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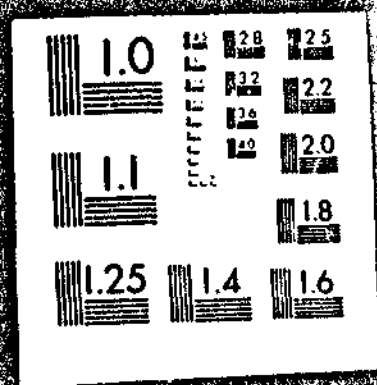
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ANALYTICAL METHODOLOGY FOR HERBICIDE
ORANGE. VOLUME II: DETERMINATION OF
ORIGIN OF USAF STOCKS

D. C. Fee, et al

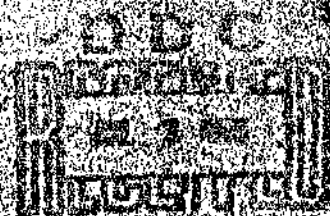
Aerospace Research Laboratories
Wright-Patterson Air Force Base, Ohio

May 1975

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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.

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PREFACE

The research and development described in this report were performed in-house by the Gaseous Ionization and Excitation Processes Group of the Chemistry Research Laboratory, Aerospace Research Laboratories (AFSC), Wright Patterson AFB, Ohio. This work was funded by Air Force Logistics Command, Assistant Deputy Chief of Staff/Distribution, Mr. Karl Merrill. Dr. Billy E. Welch, Special Assistant for Environmental Quality, Office of the Secretary of the Air Force, had overall cognizance for this effort which was undertaken to provide analytical chemistry support of USAF efforts to dispose of excess herbicide stocks in accordance with Environmental Protection Agency guidelines. The in-house work force was augmented during these studies via Contract No. F33615-73-C-4099 with Systems Research Laboratories, Inc., Dayton, Ohio 45440. These studies were performed under Project 7023, Task 702306, Work Unit 70230614, "Advanced Mass Spectrometric Analytical and Diagnostic Techniques for Materials and Research Applications."

The ARL principal investigator in these studies was Dr. Thomas O. Tiernan, ARL (LJ), Wright Patterson AFB, Ohio 45433.

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SECTION I

INTRODUCTION

Commercial herbicide formulations containing 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) have been used extensively over a period of years for brush control in the United States, and were applied for defoliation purposes in South Vietnam.¹⁻⁶ In 1970 it was discovered that some herbicide formulations containing 2,4,5-T also contain prohibitive levels (several parts-per-million) of a highly toxic contaminant, TCDD (tetrachlorodibenzo-p-dioxin).²⁻⁶ TCDD is formed as a by-product in the manufacture of 2,4,5-T and is approximately a million times more toxic than 2,4,5-T.^{1,7} TCDD is known to cause chloracne and other skin diseases in humans,⁸⁻¹¹ edema in new-born chicks,^{10,12,13} and numerous birth defects in rats, mice, and hamsters.¹⁴⁻¹⁷ In addition, the effects of TCDD may be cumulative.⁴ By 1970, the hazards of the TCDD present in 2,4,5-T were well known, and as a result further use of herbicides containing this compound was suspended in South Vietnam. The use of 2,4,5-T in the United States was also restricted. The U. S. Environmental Protection Agency placed a total ban on the use of 2,4,5-T having a "high" dioxin content. The level of TCDD which can be tolerated safely in herbicides is a subject of much controversy, and these limits may be revised in the near future.

The herbicide formulation used in South Vietnam was designated Herbicide Orange and consisted of an approximately 50-50 mixture of the butyl esters of 2,4-D (2,4-dichlorophenoxyacetic acid) and 2,4,5-T. When use of this herbicide in Vietnam was discontinued, large quantities of this material were on hand, and these remain in the USAF inventory today. Some 2.3 million gallons of this material are presently stored in 55-gallon drums in two locations--Gulfport, Mississippi, and Johnston Island in the Pacific Ocean. It is desirable to dispose of this herbicide as soon as practical, by either destroying it or (for those lots containing a "safe" level of dioxin) using it for brush-killing applications. Either procedure requires EPA approval or certification, and this, in turn, necessitates data on the chemical composition and homogeneity of the herbicide on hand.

The 15,200 barrels of herbicide presently stored in Gulfport, Miss., were originally purchased in ten lots from several different manufacturers. Unfortunately, owing to rebarreling and handling of much of the herbicide, some mislabeling has occurred. As a result, extant records may or may not be useful for assigning a given barrel of Herbicide Orange to one of the ten lots which were originally purchased. It is desirable, therefore, to develop a simple and reliable technique for characterizing the Herbicide stocks on a large-volume basis. The goal of the present work was to determine whether a rapid, routine analytical technique such as gas chromatography could be applied a) to characterize groups within the Herbicide-Orange stocks according to manufacturer or manufacturer's production run and b) to demonstrate that such groups are homogeneous, that is, that a given manufacturer's product consistently has the same composition. Achieving these goals would greatly reduce the number of analyses required to characterize the entire inventory since, hopefully, it would reduce a barrel-by-barrel analysis problem to a group analysis problem.

Reported herein are results of analyses of a limited number of barrels of Herbicide Orange. The volatile components of the samples of herbicide were analyzed by temperature-programmed gas chromatography.²⁰ All chromatographic peaks were not resolved. Greater effort could have been made to resolve overlapping peaks through more careful selection of liquid phase,²¹ poro-injector splitting of the carrier flow and multiple columns in series,²² programmed-pressure gas chromatography,²³ trapping and reinjecting,²⁴ back-flushing,²⁵ or complex valving arrangements of multiple columns in series.²⁶⁻²⁸ These techniques, while useful in analyzing mixtures with components of widely differing boiling points and physical-chemical properties, increase the time of analysis or the complexity of the analytical apparatus--both undesirable when a barrel-by-barrel determination is being performed. As will be shown, the simple gas-chromatographic analysis performed proved to be quite sufficient to identify homogeneous groups of the Herbicide-Orange stock according to manufacturer or manufacturer's production run. The data presented demonstrate the feasibility of identifying Herbicide Orange by its characteristic gas-chromatographic "fingerprint."

SECTION II

EXPERIMENTAL

SAMPLING PROCEDURE

Samples of herbicide Orange were collected by personnel from the USAF Environmental Health Laboratories, Kelly AFB, Texas, from barrels selected at random from groups representative of each of the ten lots purchased. Samples were collected in 1- or 2-oz. glass bottles, and an appropriate identification number was etched into each bottle; this number was painted on the corresponding barrel of herbicide. In order to remove a herbicide specimen from a barrel, a bottle was attached to its own "coat-hanger" plunger, and the sample bottle was plunged about 18 in. into the drum contents and swirled four to six times. The bottle with attached plunger was allowed to drip the excess herbicide back into the drum. Each bottle was then topped with new aluminum foil, tightly capped, rinsed by dipping in gasoline, and allowed to dry. Each bottle was rinsed a second time in fresh gasoline before being detached from its plunger, wiped with Kimwipes, and packed for shipment to the Aerospace Research Laboratories for analysis.

INSTRUMENTATION

The analyses were accomplished with a Varian Model 1440 Gas Chromatograph equipped with a flame ionization detector. The components were separated on an 8-ft., 1/8-in.-o.d. glass column packed with Gas Chrom Q coated with 10% DC-200. Following injection of 1 μ l of the sample, the column was temperature programmed from 110 to 240°C at a rate of 4°C/min. Other operating parameters were helium carrier flow, 30 cc/min; injector temperature, 275°C; and detector temperature, 275°C. The data were recorded with a 1-mV strip-chart recorder, and an Autolab System IV computing integrator was used to measure peak areas.

SECTION III

RESULTS

Table I lists the manufacturers of the herbicide lots sampled, the total number of drums of each in stock, the number of samples taken for analysis in the present study, and the TCDD levels reported earlier by Dow Chemical. Typical chromatograms for each of these groups of samples are displayed in Figures 1 through 11. Marked differences in the composition of the Herbicide-Orange samples from different lots are immediately apparent. Before these differences are discussed in detail, the overall reproducibility of the sampling and analysis procedures will be discussed.

