462

ETHYL CORPORATION

RESEARCH AND DEVELOPMENT DEPARTMENT

BATON ROUGE, LOUISIANA 70821

A DETERMINATION OF THE NON-MIGRATION LEVEL FOR VCM FROM PVC BOTTLES TO FOOD-SIMULATING SOLVENTS

Authors: J. L. Cannaday
G. A. Daniels
G. C. Gaeke

Date: June 7, 1977

A DETERMINATION OF THE NON-MIGRATION LEVEL FOR VCM FROM PVC BOTTLES TO FOOD-SIMULATING SOLVENTS

SUMMARY

This report summarizes the results of our five-week and 58-day storage tests with water and 50% aqueous ethanol at 120°F in PVC bottles with seven different initial levels of vinyl chloride monomer in the bottles. The proposal for this experimental program was sent to the FDA Hearing Clerk by letter of January 19, 1977.

CONCLUSIONS

With analysis by headspace and FID, both water and 50% aqueous ethanol contents show no statistical difference in extractants in the VCM region of the three (different) low level bottles which contained less than 0.09 ppm VCM. The 0.09 ppm VCM contents with both water and 50% aqueous ethanol show a significant increase in the VCM region of the chromatograms. These correspond to about 0.0006 ppm VCM with water and 0.0008 ppm VCM with 50% aqueous ethanol after 58 days at 120°F.

With analysis by GCMS, the sensitivity for VCM in water is 0.0016 ppm and in 50% aqueous ethanol is 0.005 ppm. VCM is not confirmed by GCMS in the water and 50% aqueous ethanol contents of the 0.23 ppm VCM bottles.

A non-migration level of 0.04 ppm VCM is established which corresponds to the 95% confidence level that the areas of the chromatogram blips in the VCM region for the contents in a PVC bottle shall not be greater than with no VCM.

BOTTLE PREPARATION

This study was conducted on bottles prepared from compounds containing the following VCM levels:

Compound	
1	<0.01 ppm
2	0.01 ppm
3	0.02 ppm
4	0.09 ppm
5	0.23 ppm
6	0.8 ppm
7	1.9 ppm

Four batches of resin plus stabilizer were prepared with target VCM values of <0.01, 0.4, 1.0, and 2.0 ppm. The <0.01 and 0.4 levels were prepared by using special laboratory techniques. The 1.0 and 2.0 resins were obtained by addition of VCM. The stabilizer was added to the resins to allow removal of VCM without degrading the resin. Table I shows the analyses for the resin plus stabilizer combinations. The analytical method is attached as Appendix I. Analyses in Table I are reported as VCM equivalent to the total area in the 138 to 146 second region of the chromatogram. VCM without interferences shows a sharp peak at 141 seconds. Interferences in the VCM region which are not VCM convert this sharp peak into blips which are impossible to distinguish at the 0.01 ppm VCM level and difficult to distinguish at the 0.4 ppm level. All areas and VCM equivalents in this report were obtained by hand integration of the chromatogram peaks. We found that machine integration was meaningless for some of the analyses because of broadened peaks, doublets, and side peaks. Low level resin plus stabilizer and powder blend and all compound pellets and bottles analyses were hand integrated. We believe that the very low level resin plus stabilizer contains less than 0.005 ppm as VCM. Analytical results are shown for two different batches of low level resin plus stabilizer as a second batch was prepared to provide sufficient material for intermediate blends.

Additional additives for our 8237 bottle compound were added to the resin plus stabilizer combinations and these were given similar processing in a laboratory intensive mixer to prepare powder blends and pellets with the same heat history. The target 1.0 and 2.0 ppm VCM levels show about one-half the equivalent VCM in the powder blend as in the resin plus stabilizer. The low level VCM shows an increase which is obviously due to non-VCM components because of the non-typical peaks that are observed. The powder blends were then pelletized. The pellets were analyzed by solution in DMAC. This analytical procedure is attached as Appendix II. It is apparent that sensitivity for VCM at low levels is completely lost with the pelletized compound as the apparent VCM for the low level compound is obviously essentially all non-VCM components by comparison with the resin plus stabilizer from which it was prepared. The target 1.0 and 2.0 ppm VCM compounds show reasonable agreement with the powder blends. Bottles prepared from these four compounds were also analyzed by the solution method. Additional increases in non-VCM is indicated by these chromatograms except for the target 2.0 ppm VCM bottles.

The intermediate VCM level bottles were prepared by blending the target 0.4 ppm VCM compound (assumed as 0.4 ppm VCM) with the low level compound for 0.02 and 0.04 ppm VCM blends and the target 1.0 ppm VCM compound (assumed as 0.84 ppm VCM) for the 0.1 ppm VCM blend. Two bottles of each of the <0.01, 0.02, 0.04, 0.1, 0.4 and 0.8 ppm VCM compound were sent to Dr. Breder.

(In routine production, VCM levels for bottle compound are measured and controlled on powder blend. At very low levels, it is obvious these measured values will be in error on the high side because of the noted interferences.)

Analysis of the stabilizer shows peaks at 138 and 146 seconds. The chromatograms for resin plus stabilizer for the <0.01 ppm VCM level show double peaks corresponding to the interfering components in the stabilizer. Chromatograms and tapes for this are included in Appendix III. Equivalent VCM shown in Table I for resin plus stabilizer is calculated from the double peak area. The major part of this area is in the 138 and 146 second region. The estimate of less than 0.005 ppm VCM is based upon the assumption that about 80% of the area is represented by the non-VCM components.

VCM losses appear consistent in converting resin plus stabilizer to compound at the nominal 1.0 and 2.0 ppm VCM levels. If this proportionate loss is applied to the nominal 0.4 ppm VCM level, estimated compound VCM content is 0.23 ppm. Heat history was the same for these three compounds, so this appears to be a reasonable assumption. Blending of this compound with the <0.01 ppm VCM compound would then result in 0.01 and 0.02 ppm VCM rather than the target values of 0.02 and 0.04 ppm VCM.

MIGRATION DATA

Tables II and III show the analyses for the water and the 50% aqueous ethanol contents from the PVC bottles after five weeks storage at 120°F. Tables IV and V show similar data after 58 days storage at 120°F. Triplicate analyses from three bottles at each VCM level are shown. Analyses are also reported for a fourth bottle for six VCM levels with water after five weeks storage because of inconsistencies between the analyses from the three bottles.

The following table shows the differences between the average areas of the chromatogram blips for the four high-VCM level bottles and the baseline areas (three low-VCM level bottles) in terms of VCM as a fraction of the VCM that is predicted for migration to the bottle contents with allowance for VCM loss in bottle blowing. Areas are converted to VCM by division by 5.2 for water and 1.8 for 50% aqueous ethanol.

Initial VCM Level	Fraction of Predicted Migration			
	Water		50% Aqueous Ethanol	
	Five Weeks	58 Days	Five Weeks	58 Days
1.9 ppm	0.84	0.83	0.83	0.86
0.8	0.56	0.49	0.10	0.39
0.23	0.84	0.63	*	0.27
0.09	1.30**	0.69	0.93	0.38

* The average total area for this bottle is less than that from Compound 1 bottles, but is within experimental error for these data.

** The value greater than unity is probably a result of experimental error with this low-level VCM in the contents.

The water results are observed to be reasonably consistent. The correction for the 0.23 ppm VCM bottle appears to provide about the same fraction migration as for the two higher level bottles. The 50% aqueous ethanol results are not as consistent as for the water.

Chromatograms for typical bottle content analyses are provided in Appendix III.

STATISTICAL ANALYSIS OF DATA

Tables VI to IX summarize the statistics for the water and 50% aqueous ethanol contents data for both the five-week and the 58-day experiments. Outlier bottle contents were rejected as shown. In all cases the extractable level in Compounds 2 and 3 are not significantly greater than the extractable level for Compound 1. The test for statistical significance is made by asking the following question: Is the extractable level for Compound X greater than the extractable level for Compound 1? Associated with this question is the Null hypothesis: The extractable from Compound X is not larger than the extractable from Compound 1. A value of 0.05 or smaller for the probability of the Null hypothesis is taken as evidence that the extractable level from Compound X is greater than the extractable level from Compound 1. The extractable level for Compound 4 is clearly greater for water and marginally so for the 50% aqueous ethanol for both the five-week data and the 58-day data. In all cases, except for 50% aqueous ethanol at five weeks, the extractable levels for Compounds 5 to 7 are greater than for Compound 1. Compounds 5 and 6 for 50% aqueous ethanol at five weeks appear to be anomalous as Compound 5 is less than Compound 1, while Compound 6 is only marginally greater.

