (1975-77), Dayton, OH. In addition, as the principal chemist at the Flammability Research Center (1977-1979), University of Utah, he was under Air Force contract supporting the Herbicide Orange Site Monitoring Project. He developed the isomeric identification technique currently in use at Gulf South and is considered one of the worlds leading Mass Spectroscopist in this field.

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ARL-TR-75-0110, Vol II, May 1975. D.C. Fee, B.M. Hughes, M.L. Taylor, T.O. Tiernan (ARL), and C.E. Hill, Jr. (SRL). Analytical Methodology for Herbicide Orange, Vol II. Determination of Origin of USAF Stocks. ARL & Systems Research Laboratories,Wright-Patterson AFB, OH 45433 AD A011-598. 30 p.

ARL-TR-75-0110, Vol I, May 1975. B.M. Hughes, D.C. Fee, M.L. Taylor, T.O. Tiernan (ARL), C.E. Hill, Jr., and R. L. C. Wu (SRL). Analytical Methodology for Herbicide Orange Vol I. Determination of Chemical Composition. ARL & Systems Research Laboratories, Wright-Patterson AFB, OH 45433. AD A011-597. 365 p.

OEHL-TR-78-92. October 1978. Alvin L. Young, Capt; John A. Calcagni, Lt Col; Charles E. Thalken, Lt Col; and James W. Tremblay, Major. The Toxicology, Environmental Fate, and Human Risk of Herbicide Orange and its Associated Dioxin. USAF Occupational and Environmental Health Laboratory, Aerospace Medical Division (AFSC), Brooks AFB, TX ADA062143. 247 p.

From: Young, et al. (3)

TABLE 6. Concentration, ppm, of TCDD in samples of Herbicides Orange and Purple.[a]

Source of Samples	Number of Samples		Range of TCDD (ppm)	Mean TCDD, Concentration (ppm)
	Orange	Purple		
Johnston Island Inventory, 1972[b]	200	(4)[c]	0.05-47	1.91
Johnston Island Inventory, 1974	10		0.07-5.3	1.68
NCBC, Gulfport Inventory, 1972[d]	42		0.05-13.3	1.77
NCBC, Gulfport Inventory, 1975	238		0.02-15	2.11
Eglin AFB Archived Sample		1[e]	-	45
Eglin AFB Inventory, 1972	2		-	0.04

The Weighted Mean Concentration of TCDD in Orange = 1.98 ppm

[a]Analyses for TCDD performed by Interpretive Analytical Services, Dow Chemical U.S.A., Midland Michigan; Aerospace Research Laboratories, Wright-Patterson AFB, Ohio; and The Brehm Laboratory, Wright State University, Dayton Ohio.

[b]Surplus Herbicide Orange was shipped from South Vietnam to Johnston Island for storage in April 1972.

[c]Four of 200 samples may have been Herbicide Purple, see text.

[d]The Naval Construction Battalion Center (NCBC) Gulfport, Missippi served as a storage site for Surplus Herbicide Orange from 1969 to 1977.

[e]Herbicide Purple was extensively used in the evaluation of aerial spray equipment on Test Area C-52, Eglin Air Force Base Reservation, Florida, 1962-1964.

Atch 1

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARL 75-0110, Vol II	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Analytical Methodology for Herbicide Orange. Vol. II. Determination of Origin of USAF Stocks		5. TYPE OF REPORT & PERIOD COVERED TECHNICAL — FINAL December 1972 -December 1974 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) D. C. Fee, B. M. Hughes, M. L. Taylor, T. O. Tiernan (ARL), and C. E. Hill, Jr. (SRL)		8. CONTRACT OR GRANT NUMBER(s) F33615-73-C-4099 and in-house
9. PERFORMING ORGANIZATION NAME AND ADDRESS ARL (AFSC) & Systems Research Laboratories Chemistry Research Laboratory (LJ) Wright Patterson AFB, OH 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS DOD Element 61102F 702306 14
11. CONTROLLING OFFICE NAME AND ADDRESS ARL (LJ) Building 450, Area B Wright Patterson AFB, OH 45433		12. REPORT DATE May 1975 13. NUMBER OF PAGES 36
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Air Force Logistics Command (DS) Wright Patterson Air Force Base Ohio 45433		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Analysis
Chromatography
Organochlorine Compounds
Chemistry
Gas Chromatography
Herbicide
Herbicide Orange