The reproducibility of the herbicide sampling and analysis methods is demonstrated by a comparison of the results obtained for duplicate samples taken from the same barrel at different times. Such comparisons are presented in Tables II through VII. In these tables, the area of each peak is normalized to the total area of all peaks detected for a given sample of herbicide, where the total area is taken to be 100%. The chromatographic peaks are identified in this analysis by retention time only. The detector response is assumed to be equal for all components. A thorough examination of Tables II through VII shows that the retention times and peak areas are reproducible in general to within 4%, with the exception of the data shown in Table II. (The poor peak shapes which are exhibited for this sample in Fig. 5 are probably responsible for the lack of reproducibility in the corresponding quantitative data in Table II.) This reproducibility of duplicate samples to within 4% is characteristic of the precision attainable with gas-chromatographic analysis. These results clearly indicate that a homogeneous sample was obtained from each barrel by the sampling procedure which was employed.

The results of analyses of all barrels having the same analysis sequence number and transportation control number show that peak areas of individual components are reproducible to within 30%, with one exception. (The somewhat larger uncertainty here in comparing different barrels from the same manufacturer may indicate fluctuations in reaction conditions during a given production run.) The exception is the group of barrels having Analysis Sequence No. 10, where evidence for at least two distinctly different subgroups were found.* Results suggesting two subgroups are shown in Figures 6 and 7. Each subgroup showed reproducibility to within 30%. Subgroup A included four of the ten barrels sampled. The remaining six barrels sampled belonged to Subgroup B. It may be significant that subgroups were noted only in the analysis sequence group composed of the largest number of barrels of herbicide. In all other analysis sequence groups (composed of a smaller number of barrels), the analyses showed similar results (within 30% reproducibility) for all barrels sampled. The chromatograms of the herbicide samples from all barrels tested in a given group were similar to the representative chromatograms which are shown in Figures 1-11. These results suggest that two or more separate production runs were made in the manufacture of the 6976 barrels of herbicide in Analysis Sequence Group 10, while the other analysis sequence groups (containing fewer barrels) were each manufactured in one production run.**

*Extensive TCDD analyses presented in Vol. I of this report strongly suggest the existence of two and probably more subgroups within Dow ASN 10.

**The TCDD analyses reported in Vol. I actually indicate that only two of the ASN batches are homogeneous. Conclusions above are based on a limited number of samples.

TABLE I

IDENTIFICATION DATA ON HERBICIDE-ORANGE STOCKS AT GULFPORT, MISSISSIPPI

<u>Manufacturer</u>	<u>Transportation Control No. (TCN)^a</u>	<u>Analysis Sequence No.</u>	<u>Number of TCN Drums Sampled</u>	<u>Total Number of Drums with Same TCN</u>	<u>TCDD^b (mg/kg)</u>
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

^aEach separate purchase of herbicide was designated by a separate TCN.

^bTetrachlorodibenzo-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.

^cIncluding two samples from the same barrel.

^dIncluding two samples from each of two barrels.

^eNot determined.

^fAverage value of five samples: 12, 17, 12, 15, 15. Other sample value was 0.07 with rechecks.

^gAverage value of four samples: 8.0, 8.1, 8.7, and 9.7. Other two samples each averaged < 0.05 with rechecks.

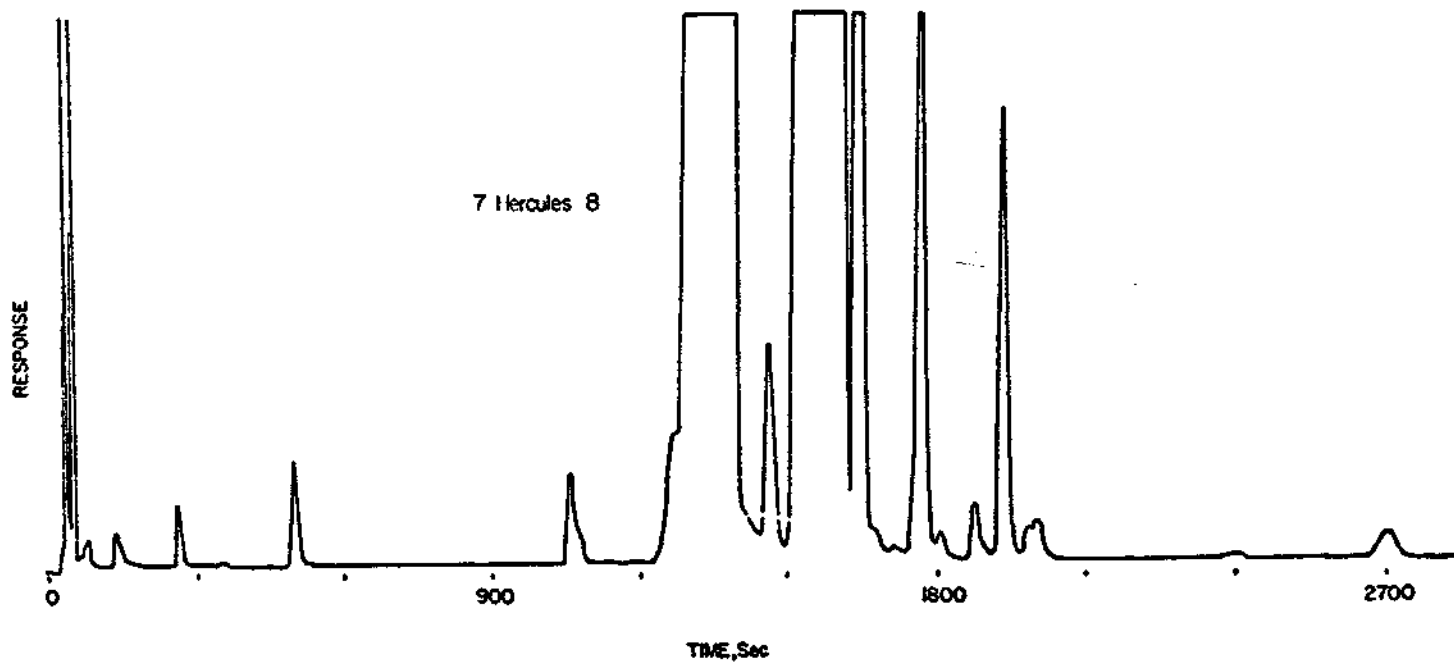


Figure 1. Characteristic Chromatogram of Analysis Sequence Group 8 (Hercules Company, TCN 9464 8156 0001); Barrel Numbers 2, 7, 11B, and Barrel 99 which was Mislabeled as Coming from Diamond Company (TCN FY9461 7165 0001AA)