An analysis of variance of the observed values of area units indicated that both the variance between analyses within bottles and the variance between bottles are approximately proportional to the square of the level of the observation in the water data at five weeks and the 50% aqueous ethanol data at past five weeks and 58 days. This suggests a logarithmic transformation of the data.

The log-transformed data for both sets of 50% aqueous ethanol data and the water data at five weeks were subjected to analysis of variance to determine the variance between analyses and the variance between the bottles on a log-scale. A Bartlett test of the variance shows that these variances on a log-scale are drawn from a homogeneous population, thereby allowing pooling of the individual variances. For the five-week data, the variances between bottles have a total of 14 degrees of freedom for each series, while the variance within bottles have 42 degrees of

freedom for each series. As the variance between bottles is the major contributor to the total variance, the tests of the various means is made with the pooled standard deviations using 14 degrees of freedom. The 50% aqueous ethanol data at 58 days has but 12 degrees of freedom for the variance between bottles.

The analysis of variance for the water data at 58 days shows two differences from the other three sets of data.

1. The variance is constituted entirely by differences in analysis rather than differences between bottles.

2. The variances are not drawn from a homogeneous population for the various compounds, whether the data are used directly or a log-transformation is used.

A two-sample t-test for the difference of the mean values, assuming that each analysis is independent, has been used to compare Compounds 2, 3, 4, and 5 with Compound 1.

VCM NON-MIGRATION LEVEL

A review of the statistical data presented in Tables VI-IX shows that VCM was not detected as a significant difference in the level of extractable from Compound 1 in the cases of Compounds 2 and 3. Compound 4 shows differences which are marginally significant for the 50% aqueous ethanol and more significant for water. It is our best estimate that Compound 2 contains about 0.01 ppm VCM and that Compound 2 contains about 0.02 ppm VCM, while Compound 3 contains about 0.09 ppm VCM. The data, then places the detectable limit of VCM as occuring with a VCM content of the compound ranging between 0.02 and 0.09 ppm VCM.

A more refined estimate of the limit of detection can be made by considering the t values which were obtained in the statistical studies. The critical t value for a 95% probability that a compound has a higher level of extractable than Compound 1 ranges from 1.76 to 1.78 for the experiments presented in this report. These t values are shown in Figure 1 for the comparisons from Compounds 2-5 with Compound 1. The intersection of a line through these t values with the critical t value defines the concentration of VCM in PVC compound where VCM should be detected in the extract. The t values describe reasonably smooth curves for 50% aqueous ethanol at 58 days and for water at five weeks. As would be expected, scatter occurs at the lowest levels. The 50% aqueous ethanol data at five weeks fall below the data for 50% aqueous ethanol at 58 days, except for the point at 0.09 ppm VCM. The data for water at 58 days are

scattered and fall well above the values for water at five weeks. The major reason for these larger t values is the greatly reduced variance between bottles for this set of data. The analyses of variance suggests 0 for the standard deviation between bottles for the 58-day data as compared to 0.1268 (on a ln scale) for the five-week data. The variance between analyses is about the same for both sets of water data. Whether this improved replication is due to the additional time of extraction or other causes is not known. A limit of detection for the 58-day water data can be considered a low estimate. The values obtained from Figure 1 are given below:

Experiment		VCM Concentration in PVC for Detection
Solvent	Time	
Water	Five Weeks	0.07
50% Aqueous Ethanol	Five Weeks	>0.09
Water	58 Days	0.04
50% Aqueous Ethanol	58 Days	0.09

It is interesting to note that if the variances established for the five-week data for water were used for the 58-day data, the t value curves would be essentially identical. This would yield a value of 0.07 for water at 58 days.

The data given in Figure 1 suggest that VCM is more readily detected in water than in 50% aqueous ethanol in this type of experiment. Water storage at 120°F for 58 days corresponds to about 1.25 years at 72°F. The VCM non-migration level of 0.04 in PVC bottles thus represents a conservative level for all applications.

GCMS ANALYSES

GCMS analyses were obtained at Spectrix Corporation, Houston, Texas. The apparatus was a Supelco 1.5 meter by 2 mm ID glass column with Carbopack C (60-80 mesh) coated with 0.2% Carbowax 1500 and a Finnegan Model 3200 gas chromatograph mass spectrometer. Standards analyses showed a sensitivity of 0.0016 ppm in water and 0.005 ppm in 50% aqueous ethanol. Analyses of the contents from the 0.23 and 0.09 ppm VCM bottles did not show VCM. A report of this work is attached as Appendix IV.

TABLE I

PVC ANALYSES; PPM VCM*

(Includes total 138-146 second material)

Target VCM Level	Resin Plus Stabilizer	Powder Blend	Compound Pellets	Bottles
<0.01	0.014**	0.052	0.50	0.64
<0.01	0.026**	0.067	0.41	-
0.4	0.44	0.39	0.60, 0.38	0.90
1.0	1.61	0.85	0.83, 0.70	0.94
2.0	3.85	2.22	1.89	1.86

* Values shown are average of triplicate analyses.

** Detailed study of the chromatogram indicates the VCM portion is < 0.005.

TABLE II

WATER CONTENT ANALYSES

Five-Week Storage

All values are area measurements as products of peak heights and width at half heights. Areas of secondary peaks are added where these occur.

			Actual Values
		Compound 1	(<0.01 ppm VCM)
Bottle	1	15.7, 15.3, 15.6	rejected
	2	20.6, 20.3, 20.8	
	3	19.3, 20.6, 20.5	
	4	22.3, 20.5, 21.0	
		Compound 2	(0.01 ppm VCM)
Bottle	1	23.1, 22.3, 22.0	
	2	19.2, 18.6, 19.6	
	3	21.0, 20.7, 20.7	
	4	26.3, 25.7, 26.1	rejected
		Compound 3	(0.02 ppm VCM)
Bottle	1	18.9, 21.2, 21.9	
	2	19.8, 21.5, 22.2	
	3	22.1, 22.8, 23.0	
	4	26.4, 27.4, 25.8	rejected
		Compound 4	(0.09 ppm VCM)
Bottle	1	19.7, 22.6, 26.3	rejected
	2	27.7, 25.7, 25.5	
	3	24.0, 23.1, 22.7	
	4	27.8, 28.5, 28.7	
		Compound 5	(0.23 ppm VCM)
Bottle	1	23.7, 24.8, 25.3	
	2	23.8, 29.1, 25.7	
	3	35.1, 35.4, 32.8	
	4	33.3, 31.6, 31.8	
		Compound 6	(0.8 ppm VCM)
Bottle	1	29.0, 27.6, 35.2	rejected
	2	15.2, 15.0, 17.5	rejected
	3	42.6, 38.0, 41.1	
	4	42.2, 40.8, 40.8	
		Compound 7	(1.9 ppm VCM)
Bottle	1	106.4, 102.6, 83.7	
	2	90.0, 90.9, 90.8	
	3	88.0, 87.7, 95.3	

TABLE III

50% AQUEOUS ETHANOL CONTENT ANALYSES

Five-Week Storage

Area values as defined in Table II.

			Actual Values (<0.01 ppm VCM)
		Compound 1	
Bottle	1	21.5, 21.3, 22.0	
	2	21.2, 22.2, 21.3	
	3	19.0, 18.0, 18.0	
		Compound 2	(0.01 ppm VCM)
Bottle	1	22.1, 19.9, 20.6	
	2	19.5, 19.9, 18.5	
	3	20.4, 20.9, 21.1	
		Compound 3	(0.02 ppm VCM)
Bottle	1	19.1, 19.0, 19.1	
	2	20.0, 20.8, 20.2	
	3	19.8, 20.9, 19.2	
		Compound 4	(0.09 ppm VCM)
Bottle	1	21.6, 22.4, 20.9	
	2	23.0, 24.5, 24.2	
	3	24.0, 24.2, 23.2	
		Compound 5	(0.23 ppm VCM)
Bottle	1	20.1, 20.9, 19.9	
	2	20.3, 19.1, 20.6	
	3	20.3, 20.4, 21.0	
		Compound 6	(0.8 ppm VCM)
Bottle	1	23.2, 24.2, 23.8	
	2	21.6, 21.5, 21.6	
	3	24.3, 22.5, 25.0	
		Compound 7	(1.9 ppm VCM)
Bottle	1	80.4, 86.2, 81.1	
	2	56.5, 56.3, 61.2	
	3	68.3, 68.8, 65.8	

TABLE IV

WATER CONTENT ANALYSES

58-Day Storage

Area values as defined in Table II.