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A method was developed for gas-chromatographic characterization of chlorophenoxy herbicide formulations; with this method the original manufacturer of the herbicide could be determined. Using a temperature-programmed flame-ionization gas chromatograph, a gas chromatogram was obtained for each of several herbicide specimens. It was found that the amount and type of impurities determined gas chromatographically are characteristic of the original manufacturer of the material. In addition,

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Atch 2

20. continued

this simple analytical method was used to determine the homogeneity of the USAF herbicide stocks. These data were used to prepare Environmental Impact Statements for the Environmental Protection Agency.

TABLE I

IDENTIFICATION DATA ON HERBICIDE-ORANGE STOCKS AT GULFPORT, MISSISSIPPI

Manufacturer	Transportation Control No. (TCN)[a]	Analysis Sequence No.	Number of TCN Drums Sampled	Total Number of Drums with Same TCN	TCDD[b] (mg/kg)
* Hercules Co.	9464 8156 0001	8	3	500	< 0.05
* Hercules Co.	9464 8192 001	14	6	2152	n.d.[e]
* Diamond Co.	FY9461 7165 0001AA	18	3	60	14.2[f]
* Diamond Co.	FY9461 8156 001AA	11	3	421	8.62[g]
Thompson Hayward Co.	9463 8155 X032	1	6[c]	1546	0.32
Dow Chemical Co.	9463 8155 X052	10	12[d]	6976	0.12
Thompson Co.	9463 7184 X011	3	3	46	n.d.
Thompson Co.	9463 8155 X012	5	4[c]	808	0.17
Monsanto Co.	FY9463 7163 X0001XX	4	4[c]	563	n.d.
Monsanto Co.	FY9463 8183 X002XX	6	7[c]	2185	7.62
				15,257	

[a] Each separate purchase of herbicide was designated by a separate TCN.

[b] Tetrachlorodibenzo-p-dioxin content (in ppm). Results reported in this column are the average of six samples collected from six different barrels of Herbicide Orange having the same TCN. The analyses were accomplished by Dow Chemical Co. under Contract No. F41608-73-C-1629, and the results were reported previously in Dow Report No. IAS-246 dated 26 December 1972.

[c] Including two samples from the same barrel.

[d] Including two samples from each of two barrels.

[e] Not determined.

[f] Average value of five samples: 12, 17, 12, 15, 15. Other sample value was 0.07 with rechecks.

[g] Average value of four samples: 8.0, 8.1, 8.7, and 9.7. Other two samples each averaged < 0.05 with rechecks.