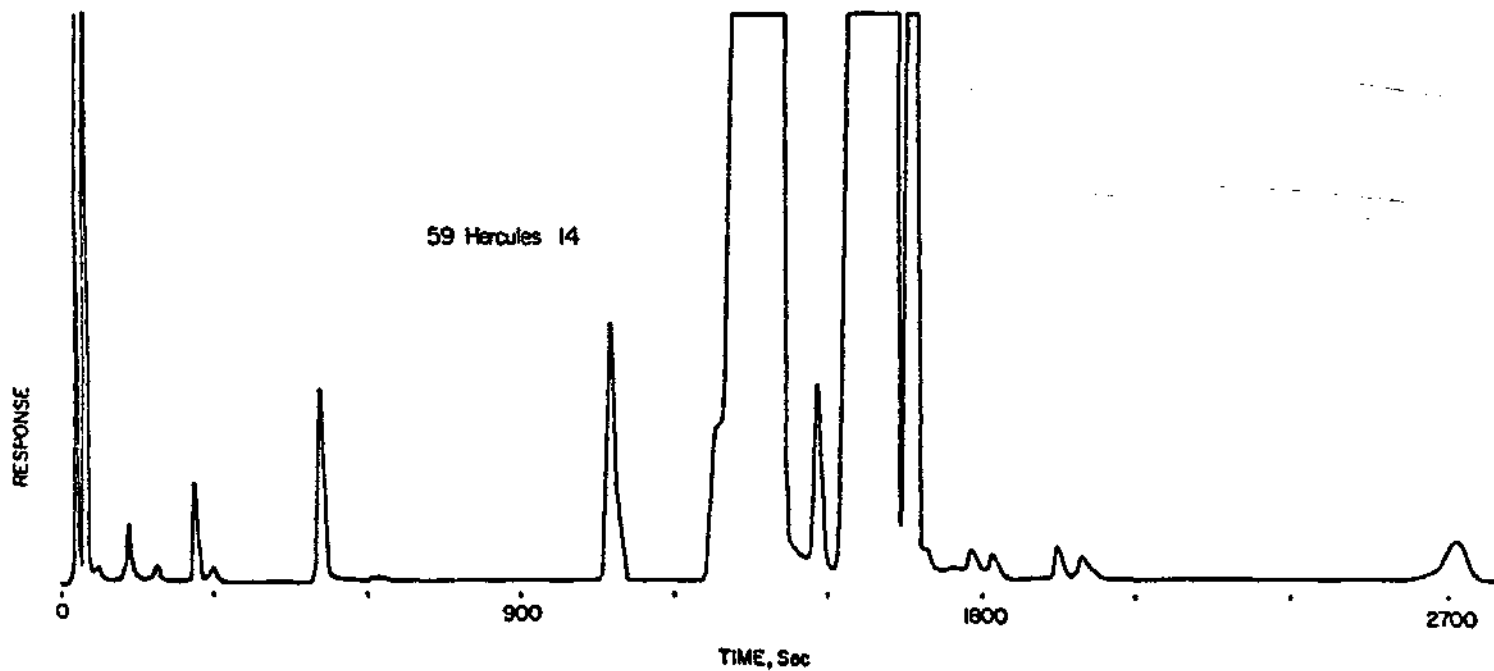


Figure 2. Characteristic Chromatogram of Analysis Sequence Group 14 (Hercules Company, TCN 9464 8192 001); Barrel Numbers 17, 27, 39, 42, 50, and 59

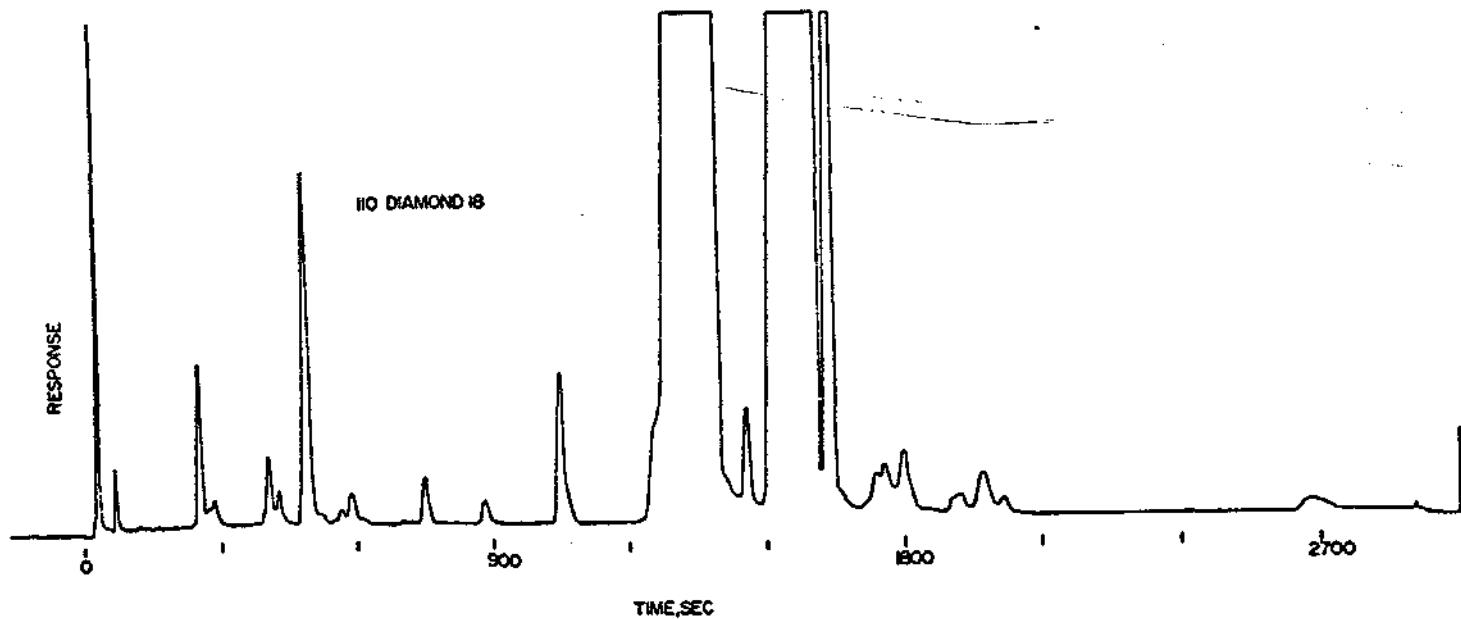


Figure 3. Characteristic Chromatogram of Analysis Sequence Group 18 (Diamond Company, TCN FY9461 7165 0001AA); Barrel Numbers 72 and 110

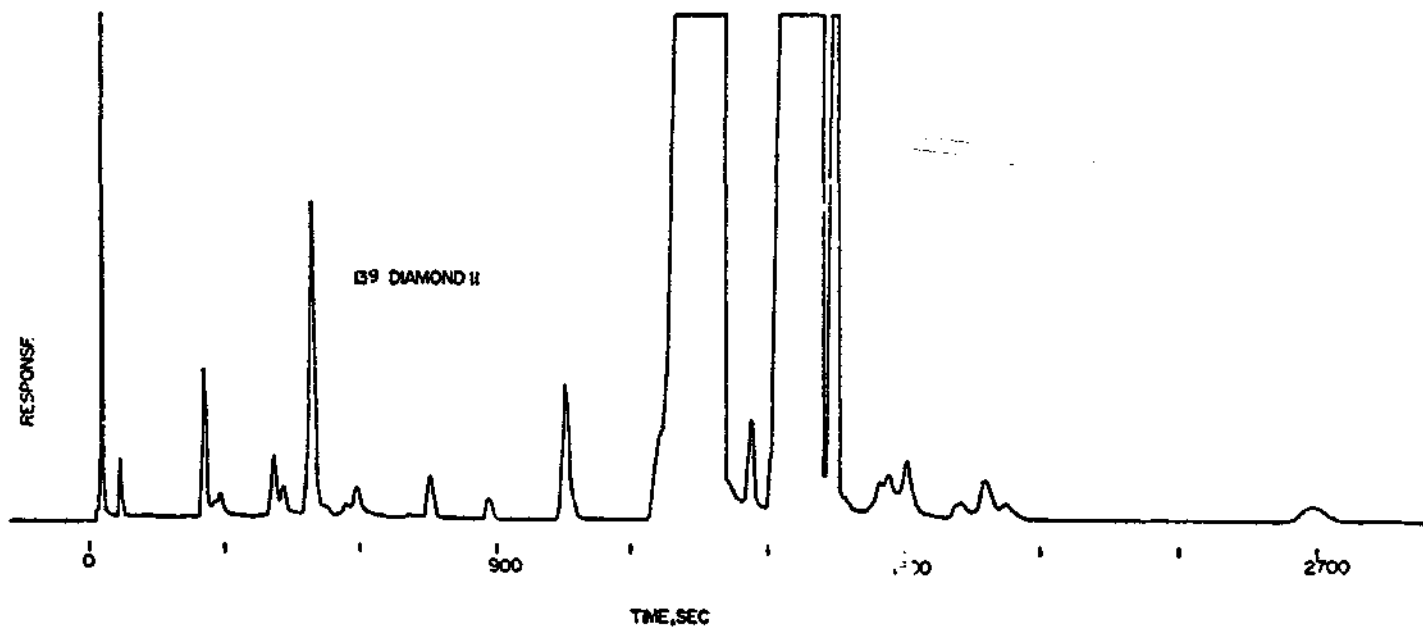


Figure 4. Characteristic Chromatogram of Analysis Sequence Group 11 (Diamond Company, TCN FY9461 8156 001AA); Barrel Numbers 139, 186, and 217