			Actual Values
		Compound 1	(<0.01 ppm VCM)
Bottle	1	16.8, 19.1, 18.3	
	2	17.8, 18.1, 17.9	
	3	18.4, 18.0, 18.0	
		Compound 2	(0.01 ppm VCM)
Bottle	1	16.4, 18.1, 16.8	
	2	17.9, 17.9, 17.6	
	3	19.5, 14.5, 17.9	
		Compound 3	(0.02 ppm VCM)
Bottle	1	18.5, 17.0, 19.0	
	2	17.0, 18.8, 17.8	
	3	18.3, 17.9, 18.2	
		Compound 4	(0.09 ppm VCM)
Bottle	1	21.3, 21.7, 21.3	
	2	24.0, 21.6, 23.0	
	3	20.8, 21.3, 21.8	
		Compound 5	(0.23 ppm VCM)
Bottle	1	27.1, 30.0, 24.3	
	2	26.2, 31.8, 26.9	
	3	30.8, 23.7, 22.6	
		Compound 6	(0.8 ppm VCM)
Bottle	1	44.1, 42.6, 40.9	
	2	26.8, 26.6, 26.0	rejected
	3	8.6, 11.1, 9.5	rejected
		Compound 7	(1.9 ppm VCM)
Bottle	1	116.1, 117.4, 115.4	
	2	86.3, 87.8, 89.3	rejected
	3	117.9, 113.6, 112.3	

TABLE V

50% AQUEOUS ETHANOL CONTENT ANALYSES

58-Day Storage

Area values as defined in Table II.

			Actual Values
		Compound 1	(<0.01 ppm VCM)
Bottle	1	18.8, 19.4, 19.3	
	2	19.7, 20.0, 19.1	
	3	18.0, 17.4, 17.4	
		Compound 2	(0.01 ppm VCM)
Bottle	1	19.3, 19.5, 19.4	
	2	19.8, 19.8, 18.2	
	3	19.6, 19.5, 20.1	
		Compound 3	(0.02 ppm VCM)
Bottle	1	18.4, 18.4, 17.5	
	2	9.2, 9.5, 8.5	rejected
	3	18.5, 19.3, 17.7	
		Compound 4	(0.09 ppm VCM)
Bottle	1	20.3, 20.7, 20.7	
	2	18.3, 19.2, 17.9	
	3	22.2, 20.6, 21.6	
		Compound 5	(0.23 ppm VCM)
Bottle	1	21.3, 22.0, 21.1	
	2	22.2, 22.8, 21.0	
	3	21.3, 20.3, 19.3	
		Compound 6	(0.8 ppm VCM)
Bottle	1	24.3, 24.2, 25.3	
	2	24.8, 26.1, 26.2	
	3	26.8, 26.3, 27.3	
		Compound 7	(1.9 ppm VCM)
Bottle	1	84.9, 78.6, 80.9	
	2	65.2, 65.8, 62.7	rejected
	3	88.2, 85.3, 85.1	

TABLE VI

STATISTICAL DATA - WATER

Five-Week Storage

Compound	Bottles Included	Area Units	
		Average	Average of Ln (Area Units)
1	2, 3, 4	20.656	3.0273
2	1, 2, 3	20.800	3.0326
3	1, 2, 3	21.489	3.0657
4	2, 3, 4	25.967	3.2532
5	1, 2, 3, 4	29.367	3.3690
6	3, 4	40.917	3.7108
7	1, 2, 3	92.822	4.5280

Comparisons vs. Compound 1

Compound	Degrees of Freedom	Difference Ln (Area Units)	t*	Probability of Null Hypothesis**
2	14	0.0053	0.050	0.4912
3	14	0.0384	0.361	0.3715
4	14	0.2259	2.126	0.0266
5	14	0.3417	3.438	0.0020
6	14	0.6835	5.753	<0.0001
7	14	1.3207	12.429	<0.0001

* t values of greater than about 1.76 indicate that the extraction from the compound is statistically significantly greater than from Compound 1.

** Values less than 0.05 indicate statistically significantly greater extraction than from Compound 1.

t values are calculated from the following estimates for the standard deviation of Ln (area units) obtained by pooling all the analyses:

Between analyses	0.0510
Between bottles	0.1268

TABLE VII

STATISTICAL DATA - 50% AQUEOUS ETHANOL

Five-Week Storage

Compound	Area Units	
	Average	Average of Ln (Area Units)
1	20.500	3.0173
2	20.322	3.0106
3	19.778	2.9845
4	23.111	3.1389
5	20.289	2.9991
6	23.067	3.1374
7	69.389	4.2289

Comparisons vs. Compound 1

Compound	Degrees of Freedom	Difference Ln (Area Units)	t*	Probability of Null Hypothesis**
2	14	-0.0067	-0.097	0.5258
3	14	-0.0328	-0.474	0.6699
4	14	0.1216	1.756	0.0518
5	14	-0.0182	-0.263	0.5911
6	14	0.1201	1.735	0.0538
7	14	1.2116	17.499	<0.0001

* t values of greater than about 1.76 indicate that the extraction from the compound is statistically significantly greater than from Compound 1.

** Values less than 0.05 indicate statistically significantly greater xtraction than from Compound 1.

t values are calculated from the following estimates for the standard deviation of Ln (area units) obtained by pooling all the analyses:

Between analyses	0.0324
Between bottles	0.0827

TABLE VIII

STATISTICAL DATA - WATER

58-Day Storage

Compound	Bottles Included	Area Units Average
1	1, 2, 3	18.044
2	1, 2, 3	17.400
3	1, 2, 3	18.056
4	1, 2, 3	21.867
5	1, 2, 3	27.044
6	1	42.533
7	1, 3	115.450

Comparisons vs. Compound 1

Compound	Approximate Degrees of Freedom	Difference (Area Units)	t*	Probability of Null Hypothesis**
2	10	-0.644	-1.275	0.8842
3	10	0.012	0.036	0.4860
4	13	3.823	9.787	<0.0001
5	8	9.000	8.159	<0.0001

* t values greater than about 1.8 indicate that the extraction from the compound is significantly greater (in the statistical sense) than from Compound 1.

** Values less than 0.05 indicate statistically significantly greater extraction than from Compound 1.

Analysis of variance for these data indicates that the variance betwe n analyses within bottles contributes essentially all the variance. These variances differ between compounds so that pooling is not indicated. A two-sample t-t st has been used to compare Compounds 2, 3, 4 and 5 with Compound 1. Each analysis has been assumed to be independent even though replication within bottles was used. This procedure is justified by the observation that the varianc is contributed by differences between analyses rather than differences between bottl s. Statistical data have not been made to compare Compounds 6 and 7 with Compound 1 as the peak areas ar much greater.

TABLE IX

STATISTICAL DATA - 50% AQUEOUS ETHANOL

58-Day Storage

Compound	Bottles Included	Area Units	
		Average	Average of Ln (Area Units)
1	1, 2, 3	18.789	2.9321
2	1, 2, 3	19.467	2.9678
3	1, 3	18.300	2.9064
4	1, 2, 3	20.167	3.0017
5	1, 2, 3	21.256	3.0555
6	1, 2, 3	25.700	3.2457
7	1, 3	83.833	4.4281

Comparisons vs. Compound 1

Compound	Degrees of Freedom	Difference Ln (Area Units)	t*	Probability of Null Hypothesis**
2	12	0.0357	0.875	0.2044
3	12	-0.0257	-0.284	0.5996
4	12	0.0696	1.706	0.0583
5	12	0.1234	3.024	0.0039
6	12	0.3136	7.685	<0.0001
7	12	1.4960	33.199	<0.0001

* t values of greater than about 1.78 indicate that the extraction from the compound is statistically significantly greater than from Compound 1.