* Archived Samples of these TCNs available, Nov 1979

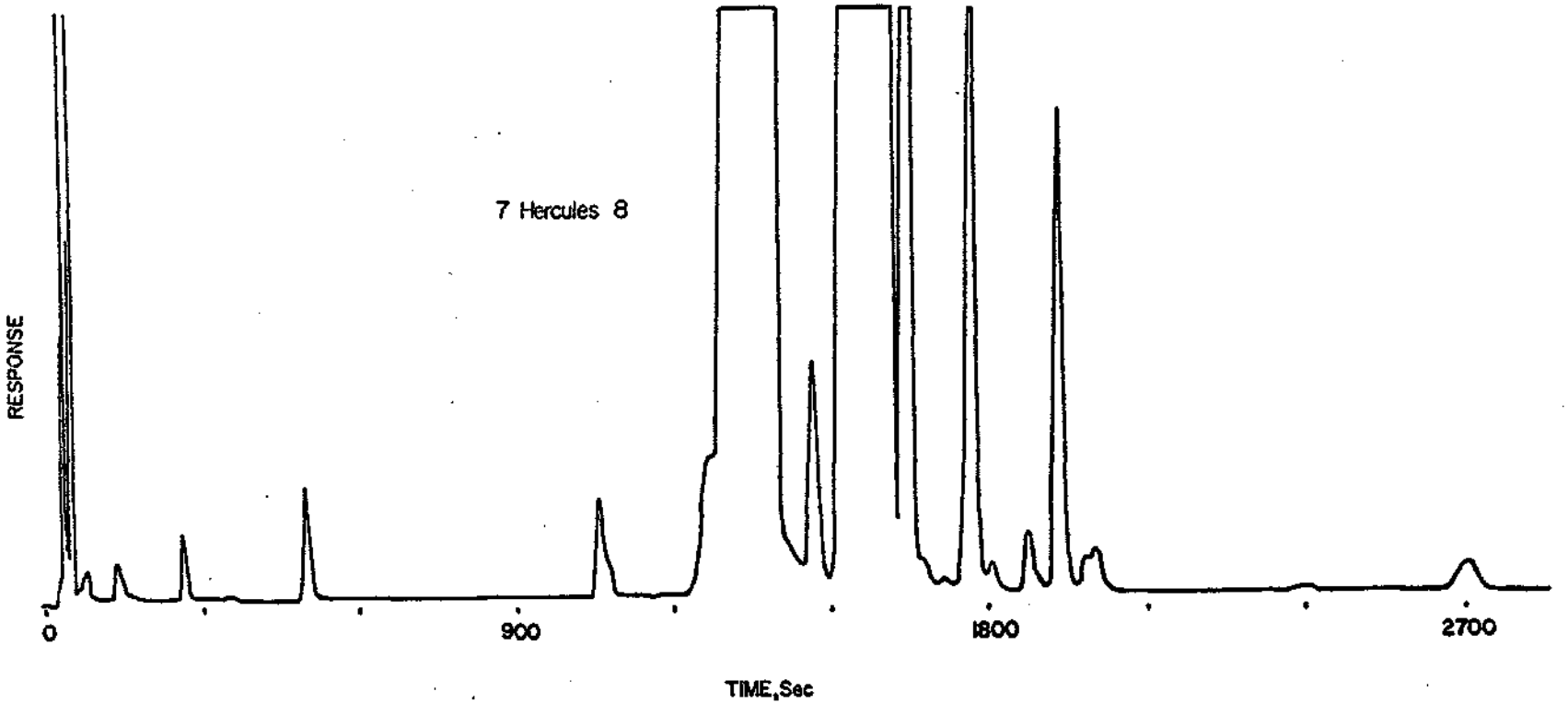

Figure 1. Characteristic Chromatogram of Analysis Sequence Group 8 (Hercules Company, TCN 9464 8156 0001); Barrel Numbers 2, 7, 11B, and Barrel 99 which was Mislabeled as Coming from Diamond Company (TCN FY9461 7165 0001AA)