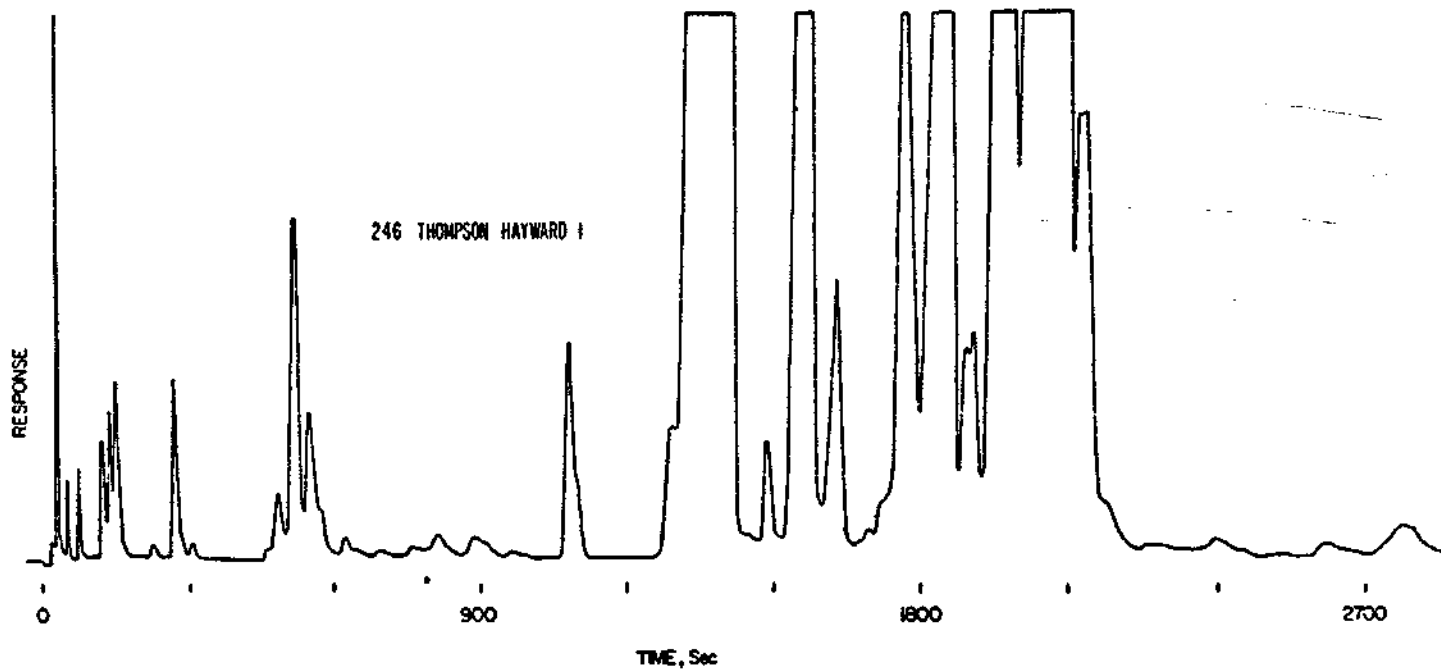


Figure 5. Characteristic Chromatogram of Analysis Sequence Group 1 (Thompson Hayward Company, TCN 9463 8155 X032); Barrel Numbers 244, 245, 246, 247, 248, and Sample 278 which was a Duplicate from Barrel 246

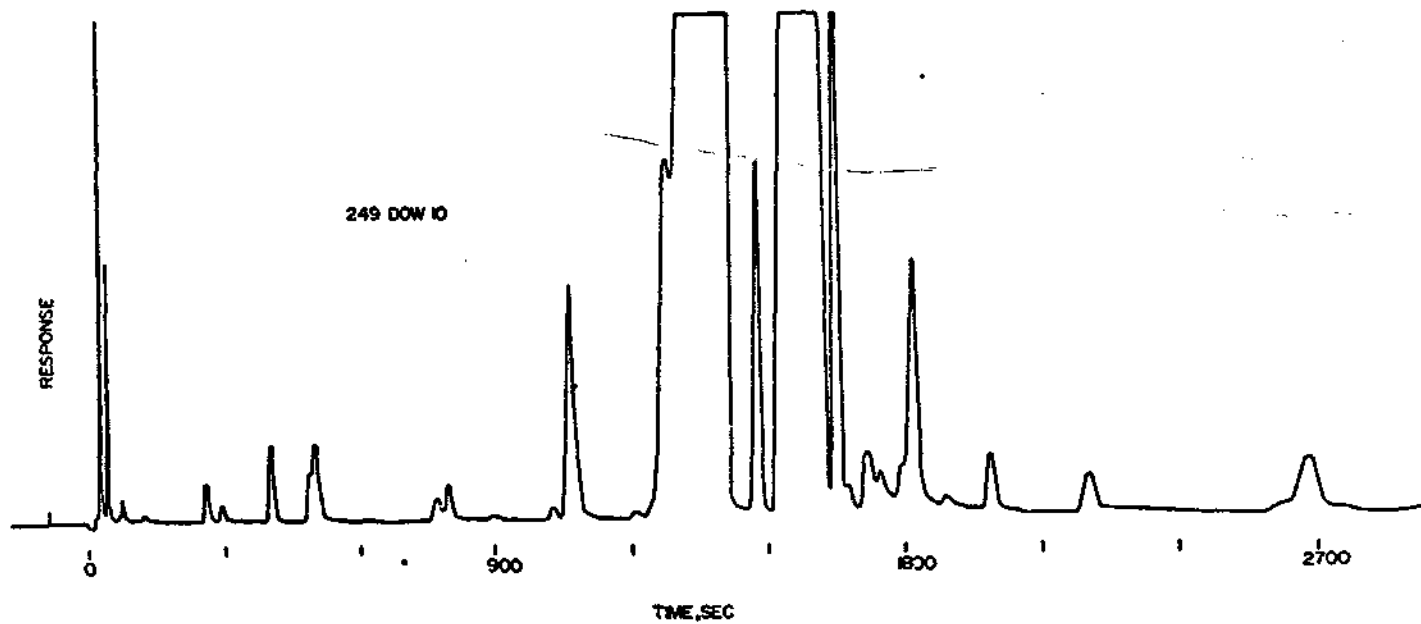


Figure 6. Characteristic Chromatogram of Analysis Sequence Group 10, Subgroup A (Dow Chemical Company, TCN 9463 8155 X052); Barrel Numbers 249, 250, 252, and 253