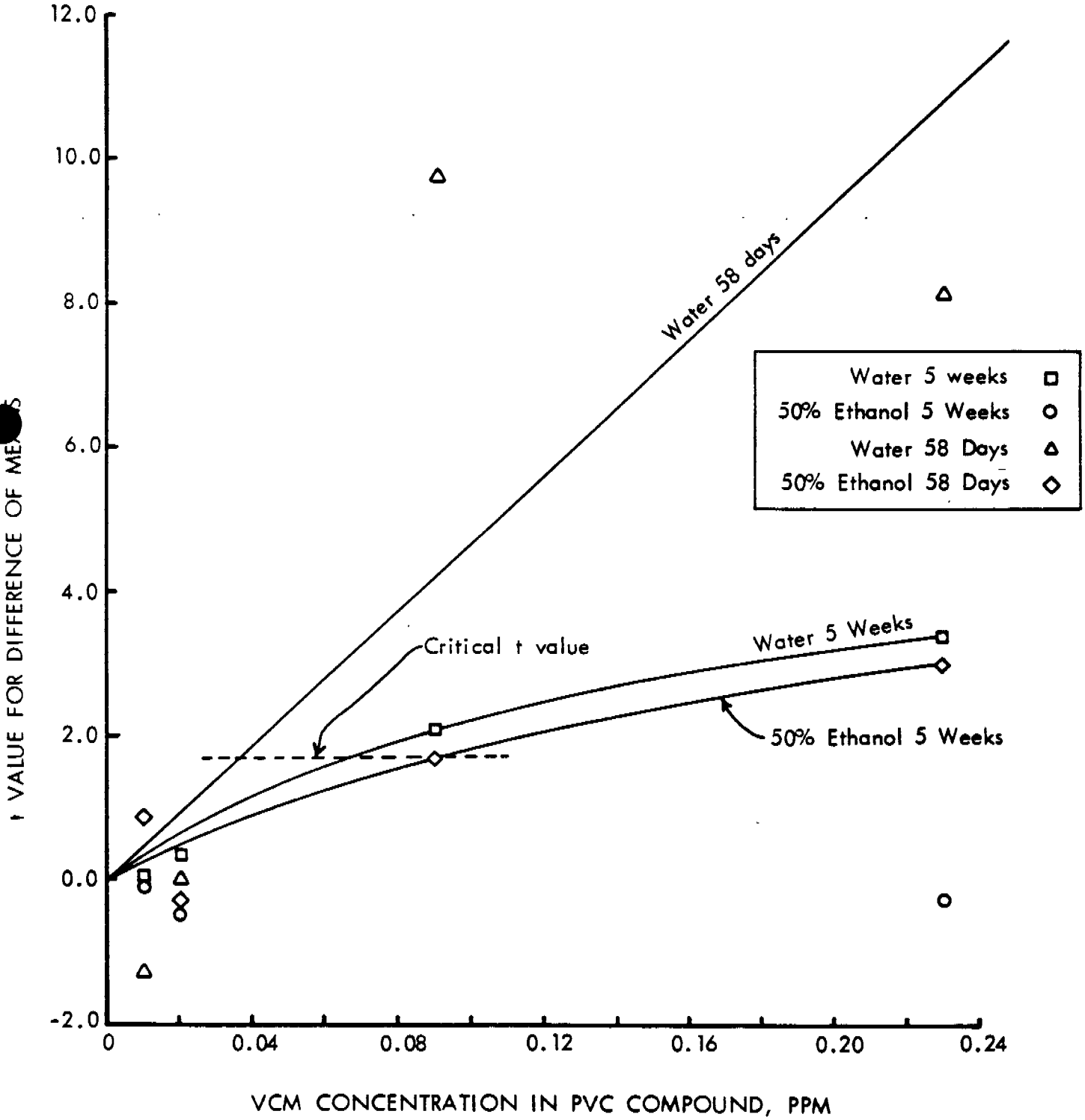
** Values less than 0.05 indicate statistically significantly greater extraction than from Compound 1.

t values are calculated from the following estimates for the standard deviation of Ln (area units) obtained by pooling all the analyses:

Between analyses	0.0287
Between bottles	0.0465

FIGURE 1

t Values for Extraction
From PVC Compounds



VC4062

Appendix I

Determination of Residual Vinyl Chloride Monomer in Polyvinyl Chloride Resins and Compounds

(Headspace Analyzer Method)

1. Scope

This method describes a procedure for the determination of ppm (w/w) levels of residual vinyl chloride monomer (VCl) in polyvinyl chloride (PVC) resins and compounds by a special automated technique (headspace analysis). Powders (resins and compound powder blends) and also pell ts or finished products (compounds) may be analyzed using one or the other of the two procedures described below. The limit of detection is approximately 0.005 ppm VCl for powders and 0.03 ppm for pellets.

2. Outline of the Method

a) Powders: Resins and compound powder blends are analyzed as solids. A weighed (4.0 g) sample is placed in a 25 ml vial and sealed with a serum stopper. The sample is equilibrated for one hour at 90°C (above the glass transition temperature of PVC). A sample of the vapor above the sample (headspace) is then injected into a gas chromatograph. By use of an automated turntable and sequencer up to 30 samples may be prepared and then analyzed without additional operator attention. Standard gas samples are analyzed along with the powder samples to calibrate the instrument. Peak areas are determined with an automatic integrator. From the calibration standards the concentration of VCl in the headspace is determined and the residual VCl monomer content of the resin is calculated.

b) Pellets: Pelletized compounds and finished products (cut into small pieces) must be dissolved to determine residual VCl monomer content. A weighed (0.5-0.7 g) sample is placed in a 25 ml vial containing 10.0 ml of DMAC (N,N-dimethylacetamide) as solvent. The vial is then sealed with a serum stopper and the samples are warmed (~ 50C) and shaken occasionally until the PVC is in solution (4-6 hrs). The vials are then placed in the water bath equilibrated at 90° for one hr. A sample of the vapor above the solution (headspace) is then injected into the gas chromatograph. Standard samples (VCl dissolved in DMAC) are analyzed concurrently with the samples. Peak areas are determined with an automatic integrator. Calculation of the residual VCl monomer content of the sample is straightforward, based on the headspace VCl concentration of the standards, the sample, and the sample weight.

3. Apparatus

a) Headspace Analyzer: Perkin Elmer Model F-42, equipped with a flame ionization detector, thermostated sample turntable, backflush assembly, and automatic timing sequencer.

b) Sample Vials: 25 ml complete with butyl rubber septum caps and aluminum caps.

c) Column: 3' x 1/8" SS plus 6' x 1/8" SS both packed with 0.2% Carbowax 1500 on Carbopak C. The two columns are connected in s ries (3' column closest to injection port) with the backflush "T" between them.

d) Recorder: 1 mv, 15"/hr.

e) Integrator: Spectra Physics System I (Perkin Elmer Model 1).

f) Syringes, Gas Tight: 10, 50, 100, 500 µl and 1, 2, 5 ml.

g) Ordinary Laboratory Glassware.

4. Reagents and Materials

a) Vinyl Chloride: 99.9+% pure.

b) Vinyl Chloride in Nitrogen Standards: 10 ppm (v/v), 50 ppm (v/v), 100 ppm (v/v), 1000 ypm (v/v). Available from Supelco, Inc.

c) N, N-dimethylacetamide (DMAC): reagent grade.

d) Nitrogen: Zero grade carrier gas.

e) Hydrogen: high purity for FID.

f) Air: high purity for FID.

5. Instrument Operating Conditions

a) Water Bath: 90.0C ± 0.1°

b) Gas Flow Controllers
N_2 (reference col): 10 ml/min (~ 1 Kg (cm^2)
N_2 (analytical col): 10 ml/min (~ 1.2 Kg/cm^2)
N_2 (backflush)" 10 ml/min (~ 0.8 Kg/cm^2)
H_2: 25-30 ml/min (2.0 Kg/cm^2)
Air: 250-300 ml/min (3.2 Kg/cm^2)

c) Gas Chromatograph Conditions:
Oven: 55C
Injector: 100C
Detector: 150C
Dosing Needle: 100C

d) Sequencer (Programmer) Controls
Backflush: On
P: 30 sec (internal setting)
I: 3 sec
A: 0.8 min
BF: 8' (10X internal setting)
S: 1'

e) Integrator Controls
PW: 5 (peak width)
SS: 15 (slope sensitivity = 1.2 μv/sec)
FP: 5 (fused peaks)
BL: 2 (baseline)
T1: 60 (initial delay)
T4: 250 (stop time)
MA: 0 (minimum area)
Program: 3 (external standard)

6. Calibration

a) Powders (resins and compound powder blends only). Calibrate the analytical system using gaseous vinyl chloride in nitrogen standards as follows: Take two or three empty vials, close each with a septum stopper and seal with an aluminum cap. Insert a 3" needle (22 gauge) and a short (1/2", 22 gauge) needle through the septum of the vial. Connect (metal tubing) the long (3") needle to a cylinder containing the vinyl chloride standard (10-100 ppm VCl in N_2) and slowly flush (15-25 ml/min) the vial with the standard for 4-6 min. After the vial has been filled with the VCl standard remove first the 3" needle and then the 1/2" needle from the vial. Repeat to fill additional vials. Label the vials containing the standards and use within 24 hours.

To calibrate the instrument, take two or three vials each of four or more standards and insert in the F-42 turntable (at operating temperature). Allow the standards to come to thermal equilibrium (one hr) and then analyze using the instrument conditions shown in section 5.