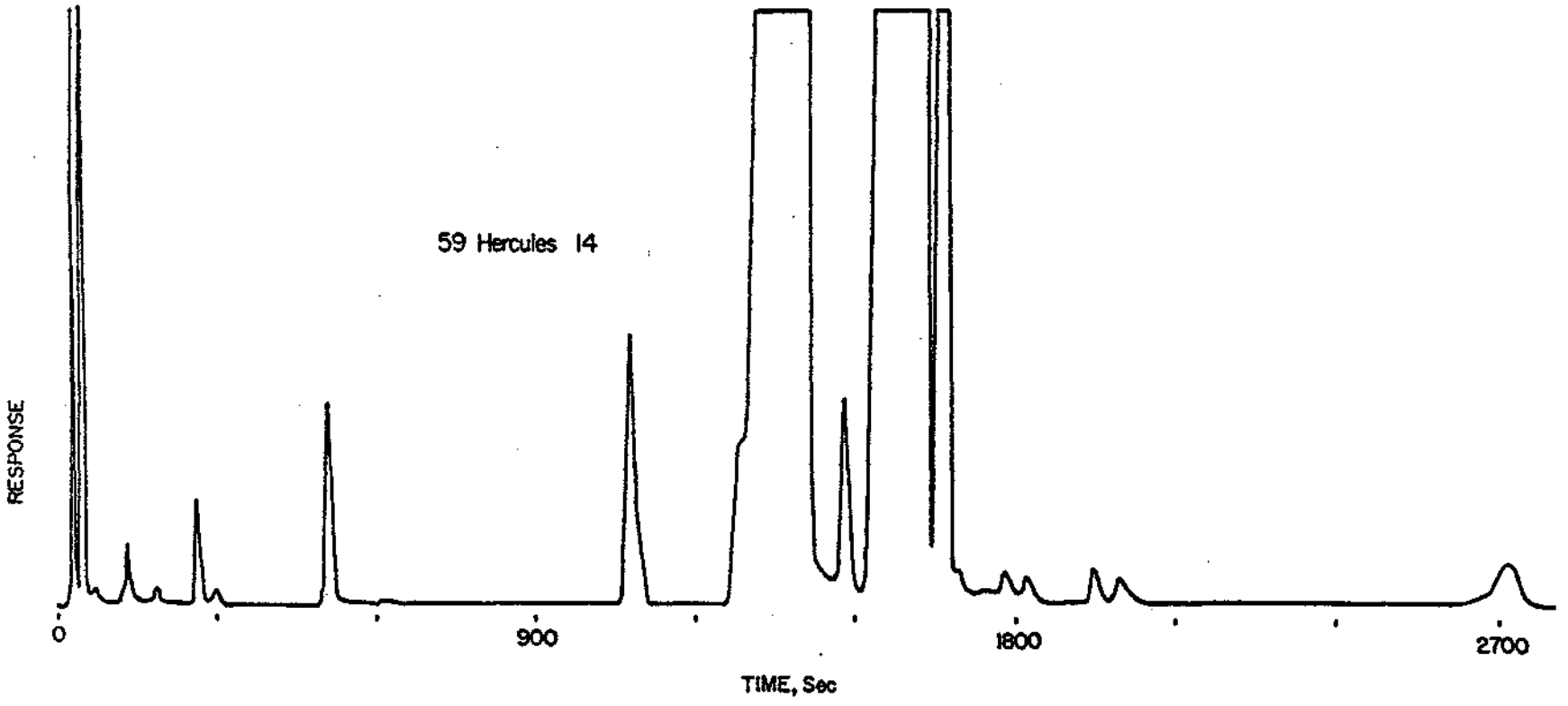

Figure 2. Characteristic Chromatogram of Analysis Sequence Group 14 (Hercules Company, TCN 9464 8192 001); Barrel Numbers 17, 27, 39, 42, 50, and 59