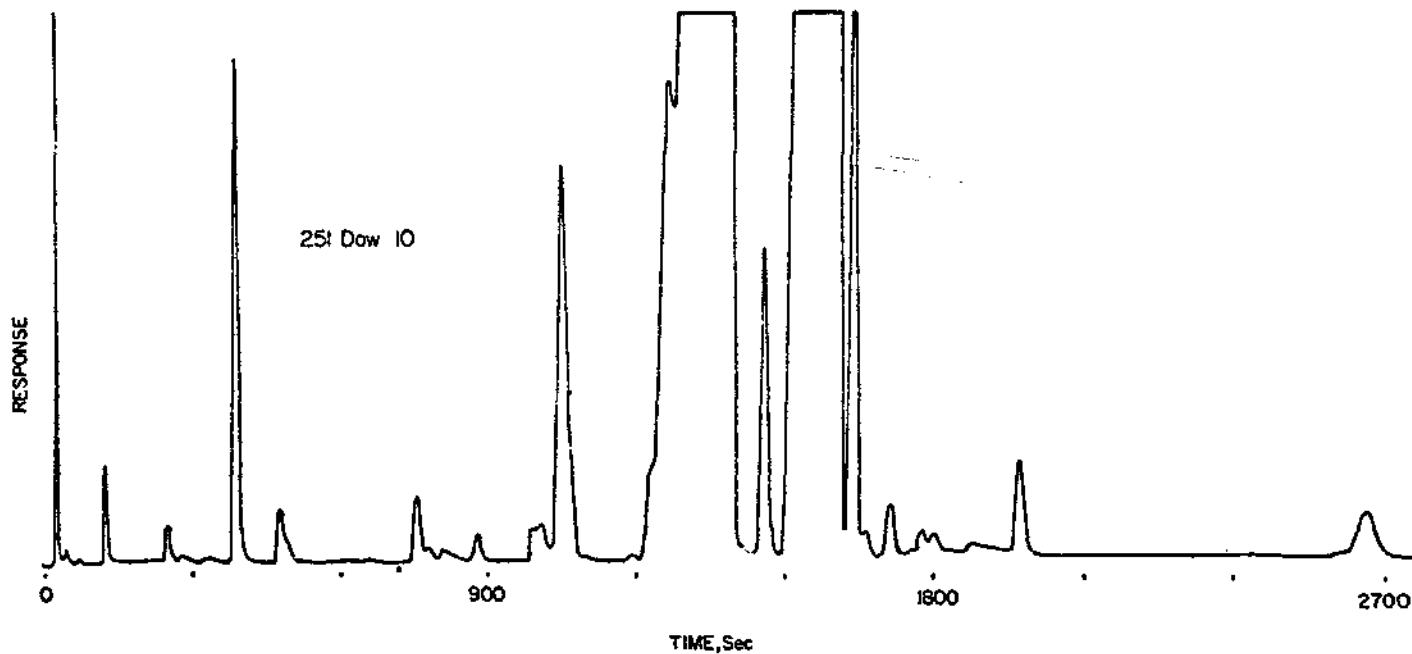


Figure 7. Characteristic Chromatogram of Analysis Sequence Group 10, Subgroup B (Dow Chemical Company, TCN 9463 8155 X052); Barrel Numbers 251, 254, 255, 256, 257, and 258, and Samples 275 and 276 which are Duplicate Samples from Barrels 251 and 256, Respectively

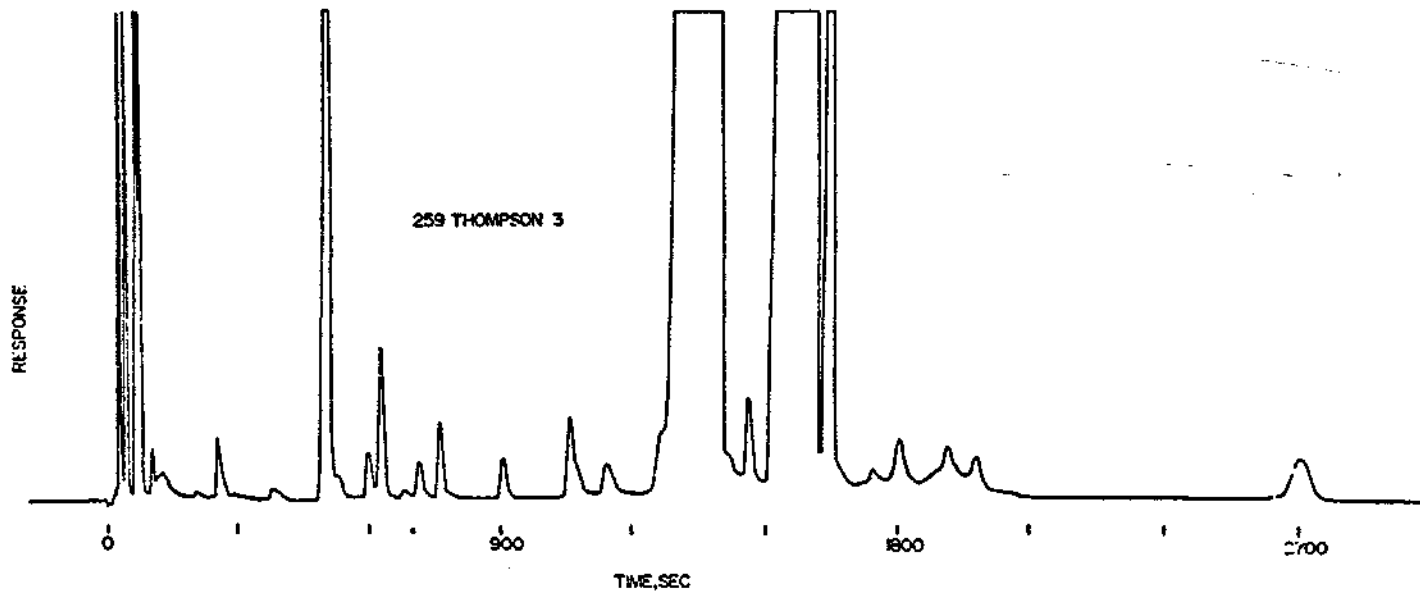


Figure 8. Characteristic Chromatogram of Analysis Sequence Group 3 (Thompson Company, TCN 9463 7184 X011); Barrel Numbers 259, 260, and 261

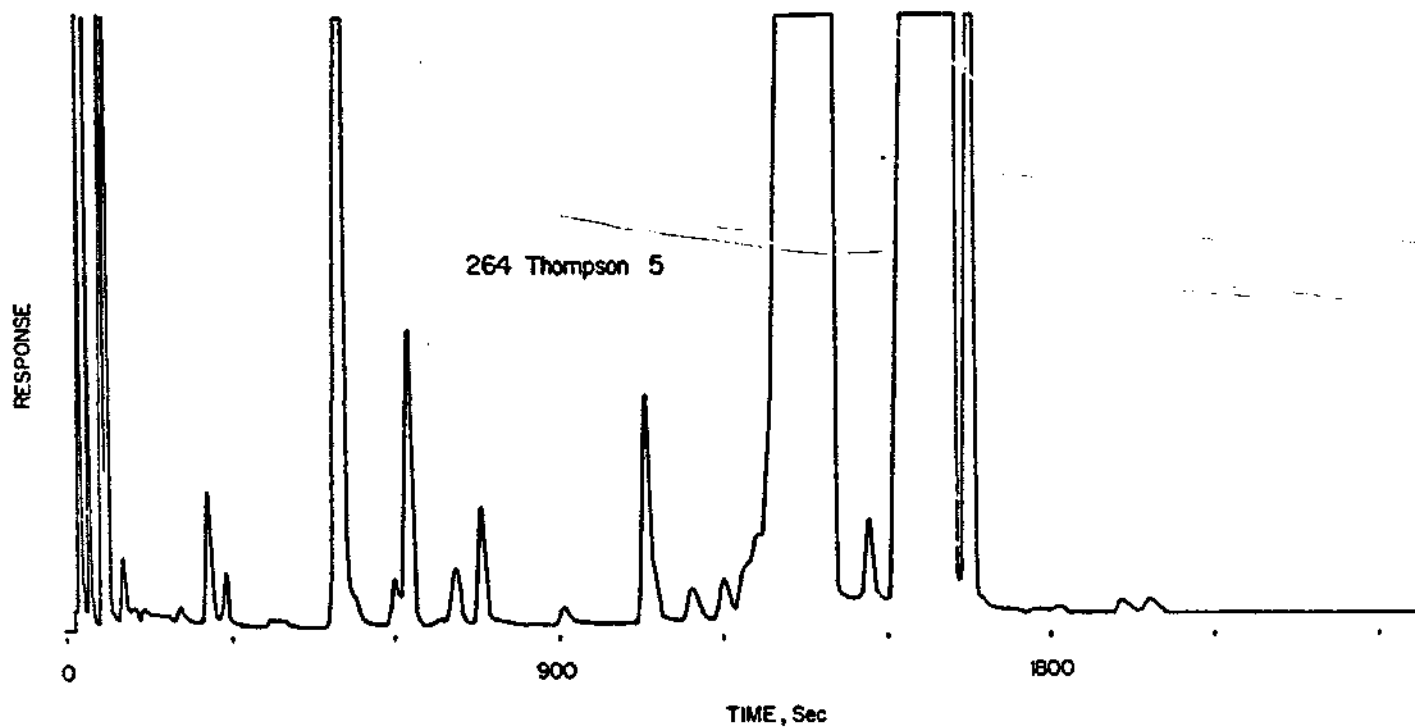


Figure 9. Characteristic Chromatogram of Analysis Sequence Group 5 (Thompson Company, ICN 9463 8155 X012); Barrel Numbers 262, 263, 264, and Sample 274 which is a Duplicate from Barrel 263