Calculate the calibration factor as follows:

$$F_{(P)} = \frac{C \times 0.0194}{A}$$

where: $F_{(P)}$ = calibration factor for powder samples

C = Concentration of VCl in the gas standard in ppm (v/v).

A = Area of the VCl peak

0.0194 = Factor which relates vapor VCl concentration (ppm) to original VCl concentration in powder. Based on 4 g sample, 25 ml vial, 90.0C and Henry's law relation. (See section 8.)

Average the calibration factor for the number of standards analyzed (results should agree within ± 5% relative).

Recalibration should be performed on a regular basis (weekly or biweekly). If the daily standard (section 7) varies more than ± 10% from the correct value then the analytical system should be recalibrated.

b) Solutions: (pellets and finished products - may also be used for powders with reduced sensitivity). Calibrate using vinyl chloride in DMAC solution standards as follows: Fill a 100 ml volumetric flask to the mark with DMAC at room temperature. Seal the flask with a septum stopper and chill in an ice bath (about 30 min). Using a gas tight syringe, take a sample of pure vinyl chloride gas from a small cylinder. Inject exactly 1.0 ml of pure VCl gas into the cold DMAC contained in the volumetric flask. Mix thoroughly and allow the solution to warm to room temperature. Since 1.0 ml of VCl weighs 2550 µg (25C, 760 mm Hg) the solution contains 255 µg VCl/10 ml DMAC.

Remove the septum stopper from the volumetric flask. Pipet 10.0 ml of the 255 µg VCl/10 ml DMAC standard into a second 100 ml volumetric flask; dilute to the mark with pure DMAC and mix. This solution contains 25.5 µg VCl/10 ml DMAC. In the same manner, prepare standards containing 2.55 µg VCl/10 ml DMAC and 0.26 µg VCl/10 ml DMAC.

By means of a 10.0 ml pipet, transfer 10 ml aliquots of each standard to a series of properly labeled 25 ml vials. Seal th vials with septum stoppers and aluminum caps. These DMAC solution standards in sealed vials are stable for at least two months under ordinary conditions (room temperature).

To calibrate the instrument, take a set (4) of standards and insert in the F-42 turntable (at operating temperature). Allow the samples to come to thermal equilibrium (one hour) and then analyze them using the conditions described in section 5.

Calculate the calibration factor as follows:

$$F_{(S)} = \frac{W}{A}$$

where: $F_{(S)}$ = calibration factor for solution

W = weight of VCl in solution (µg VCl/10 ml DMAC)

A = Area of VCl peak

Average the calibration factor for the number of standards analyzed (results should agree with ± 5% relative.

Recalibration should be performed on a regular basis (weekly or biweekly). If the daily standard (section 7) varies more than ± 10% from the correct value then the analytical system should be recalibrated.

7. Procedure

a) Powders (resins and compound powder blends only). Weigh 4.00 ± 0.01 g of PVC resin powder or PVC compound powder blend into a 25 ml vial. Close the vial with a septum stopper and seal with an aluminum cap. Analyze each sample in duplicate by weighing separate aliquots into separat vials. Also prepare an air blank by sealing an empty vial. Place the air

blank vial in the turntable (at operating temperature) followed by a vial containing a VCl in N_2 standard followed by the two sample vials. Additional samples may be inserted in the turntable at this time. Make sure that the F-42 operating parameters are set as indicated in section 5. Allow the samples to come to thermal equilibrium (one hour).

Start the analysis sequence and analyze the samples (VCL elutes at 103-104 sec). After the samples have been analyzed, insert a needle (1/2", 22 gauge) into each vial to vent the internal pressure before removing the vials from the turntable.

b) Solutions (pellets and finished products). Weigh a 0.5-0.7 g (to ± 0.0001 g) sample into a 25 ml vial. Add 10.0 ml (pipet) of DMAC to the vial and seal with a septum stopper and aluminum cap. Analyze each sample in duplicate by weighing separate samples into separate vials. Warm the sample vials to ~ 50C and shake occasionally until the PVC has dissolved (4-6 hrs). Samples must be completely dissolved (except for fillers and pigments present in some compounds) before proceeding. Prepare a DMAC blank by pipeting 10.0 ml of pure DMAC into a vial and sealing as outlined above. Additional samples may be prepared in the manner outlined above at the same time.

Place the DMAC blank in the turntable (at operating temperature) followed by one or more VCl in DMAC standards. Then insert the sample(s) in the turntable in known sequence. Make sure that the F-42 operating parameters are set as indicated in section 5. Allow the samples to come to thermal equilibrium (one hr).

Start the analysis sequence and analyze the samples (VCl elutes at 103-104 sec). After the samples have been analyzed, insert a needle (1/2", 22 gauge) into each vial to vent the pressure before removing the vials from the turntable. A typical chromatogram is shown in Figure 1.

8. Calculations

a) Powder (resins and compound powder blender only). The following equation relates the concentration of VCl in the PVC to the headspace concentration:

$$C_{VCl} = \frac{C_{HS} \times Pa}{Ti} \left(\frac{Mv\ Vg}{m_t\ R} + KT_2 \right)$$

where: C_{VCl} = concentration of VCl in the PVC before equilibration, ppm (wt/wt).

C_{HS} = concentration of VCl in the headspace after equilibration, ppm (v/v)

Pa = barometric pressure, mm Hg

Ti = ambient temperature, °K

Mv = molecular weight of VCl (62.5)

Vg = volume of gas phase in the vial, ml

m_t = weight of PVC sample

R = gas constant (62360)

K = Henry's Law constant for PVC (6.52×10^{-6})

T_2 = equilibration temperature, °K

Under ordinary laboratory conditions, the above may be reduced to the following (based on 4.00 g sample).

$$C_{VCl} = C_{HS} \times 0.0194$$

or

$$C_{VCl} = F_{(P)} \times A$$

where: $F_{(P)}$ = calibration factor from section 6

A = area of the VCl peak

The integrator may be programmed to automatically calculate the concentration of VCl in the PVC (see instruction manual for details).

b) Solutions (pellets and finished products). Calculate the VCl content of the PVC sample as follows:

$$C_{VCl} = \frac{F_{(s)} \times A}{S}$$

where: C_{VCl} = concentration of VCl in the PVC sample before equilibrium, ppm (wt/wt).

$F_{(s)}$ = calibration factor from section 6.

A = area of the VCl peak

S = sample wt, g.

The integrator may be programmed to automatically calculate the concentration of VCl in the PVC (see instruction manual for details).

9. Precision and Accuracy

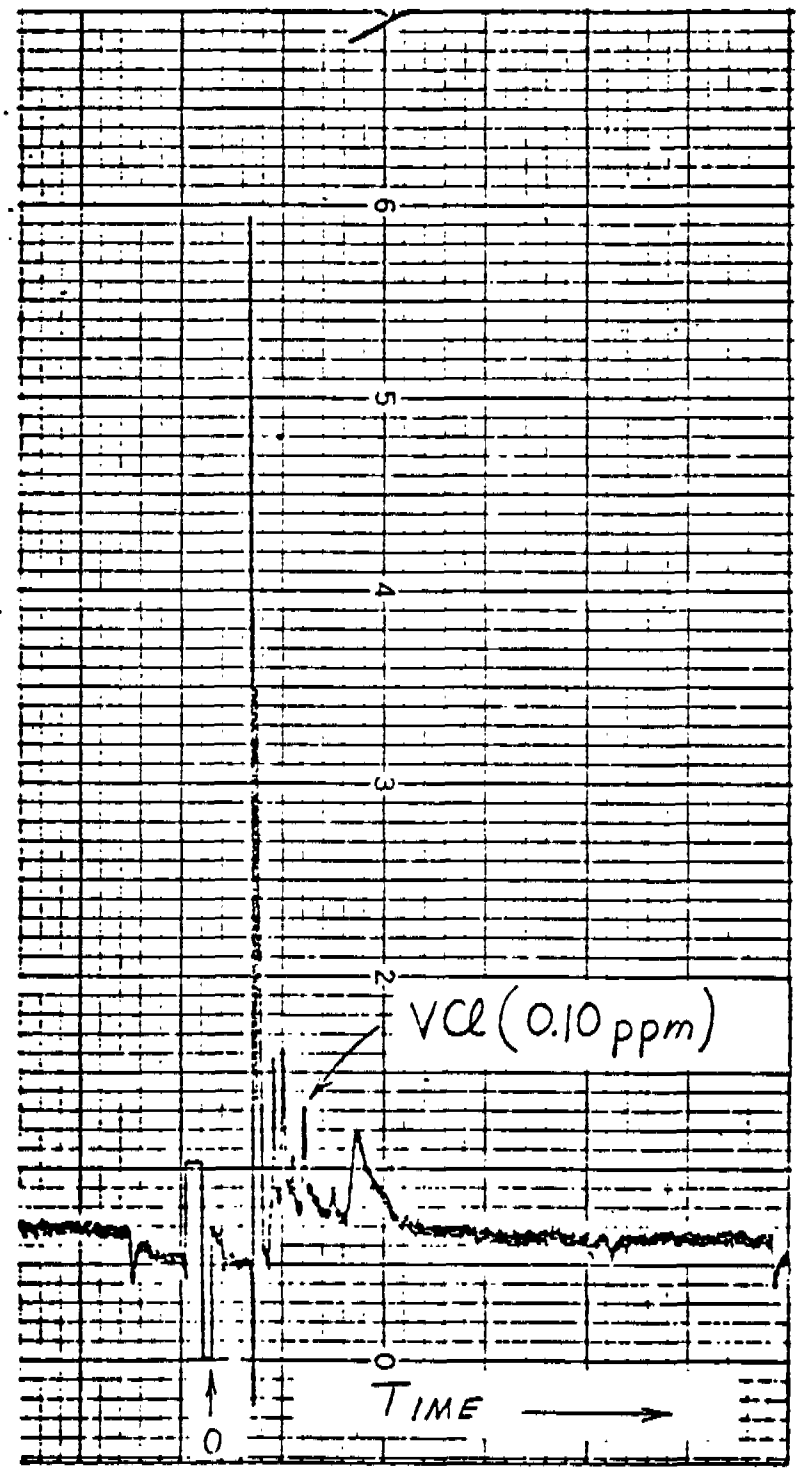
For powder samples, the precision has been found to be ±5% relative at the 1.0 ppm VCl level. The accuracy depends on the accuracy of the standards used for the calibration (generally ±5% relative). The lower limit of detection has been found to be 0.005 ppm VCl.