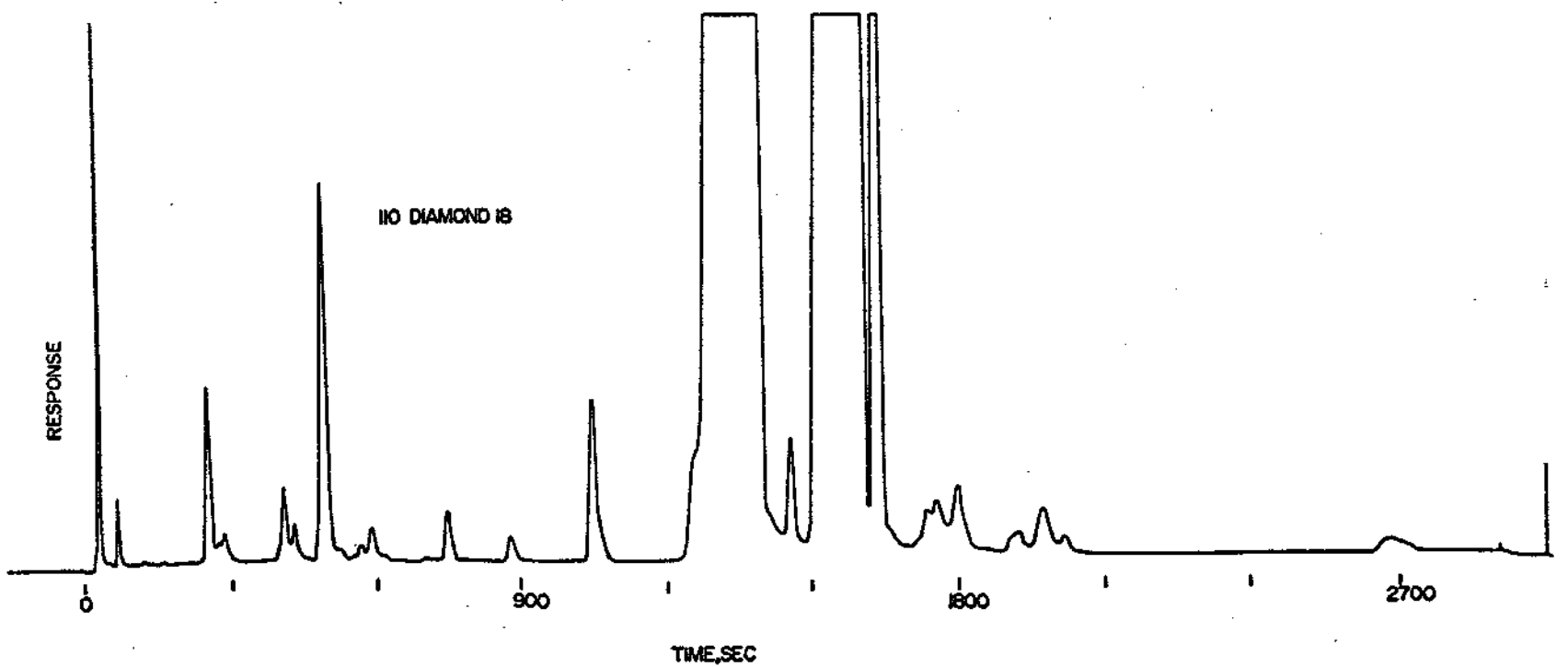

Figure 3. Characteristic Chromatogram of Analysis Sequence Group 18 (Diamond Company, TCN FY9461 7165 0001AA); Barrel Numbers 72 and 110