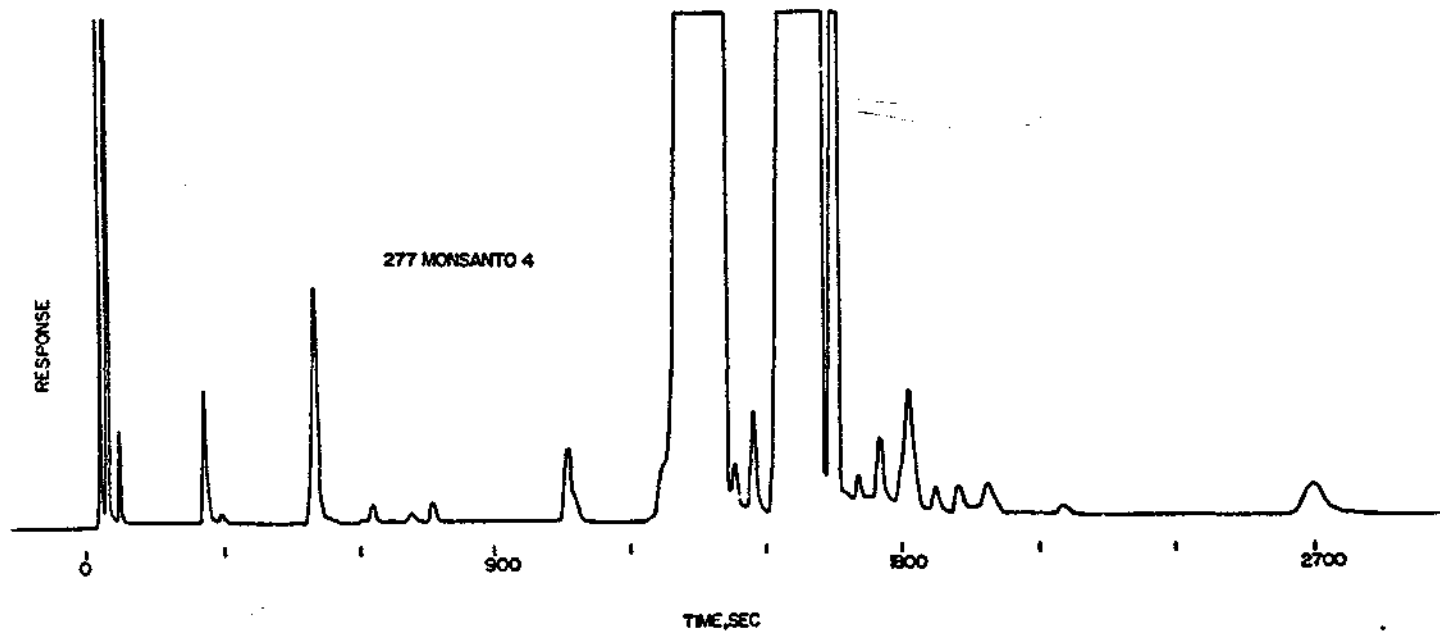


Figure 10. Characteristic Chromatogram of Analysis Sequence Group 4 (Monsanto Company, TCN FY9463 7163 X001XX); Barrel Numbers 265, 266, and 267, and Sample 277 which is a Duplicate from Barrel 266

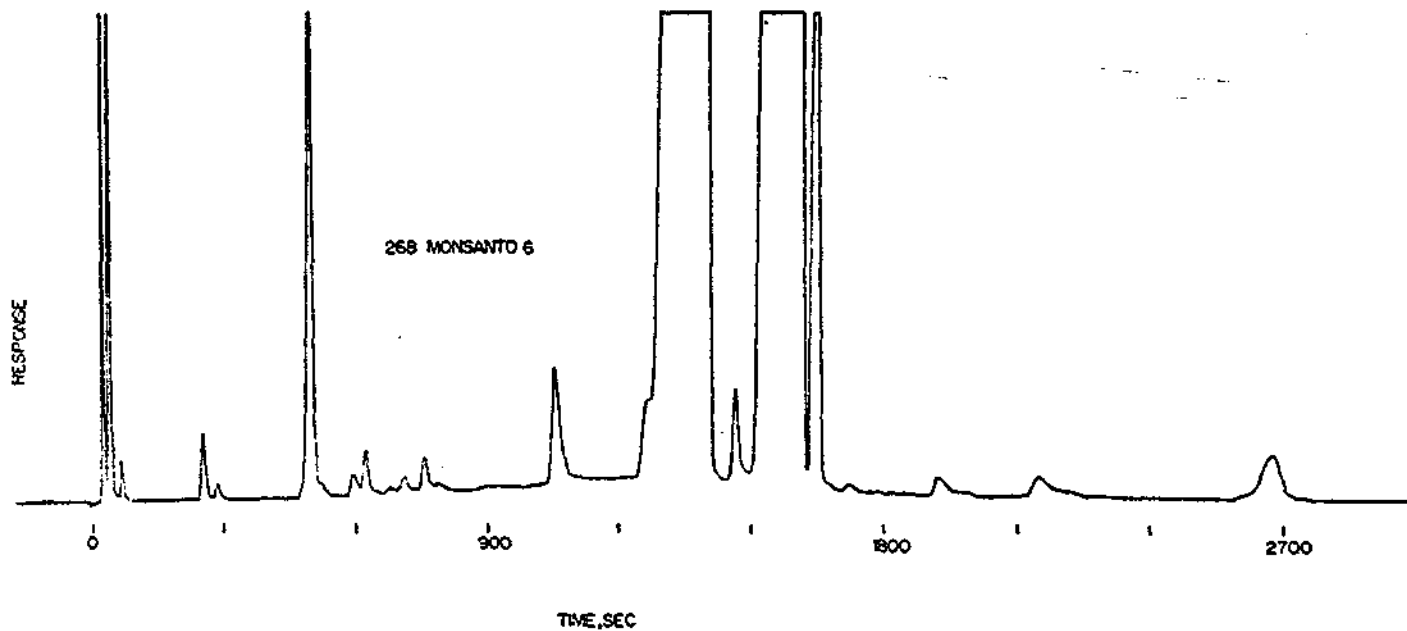


Figure 11. Characteristic Chromatogram of Analysis Sequence Group 6 (Monsanto Company, TCN FY9463 S183 X002XX): Barrel Numbers 268, 269, 270, 271, 272, and 273, and Sample 279 which is a duplicate from Barrel 270

TABLE II

COMPARISON OF ANALYSES OF DUPLICATE SAMPLES FROM THE
 SAME BARREL OF HERBICIDE ORANGE
 (THOMPSON-HAYWARD, ANALYSIS SEQUENCE NO. 1)