For pellet samples (analyzed as solutions) th precision has been found to be ±10% relative at the 1.0 ppm VCl level. The accuracy depends on the accuracy of the calibration standards (generally ±5% relative). The lower limit of detection has b en found to be 0.03 ppm VCl.

The value for Henry's Low Constant for PVC is taken from A. R. Berens, Polymer Reprints, 197, September, 1974.

FIGURE 1

Vinyl Chloride in PVC (DMAC Solution)



HEWLETT-PACKARD 9280-0222

VC4069

Appendix II

Determination of Low Levels of Vinyl Chloride in Various Solvents (Headspace Analyzer Method)

1. Scope

This method describes a procedure for the determination of low levels (ppb to low ppm range) of vinyl chloride (VCl) in various solvents such as water and dilute aqueous solution, 50% ethanol, and oils by a automated technique (headspace analysis). The lower limit of detection is dependent on the solvent to be analyzed but, in general, ranges from 1 - 2 ppb for water up to 6 - 8 ppb for oils.

2. Outline of the Method

a) A 10.0 ml sample of the liquid to be analyzed is transferred to a 25 ml vial and sealed with a serum stopper. The sample is then equilibrated for one hour at an elevated temperature (90C for water, aqueous solution, and oils; 65C for 50% ethanol solution). A sample of the vapor (headspace) above the liquid is then injected into a gas chromatograph equipped with a flame ionization detector. By use of an automated turntable and sequencer up to 30 samples may be prepared and analyzed without additional operator attention. Standard gas samples and standard liquid samples containing known amounts of vinyl chloride are analyzed along with the unknown samples to calibrate the instrument. Calibration may be either based on measurement of peak height with a ruler or peak area measured with an automatic integrator. From the calibration standards the VCl content of the unknown sample is determined.

3. Apparatus

a) Headspace Analyzer: Perkin Elmer Model F-42, equipped with a flame ionization detector, thermostatted sample turntable, back-flush assembly, automatic timing sequencer.

b) Sample Vials: 25 ml complete with butyl rubber septum caps and aluminum caps. These vials are available from Perkin Elmer to fit the F-42 turntable.

c) Column: 5' x 1/8" SS packed with 10% Carbowax 20 M on 60/80 Chromosorb W HP followed by 10' x 1/8" SS packed with 10% OV-17 on 60/80 Chromosorb W HP. The two columns are connected in series (Carbowax 20 M section closest to injection port) with the back-flush "T" between the two columns.

d) Recorder: 1 mv full scale, 15"/hour.

e) Integrator: Spectra-Physics System I (Perkin-Elmer Model 1).

f) Syringes, Gas Tight: 10, 50, 100, 500 µl and 1, 2, 5 ml.

g) Ordinary Laboratory Glassware.

4. Reagents and Materials

a) Vinyl Chloride: 99.9+% pure.

b) Vinyl Chloride in Nitrogen Standards: 1 ppm (v/v), 10 ppm (v/v), 50 ppm (v/v), 100 ppm (v/v), 1000 ppm (v/v). Available from Supelco Inc.

c) Nitrogen: Zero grade carrier gas.

d) Hydrogen: High purity for FID.

e) Air: High purity for FID.

5. Instrument Operating Conditions

a) Water Bath: 90.0 C $\pm$ 0.1° (for water and oil samples)
65.0 C $\pm$ 0.1° (for 50% ethanol samples)

b) Gas Flow Controllers

N_2 (reference col.): 10 ml/min ($\sim$ 1 Kg/cm^2)
N_2 (analytical Col.): 10 ml/min ($\sim$ 1.2 Kg/cm^2)
N_2 (backflush): 10 ml/min ($\sim$ 0.8 Kg/cm^2)
H_2: 25 - 30 ml/min (2.0 Kg/cm^2)
Air: 250 - 300 ml/min (3.2 Kg/cm^2)

c) Gas Chromatograph Conditions

Oven: 75 C
Injector: 100 C
Detector: 150 C
Dosing Needle: 100 C

d) Sequencer (Programmer) Controls

Backflush: On
P: 30 sec. (internal setting)
I: 4 sec.
A: 1.5 min.
BF: 15 min. (internal 10X setting)
S: 1 min.

e) Integrator Controls

PW: 5 (peak width)
SS: 15 (slope sensitivity = 1.2 μv/sec)
FP: 5 (fused peaks)
BL: 2 (baseline)
T1: 100 (initial delay)
T4: 250 (stop time)
MA: 0 (minimum area)
Program: none; i.e. print areas and times only.

6. Calibration: Determination of Henry's Law Constant

a) Prepare gas standards as follows: Close an empty vial with a serum stopper and seal with an aluminum cap. Insert a 3" needle (22 gauge) through the septum of the vial. Connect this needle with metal tubing to a cylinder containing a VCl in nitrogen standard (1 - 1000 ppm). Insert a short 1/2" needle (22 gauge) through the setpum to act as a vent. Slowly flush (15 - 25 ml/min) the vial with the vinyl chloride standard for approximately 10 min. After the vial has been filled with the VCl standard, remove first the 3" needle and then the 1/2" needle from the vial. Repeat to fill additional vials with the various standards. At least five vials should be filled with each standard. If the Henry's Law constant for water is being determined, inject 20 - 25 μl of distilled water into each vial. If the Henry's Law constant for 50% ethanol or oil is being determined then the gas standards are used dry. Label the vials and use within 24 hours.

b) Prepare liquid standards as follows: Add 10.0 ml of the liquid to a vial and seal as above. By means of a microliter syringe, add an appropriate amount of pure vinyl chloride gas to the liquid. A convenient range of concentrations to prepare is from 2 ppb to 10 ppm. Prepare at least five vials of each standard. Label and use within 24 hours.

c) Analyze both the gas standards and the liquid standards as described in the Procedure (Section 7). From the areas (or peak heights) obtained on the gas standards plot concentration vs. peak area. From the area of the VCl peak obtained on each liquid standard and the calibration curves plotted for gas standards, determine the concentration of vinyl chloride in the headspace above each liquid standard. Calculate the Henry's Law Constant from the relationship on the following page.

$$K = \frac{1}{T_2}\left(\frac{C_{VC1}T_1}{C_{HS}P_a} - \frac{M_V V_g}{M_t R}\right)$$

where:

K = Henry's Law constant
T_g = equilibration temperature, °K (363 for water and oil; 338 for 50% ethanol).
C_{VC1} = concentration of VC1 in the liquid before equilibration 1 ppm (wt/wt).
T_1 = ambient temperature, °K.
C_{HS} = concentration of VC1 in the headspace after equilibration, ppm (v/v).
P_a = barometric pressure, mm Hg.
M_V = molecular weight of VC1 (62.5)
V_g = volume of gas phase in the vial, ml.
m_t = weight of liquid, g.
R = gas constant (62360).

d) The following values for Henry's Law constants have been obtained by the R&D laboratories of the Ethyl Corp., Baton Rouge, LA.