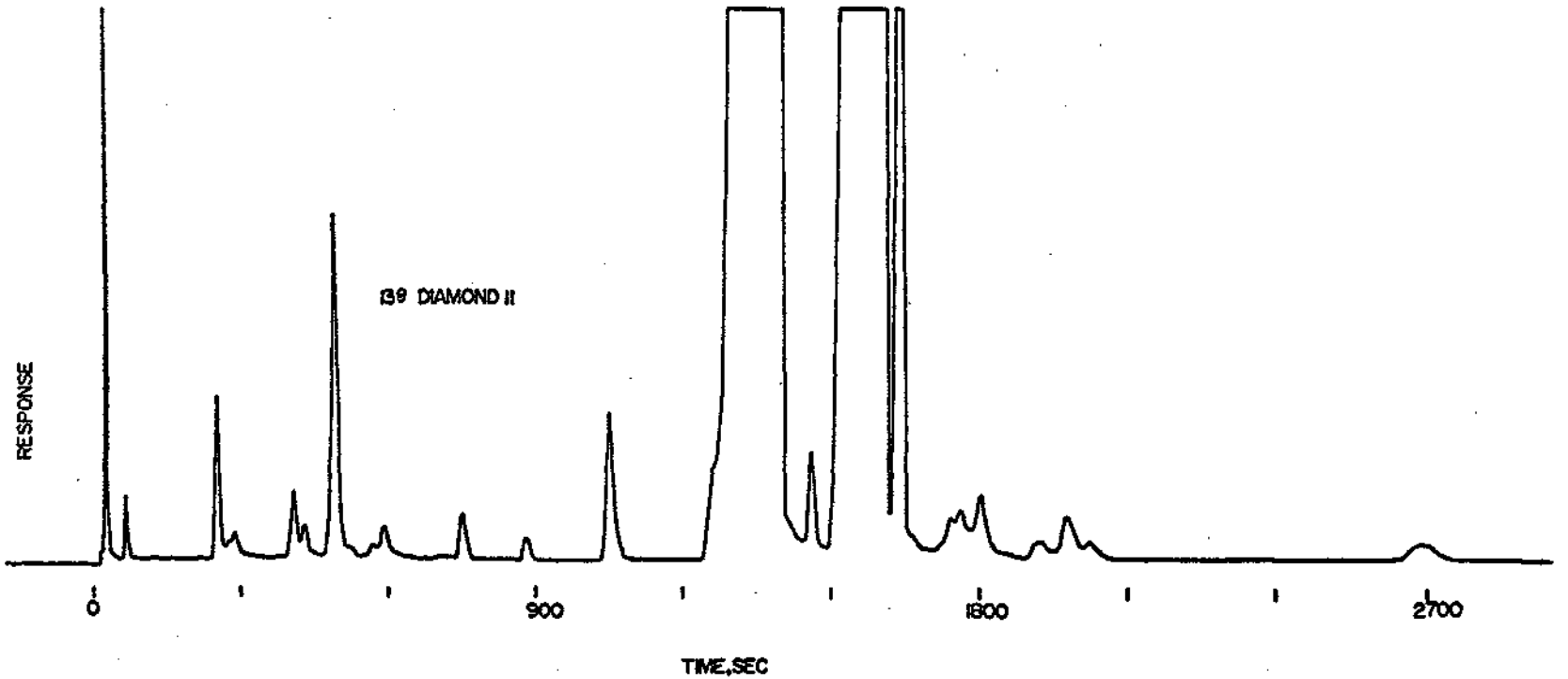

Figure 4. Characteristic Chromatogram of Analysis Sequence Group 11 (Diamond Company, TCN FY9461 8156 001AA); Barrel Numbers 139, 186, and 217

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11. CONTROLLING OFFICE NAME AND ADDRESS ARL (LJ) Building 450, Area B Wright-Patterson AFB, OH 45433		12. REPORT DATE May 1975 13. NUMBER OF PAGES 365
14. MONITORING AGENCY NAME & ADDRESS(*if different from Controlling Office*) Air Force Logistics Command (DS) Wright-Patterson Air Force Base Ohio 45433		15. SECURITY CLASS. *(of this report)* UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT *(of this Report)* Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)* Analysis Chlorophenoxy-Type Herbicide Gas Chromatograph-Mass Spectrometer Computerized Data Acquisition Tetrachlorodibenzo-p-dioxin (TCDD) Dioxin Organochlorine Compounds Herbicide Orange		
20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)* This report describes research performed by ARL at the request of the Air Force Logistics Command to develop and apply analytical methodology to characterize the USAF inventory of Herbicide Orange stocks. A computerized Gas Chromatograph-Mass Spectrometer (GC-MS) system was developed which permitted determination of the 15 to 25 major and minor herbicide components which are typically present in the stocks located at Gulfport, Mississippi. For determination of tetrachlorodibenzo-p-dioxin (TCDD), a fully automated GC-Quadrupole MS was developed and used in conjunction with an improved column-chromatography		

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Atch 3.

Item 20 Continued

sample-clean-up technique. The analytical methodology is described in detail.

TABLE XVI

COMPOSITION OF VARIOUS DRUMS OF HERBICIDE ORANGE IN THE LOT DESIGNATED ANALYSIS SEQUENCE NUMBER 8 (HERCULES CO.)†

Compound		Drum Number 2	Drum Number 7	Drum Number 11B	Average[a]
Butanol	(b)	0.71	0.81	1.36	0.96
	(c)	26	27	25	26
Toluene		1.47	1.32	1.75	1.51
		43	43	41	42
Butyl Chloride		0.07	0.11	0.11	0.10
		134	136	137	136
Dichlorophenol		0.25	0.19	0.26	0.23
		265	255	256	259
Trichlorophenol		0.43	0.41	0.42	0.42
		511	493	497	500
Butyl monochlorophenoxyacetate		0.59	0.49	0.58	0.55
		1075	1052	1057	1061
Butyl dichlorophenoxyacetate		(d)	0.78	0.37	0.58
			1262	1267	1265
Butyl dichlorophenoxyacetate		42.8	42.5	39.8	41.7
		1382	1357	1367	1369
Butyl trichlorophenoxyacetate		0.90	0.92	0.85	0.89
		1486	1462	1467	1472
Butyl trichlorophenoxyacetate		39.3	39.0	38.6	38.9
		1608	1583	1593	1595
Butyl methoxydichlorophenoxyacetate		5.87	5.40	6.00	5.76
		1673	1650	1656	1660
Octyl dichlorophenoxyacetate		3.32	3.21	3.46	3.33
		1793	1768	1777	1779
Octyl dichlorophenoxypropionate		0.32	0.32	0.35	0.33
		1894	1869	1878	1880
Octyl trichlorophenoxyacetate		2.29	2.05	2.33	2.22
		1957	1931	1941	1943
Octyl methoxydichlorophenoxyacetate		0.38	0.37	0.37	0.37
		2002	1986	1976	1988

TABLE XVI (continued)

Compound	Drum Number			Average[a]
	2	7	11B	
Butyl (bis-dichlorophenoxy)acetate	0.34 2691	0.41 2700	0.38 2717	0.38 2703
Butyl (bis-trichlorophenoxy) acetate	(e)	1.8	(e)	
Butyl (methoxydichlorophenoxy) tri-chlorophenoxyacetate	(e)	0.21	(e)	
Tetrachlorodibenzo-p-dioxin (µg/g)	<0.05	<0.05	<0.05	<0.05[f]

†This lot obtained from Hercules Company (TCN 9464 8156 0001) contains 500 drums.