<u>Sample I.D. No. 278</u>		<u>Sample I.D. No. 247</u>	
<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>	<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>
25	0.38	26	0.39
113	0.07	114	0.11
127	0.05	127	0.07
138	0.19	138	0.23
251	0.15	249	0.16
458	0.18	457	0.26
494	0.86	493	0.88
524	0.68	522	0.65
594	0.05	593	0.05
660	0.05	658	0.05
782	0.09	780	0.10
858	0.17	856	0.18
1059	1.60	1056	1.60
1399	34.3	1396	44.9
1467	1.05	1464	0.86
1535	5.70	1537	5.00
1601	1.10	1598	1.00
1738	1.44	1734	1.28
1815	5.29	1811	4.54
1858	0.12	1854	0.11
1877	0.25	1874	0.24
1956	13.2	1951	10.9
2068	31.3	2063	24.7
2100	0.16	2098	0.13
2112	0.33	2108	0.36
2228	0.10	2224	0.10
2731	0.75	2727	0.73

TABLE III

COMPARISON OF ANALYSES OF DUPLICATE SAMPLES FROM THE
 SAME BARREL OF HERBICIDE ORANGE
 (DOW, ANALYSIS SEQUENCE NO. 10)

<u>Sample I.D. No. 251</u>		<u>Sample I.D. No. 275</u>	
<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>	<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>
26	0.28	27	0.30
126	0.14	128	0.14
252	0.10	255	0.10
390	1.24	393	1.26
476	0.15	482	0.15
757	0.22	761	0.31
781	0.09		
808	0.06	818	0.06
881	0.11	887	0.11
990	0.09	999	0.05
1054	1.59	1060	1.59
1190	0.64	1197	0.58
1265	3.06	1272	2.99
1390	43.2	1398	43.4
1464	0.96	1470	0.99
1618	44.1	1625	43.6
1646	1.97	1654	1.99
1668	0.08	1676	0.06
1717	0.25	1724	0.21
1759	0.04		
1780	0.11	1787	0.09
1803	0.11	1812	0.07
1840	0.06		
1876	0.07	1884	0.04
1974	0.36	1982	0.36
2665	0.47	2677	0.33

TABLE IV
 COMPARISON OF ANALYSES OF DUPLICATE SAMPLES FROM THE
 SAME BARREL OF HERBICIDE ORANGE
 (DOW, ANALYSIS SEQUENCE NO. 10)

<u>Sample I.D. No. 256</u>		<u>Sample I.D. No. 276</u>	
<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>	<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>
26	0.23	27	0.23
254	0.10	258	0.10
393	0.33	398	0.33
483	0.12	487	0.11
764	0.13	768	0.13
891	0.04	895	0.04
1052	1.25	1066	1.26
1202	0.42	1206	0.47
1277	2.70	1280	2.78
1403	45.5	1408	45.7
1475	0.85	1479	0.85
1631	44.8	1635	44.5
1659	2.19	1663	2.19
1681	0.08	1685	0.08
1728	0.19	1732	0.18
1793	0.10	1796	0.10
1816	0.15	1819	0.14
1853	0.05		
1889	0.12	1892	0.06
1987	0.29	1990	0.29
2680	0.29	2680	0.39

TABLE V

COMPARISON OF DUPLICATE SAMPLES FROM THE
 SAME BARREL OF HERBICIDE ORANGE
 (THOMPSON CO., ANALYSIS SEQUENCE NO. 5)

<u>Sample I.D. No. 263</u>		<u>Sample I.D. No. 274</u>	
<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>	<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>
27	1.60	27	1.80
42	0.68	43	0.62
67	2.52	68	2.54
75	0.99	76	1.00
103	0.14	105	0.14
159	0.05	163	0.05
203	0.07	208	0.08
254	0.34	259	0.36
287	0.14	293	0.14
501	4.27	510	4.30
594	0.16	603	0.16
625	0.90	634	0.91
708	0.21	717	0.21
756	0.42	766	0.42
1057	0.96	1066	0.97
1200	0.14	1209	0.14
1212	0.14	1220	0.17
1236	0.39	1245	0.39
1264	0.54	1276	0.52
1397	41.0	1407	41.1
1464	0.36	1473	0.36
1590	38.3	1600	38.2
1649	4.60	1659	4.56
2689	0.38	2700	0.34

TABLE VI

COMPARISON OF DUPLICATE ANALYSES OF SAMPLES FROM THE
 SAME BARREL OF HERBICIDE ORANGE
 (MONSANTO CO., ANALYSIS SEQUENCE NO. 4)

<u>Sample I.D. No. 266</u>		<u>Sample I.D. No. 277</u>	
<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>	<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>
26	0.70	26	0.70
42	1.84	43	1.87
68	0.14	70	0.13
252	0.41	258	0.40
491	1.00	501	0.99
618	0.08	629	0.08
704	0.05	715	0.05
751	0.10	763	0.10
1051	0.42	1063	0.41
1398	44.0	1411	43.2
1419	0.44	1432	0.45
1461	0.91	1474	0.71
1591	41.4	1604	41.6
1647	4.70	1659	4.63
		1681	0.05
1693	0.16	1705	0.17
1804	0.88	1817	0.87
1861	0.13	1873	0.13
1911	0.18	1923	0.17
1975	0.27	1987	0.26
2135	0.09	2148	0.09
2684	0.54	2695	0.38

TABLE VII

COMPARISON OF DUPLICATE SAMPLES FROM THE
 SAME BARREL OF HERBICIDE ORANGE
 (MONSANTO CO., ANALYSIS SEQUENCE NO. 6)

<u>Sample I.D. No. 270</u>		<u>Sample I.D. No. 279</u>	
<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>	<u>Retention Time</u> <u>(sec.)</u>	<u>Peak Area</u> <u>(rel. %)</u>
26	0.73	26	0.70
42	0.88	41	0.88
68	0.06	67	0.06
252	0.18	248	0.17
285	0.04	280	0.04
493	1.67	487	1.67
593	0.07	585	0.07
618	0.16	611	0.16
703	0.07	696	0.06
751	0.13	743	0.13
1052	0.54	1043	0.54
1355	46.5	1385	46.9
1465	0.62	1455	0.36
1620	43.3	1611	43.2
1653	2.98	1643	2.99
1719	0.05	1709	0.06
1918	0.09	1907	0.09
2139	0.10	2132	0.32
2665	0.48	2658	0.53

Quantitative data representing each of the analysis sequence groups are given in Table VIII. Identification of each analysis group (or subgroup) can be made from specific peaks in the chromatograms as shown in Table IX.

1) Analysis Sequence Group 8 (Hercules Company, see Figure 1) is uniquely identified by the large peaks at 1773 and 1993 sec. and by the region between 600 and 900 sec. where no peaks are observed.

2) Analysis Sequence Group 14 (Hercules Company, see Figure 2) is uniquely identified by the four small peaks at 1773, 1816, 1933, and 1984 sec. and by the region between 600 and 900 sec where no peaks are observed.

3) Analysis Sequence Group 18 (Diamond Company, see Figure 3) is identified by the single large peak near the beginning of the analysis (26 sec.) and by the six small peaks at 1744, 1773, 1816, 1933, 1984, and 2024 sec.

4) Analysis Sequence Group 11 (Diamond Company, see Figure 4) has a fingerprint identical to that observed for Analysis Sequence Group 18. These are the only two groups examined in this study which cannot be distinguished from each other by means of chromatographic patterns.

5) Analysis Sequence Group 1 (Thompson Hayward Company, see Figure 5) is uniquely identified by the very large peak at 2070 sec.

6) Analysis Sequence Group 10, Subgroup A (Dow Chemical Company, see Figure 6) is uniquely identified by the relatively large peak at 1816 sec.

7) Analysis Sequence Group 10, Subgroup B (Dow Chemical Company, see Figure 7) is uniquely identified by the single large peak early in the chromatogram (26 sec.), by the large peak at 394 sec., and by the small peak at 1984 sec.

8) Analysis Sequence Group 3 (Thompson Company, see Figure 8) is uniquely identified by the four large peaks near the beginning of the analysis, particularly the peaks at 69 and 75 sec., by the peak larger than 4% at 500 sec., by the relatively large peak at 631 sec., and by the four small peaks at 1744, 1816, 1933, and 1984 sec.