$K_{H_2O} = 1.5 \times 10^{-6}$ (wet gas standard)

$K_{50\%E+OH} = 7.1 \times 10^{-6}$ (dry gas standard)

$K_{soya\ oil} = 26.8 \times 10^{-6}$ (dry gas standard)

$K_{mineral\ oil} = 19.5 \times 10^{-6}$ (dry gas standard)

e) Gas standards must be analyzed with each batch of samples analyzed.

f) The determination of Henry's Law constant for each liquid should be repeated whenever extreme accuracy is desired for the analysis of a group of samples or whenever any major operating parameter is changed.

7. Procedure

a) Transfer 10.0 ml of the liquid to be analyzed to a vial, close with a serum stopper and seal with an aluminum cap. For highest accuracy each sample should be analyzed in triplicate. Sample weight may be determined from tables of density or by weighing a seprate 10.0 ml portion of the sample.

b) Place the sample(s) in the turntable (at operating temperature). Make sure that all operating parameters as described in Section 5 are set on the instrument.

c) Also place several gas standards in the turntable.

d) Allow the samples and standards to equilibrate for one hour.

e) Analyze the samples using the automated sequencer. Vinyl chloride elutes at 141 - 142 sec. under the conditions given in Section 5. A typical chromatogram is shown in Figure 1.

f) After all of the samples and standards have been analyzed remove the vials from the turntable (relieve the internal pressure in each vial by venting with a 1/2" 22 gauge needle).

g) From the data obtained on the gas standards, determine the headspace concentration of VCl for each sample.

8. Calculations

a) Calculate the concentration of VCl in the liquid sample from the following relationship:

$$C_{VCl} = \frac{C_{HS}\ P_a}{T_1}\left(\frac{M_V\ V_g}{m_t R} + KT_2\right)$$

where:

C_{VCl} = concentration of VCl in the liquid before equilibration, ppm (wt/wt).

C_{HS} = concentration of VCl in the headspace after equilibration, ppm (v/v).

P_a = barometric pressure, mm Hg.

T_1 = ambient temperature, °K.

M_V = molecular weight of VCl (62.5)

m_t = sample weight

R = gas constant (62360)

K = Henry Law Constant (Section 6)

T_2 = equilibration temperature, °K (363 for water and oil; 338 for 50% ethanol).

b) Under ordinary conditions, most of the terms in the above equation are constant i.e., Pa = 760; T_l = 298; V_g = 13.8 ml; etc. Therefore, the following simplified equations may be used:

Water:	$C_{VCl} = C_{HS} \times 0.0049$ (wet gas standard)
50% E+OH:	$C_{VCl} = C_{HS} \times 0.0099$ (dry gas standard)
Soya Oil:	$C_{VCl} = C_{HS} \times 0.029$ (dry gas standard)
Mineral Oil:	$C_{VCl} = C_{HS} \times 0.022$ (dry gas standard)

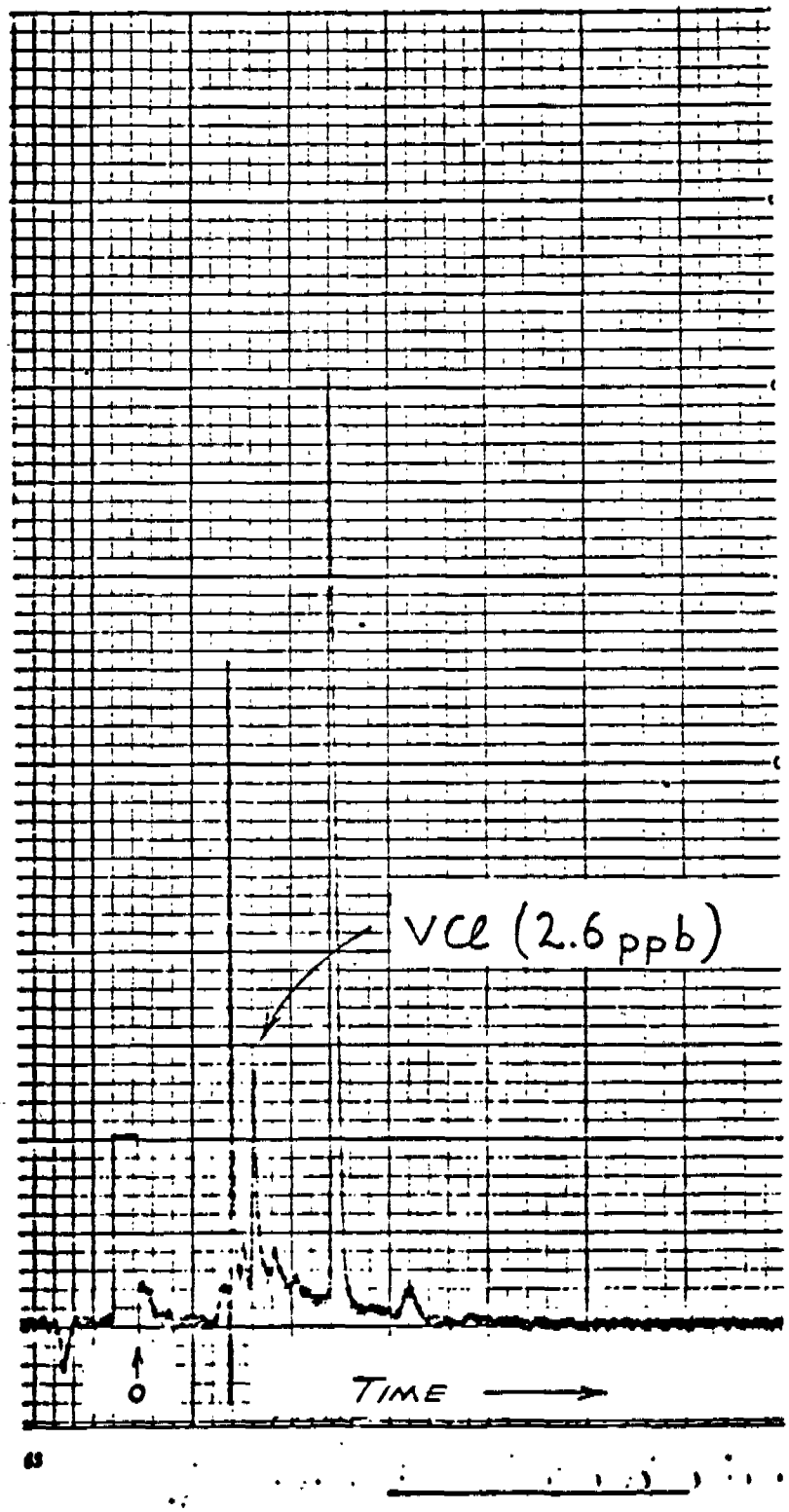
9. Precision and Accruacy

a) The precision of the analysis is dependent on two measurements. (1) the precision of the gas standards (generally $\pm$ 5% relative) and, (2) the precision of the determination of Henry's Law Constant. The latter varies from $\pm$ 20% for water to $\pm$ 5% or better for 50% ethanol and the oils. The accuracy is also dependent on these same two measurements i.e., preparation of gas standards and liquid standards, and is generally of the same order as the precision.

b) The limit of detection is dependent on the lowest concentration of VCl that can be measured in the headspace ($\sim$ 0.2 ppm) and the Henry's Law Constant for each liquid. For water the lower limit of detection is therefore 1 - 2 ppb (wt/wt) while for Soya oil the lower limit of detection is 5 - 8 ppb (wt/wt).