(a) Average relative percent and retention time for the respective compounds found in these samples.

Table shows two values for each volatile compound.

(b) Relative amount (%) of the compound

(c) Gas chromatographic retention time of the compound (sec.)

(d) Present in chromatogram but no numerical value obtained. Quantity present appears to be similar to amount found in other samples. The average was determined by dividing the sum of the values obtained by the number of actual observations.

(e) Analyses not performed.

(f) Additional TCDD analyses are summarized in Figure 9, p. 65.

TABLE XVII

COMPOSITION OF VARIOUS DRUMS OF HERBICIDE ORANGE IN THE LOT DESIGNATED ANALYSIS SEQUENCE NUMBER 14 (HERCULES COMPANY)†

Compound		Drum Number						Average[a]
		17	27	39	42	50	59	
Butanol	(b)	0.79	0.67	0.87	0.77	0.82	0.75	0.78
	(c)	25	27	26	27	31	27	27
Toluene		2.57	2.31	2.75	2.40	2.85	2.24	2.52
		39	43	42	43	49	43	43
Butyl Chloride		0.17	0.17	0.17	0.15	0.14	0.16	0.16
		122	129	126	130	147	132	131
Dichlorophenol		0.34	0.32	0.33	0.30	0.30	0.26	0.31
		249	257	250	258	287	261	260
Trichlorophenol		0.75	0.55	0.77	0.71	0.76	0.67	0.70
		492	487	498	501	543	506	505
Butyl monochlorophenoxyacetate		1.42	1.39	1.44	1.28	1.34	1.16	1.34
		1063	1063	1051	1068	1125	1075	1074
Butyl dichlorophenoxyacetate		1.03	1.09	0.79	0.92	0.65	(d)	0.90
		1274	1273	1260	1278	1338		1285
Butyl dichlorophenoxyacetate		43.1	42.6	42.3	42.7	43.4	44.4	43.2
		1380	1380	1361	1385	1434	1393	1389
Butyl trichlorophenoxyacetate		2.51	2.02	1.82	1.79	1.65	0.70	1.75
		1473	1471	1461	1476	1538	1482	1484
Butyl trichlorophenoxyacetate		40.6	41.2	40.3	41.1	40.4	42.1	41.0
		1606	1607	1588	1612	1662	1620	1616
Butyl methoxydichlorophenoxy-acetate		5.62	5.71	6.16	5.70	6.69	5.44	5.89
		1665	1662	1653	1666	1731	1671	1675
Butyl (bis-dichlorophenoxy)-acetate		0.45	0.46	0.53	0.39	0.38	0.58	0.47
		2687	2706	2670	2704	2814	2711	2715
Butyl (bis-trichlorophenoxy)-acetate		(e)	(e)	(e)	(e)	(e)	1.8	
Butyl (methoxydichlorophenoxy)-trichlorophenoxyacetate		(e)	(e)	(e)	(e)	(e)	0.21	
Tetrachlorodibenzo-p-dioxin (µg/g)		<0.05	<0.05	0.08	0.06	0.07	0.07	(f)

†This lot obtained from Hercules Company (TCN 9464 8192 001) contains 2152 drums.

(a) Average relative percent and retention time for the respective compounds found in these samples.

Table shows two values for each volatile compound.

TABLE XVII (continued)

(b) Relative amount (%) of the compound.

(c) Gas chromatographic retention time (sec).

(d) Present in chromatogram but no numerical value obtained. Quantity present appears to be similar to amount found in other samples. In this case the average value was calculated by dividing the sum of the values obtained by the number of actual observations.

(e) Analyses not performed.

(f) Additional TCDD analyses are summarized in Figure 6, p. 62.