9) Analysis Sequence Group 5 (Thompson Company, see Figure 9) is uniquely identified by the four large peaks near the beginning of the analysis (69 and 75 sec.), by the peak larger than 4% at 500 sec., by the relatively large peak at 631 sec., and by the absence of the four small peaks at 1744, 1816, 1933, and 1984 sec. which are characteristic of the Group 3 chromatograms noted above.

10) Analysis Sequence Group 4 (Monsanto Company, see Figure 10) is uniquely identified by three peaks at the beginning of the analysis (large peaks at 26 and 42 sec. and a small peak at 69 sec.), by the absence of peaks at 900 ± 50 sec., and by the five small peaks at 1744, 1816, 1875, 1933, and 1984 sec.

TABLE VIII

SUMMARY OF ANALYSES OF HERBICIDE-ORANGE STOCKS FROM GULFPORT, MISSISSIPPI

Retention Time (sec.)	Analysis Sequence Number ^a										
	1	10A	10B	3	5	4	6	8	14	18	11
26	0.43	0.36	0.27	1.53	1.60	0.71	0.78	0.96	0.78	1.00	0.86
42		0.36		1.01	0.66	1.72	0.94	1.51	2.52		
69				1.87	2.39	0.13	0.62			0.12	0.13
75				0.08	0.93						
121	0.15			0.14							
130	0.12			0.10				0.08	0.16		
208					0.06						
258	0.16	0.11	0.10	0.21	0.33	0.35	0.19	0.25	0.291	0.55	0.49
274										0.08	
291					0.13		0.05		0.05	0.20	0.07
394			0.62								
413		0.23								0.27	0.24
433										0.15	0.38
460	0.16										
490		0.11	0.13								
500	0.93	0.27		4.97	4.17	0.90	1.83	0.42	0.70	1.37	1.23
535	0.66										
580	0.05										
600				0.22	0.16		0.08			0.13	0.11

TABLE VIII (Continued)

Retention Time (sec.)	Analysis Sequence Number ^a										
	<u>1</u>	<u>10A</u>	<u>10B</u>	<u>3</u>	<u>5</u>	<u>4</u>	<u>6</u>	<u>8</u>	<u>14</u>	<u>18</u>	<u>11</u>
631				0.70	0.88	0.08	0.16				
680				0.05			0.04				
713				0.18	0.20	0.05	0.06				
758			0.14	0.39	0.38	0.09	0.16			0.22	0.15
773		0.11									
797		0.17									
868	0.05										
890			0.06							0.12	0.11
909				0.17							
1030		0.16	0.08								
1060	1.59	1.17	1.42	0.39	0.96	0.41	0.60	0.58	1.28	0.78	0.68
1150				0.29	0.36						
1200					0.14						
1260		2.0	3.06		0.41						
1387	36.9	43.2	43.1	41.6	41.9	44.1	44.4	41.4	42.4	46.3	45.8
1410						0.2					
1471	1.02	1.0	0.85	0.43	0.37	0.44	0.70	0.89	1.6	0.40	0.36
1545	5.98										
1597	1.15	41.8	44.1	39.5	40.0	41.4	43.5	38.5	42.0	41.5	42.8
1661		2.2	2.2	4.50	2.55	4.70	3.92	6.0	5.61	4.1	3.6
1670			0.08								
1694						0.14					
1744	1.95	0.42	0.22	0.06		0.24	0.06			0.19	0.17

TABLE VIII (Continued)

Retention Time (sec.)	Analysis Sequence Number ^a										
	<u>1</u>	<u>10A</u>	<u>10B</u>	<u>3</u>	<u>5</u>	<u>4</u>	<u>6</u>	<u>8</u>	<u>14</u>	<u>18</u>	<u>11</u>
1773		0.23	0.12					3.33	0.10	0.25	0.22
1816	6.08	1.57	0.14	0.21		0.66		0.09	0.10	0.44	0.38
1875	0.26	0.10	0.06			0.11		0.33			
1933				0.53		0.16	0.10	2.22	0.11	0.16	0.15
1984		0.37	0.35	0.41		0.26		0.14	0.16	0.35	0.29
2024	10.7							0.23		0.11	0.09
2070	24.5										
2100	0.13										
2130	0.27										
2150						0.08	0.12				
2200	0.10	0.23									
2230											
2700	0.76	0.52	0.39	0.61	0.31	0.47	0.53	0.37	0.46	0.29	0.27

^aSee Table I to relate Analysis Sequence Number to TCN. Results listed represent relative peak areas of respective components.

TABLE IX

CHARACTERISTIC GAS CHROMATOGRAPHIC PEAKS FOR
IDENTIFICATION OF HERBICIDE ORANGE BY TRANSPORTATION CONTROL NUMBER

Retention Time (sec.)	Analysis Sequence Number ^a										
	8	14	18	11	1	10	10	3	5	4	6
26±2	0.96±0.4	0.78±0.1	1.00±0.1	0.86±0.1	0.43±0.1	0.36±0.3	0.27±0.1	1.53±0.1	1.60±0.40	0.71±0.2	0.78
42±2	1.51±0.2	2.52±0.3				0.36±0.3		1.01±0.2	0.66±0.1	1.72±0.3	0.94
69±2			0.12 ^b	0.13				1.87±0.1	2.39±0.4	0.13	0.06
75±2								0.82±0.1	0.93±0.2		
394±5								0.62 ^{+0.6} -0.3			
500±15	0.42±0.1	0.70±0.2	1.37±0.2	1.23±0.1	0.93±0.1	0.27±0.1		4.97±0.8	4.17±0.5	0.90±0.1	1.83±0.1
631±11								0.70±0.2	0.88±0.1		0.16
890±10			0.12	0.11				0.06			
909±10									0.17		
1744±10			0.19	0.17	1.95±1	0.42±0.2	0.22	0.06		0.24	0.06
1773±20	3.33±0.1	0.10	0.25	0.22		0.23	0.12				
1816±16	0.10	0.10	0.44±0.1	0.38±0.1	6.08±1	1.57±0.3	0.14	0.31		0.66	
1875±20	0.33				0.26	0.10	0.06			0.11	
1933±20	2.22±0.2	0.11	0.16	0.15				0.53		0.16	0.10
1984±15	0.14	0.16	0.35	0.29		0.37±0.1	0.35±0.1	0.41		0.26	
2024±8			0.11	0.09	10.7±1.4						
2070±21					24.5±4.0						

^aSee Table I to relate TCN to Analysis Sequence Number. Results listed represent relative peak areas of respective components.

^bThe typical range is ± 20%, unless otherwise indicated.

11) Analysis Sequence Group 6 (Monsanto Company, see Figure 11) is uniquely identified by three peaks at the beginning of the analysis (large peaks at 26 and 42 sec. and a small peak at 69 sec.), by the absence of peaks at 900 ± 50 sec., and by the small peaks at 1744 and 1933 sec.

The identification of Herbicide Orange by the characteristic chromatogram of each analysis sequence group as described above has already proved to be highly successful. As an example, one barrel of herbicide used in degradation studies was indicated by extant records to belong to Analysis Sequence Group 18 (Diamond Company). Subsequent fingerprinting of the barrel residue following these tests clearly established that the herbicide in question was from Analysis Sequence Group 8 (Hercules Company). Knowledge of the original source of the herbicides is vital if valid conclusions are to be drawn regarding the effectiveness of degradation techniques, because the composition of the various lots varies quite markedly. If the decomposition of specific herbicide components is being monitored, obviously it is necessary to know the quantities of these components present in the original herbicide test sample.

In summary, the data indicate that among the 15,200 barrels of Herbicide Orange stored at Gulfport, Mississippi, homogeneous groups can be identified by using a simple temperature-programmed gas-chromatographic analysis of the volatile components of this herbicide. It is thus possible to determine the original manufacturer of any herbicide sample in these stocks by a rapid, simple analysis. This identification does not depend upon knowledge of the chemical identity of any component of the Herbicide Orange. In another, more extensive report from this laboratory, however, identification of all individual components in selected lots of the herbicide stocks has been made by using combined gas chromatography-mass spectrometry instrumentation.²⁹

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