FIGURE 1

Vinyl Chloride in Water



VC4076

APPENDIX III

5 FILE 1
5 XD IL

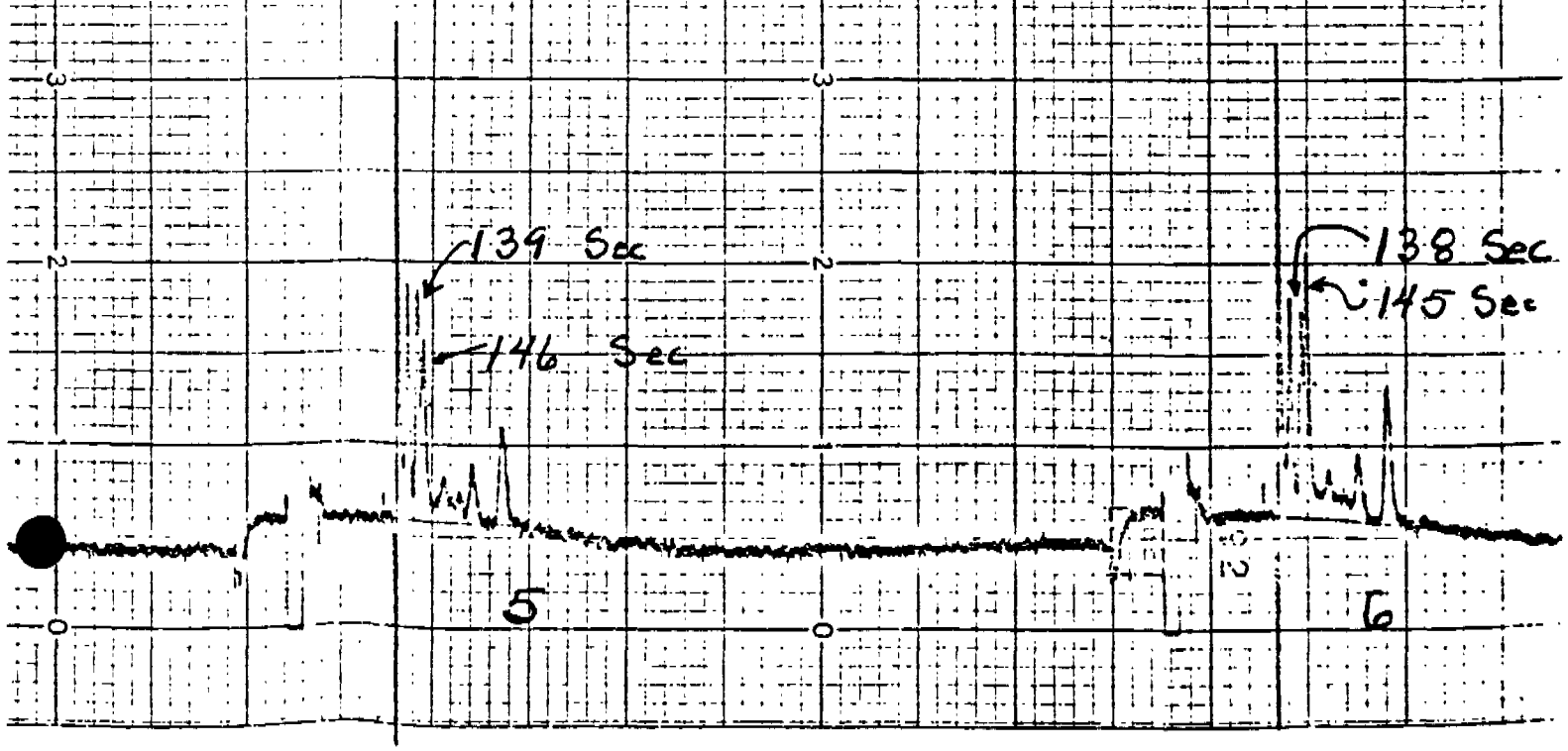
TIME	AREA
112	1537
125	464
139	297
146	161
206	171
243	408 4
	3058

6 FILE 1
6 XD ID

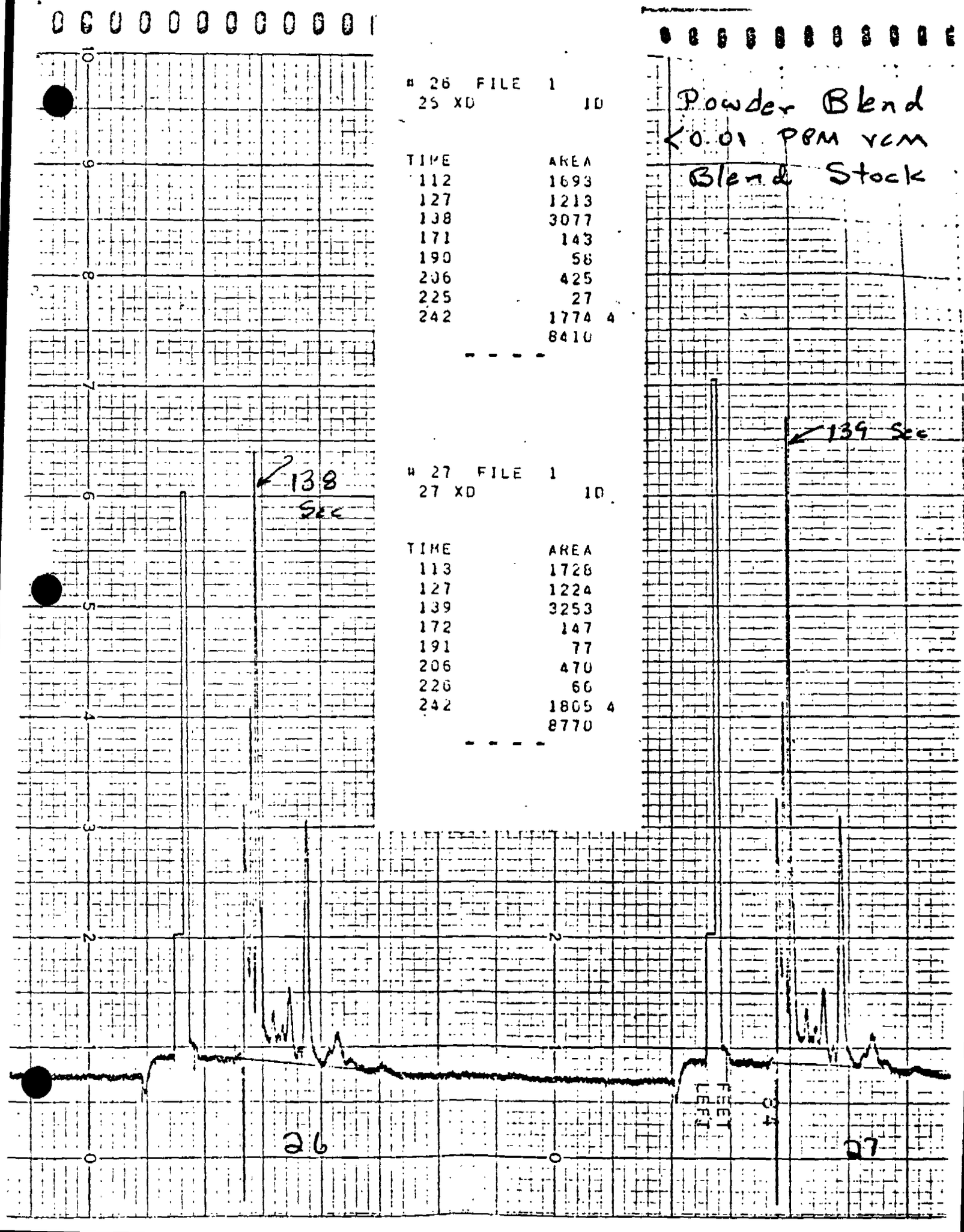
TIME	AREA
112	1442
125	390
138	242
145	390
170	62
205	221
241	559 4
	3306

7 FILE

Resin Plus Stabilizer
< 0.01 PPM VCM
Blend Stock



VC4078


26 FILE 1
25 XD ID
TIME AREA
112 1693
127 1213
138 3077
171 143
190 58
206 425
225 27
242 1774 4
8410
27 FILE 1
27 XD ID
TIME AREA
113 1728
127 1224
139 3253
172 147
191 77
206 470
226 60
242 1805 4
8770
Powder Blend
<0.01 PPM VCM
Blend Stock
138 Sec
139 Sec
26
27
FEET LEFT
VC4079

RETENTION TIME OF GAS STANDARDS

Water at Five Weeks

File No.	Retention Time, Sec.
1 - 5	140 - 142*
45 - 49	143 - 144
89 - 93	143 - 144

* No. 1 has a retention time of 134 seconds. First analysis on startup of analyzer has an anomolous retention time.

1-W-2A

9 FILE 1

9 XD ID

TIME	AREA
110	1420
128	303
139	391
145	26
109	63
241	2275 4
	5068

1-W-2B

10 FILE 1

10 XD ID

TIME	AREA
110	1469
127	287
138	382
240	3100 4
	5244

Water, 5 Weeks

Compound 1

Bottle 2 A, B

139 Sec

145 Sec

138 Sec.

9
A

10
B

VC4081

Water 5 Weeks

Compound 3

Bottle 2 B, C

3-W-2B

TIME	AREA
109	1171
123	359
137	258
144	112
153	95
239	8762 4
	10777

3-W-2C

29 FILL 1

29 XU ID

TIME	AREA
110	1225
126	344
137	244
144	94
153	80
238	8839 4
	10832

137 Sec

144 Sec

137 Sec

144 Sec

28 B

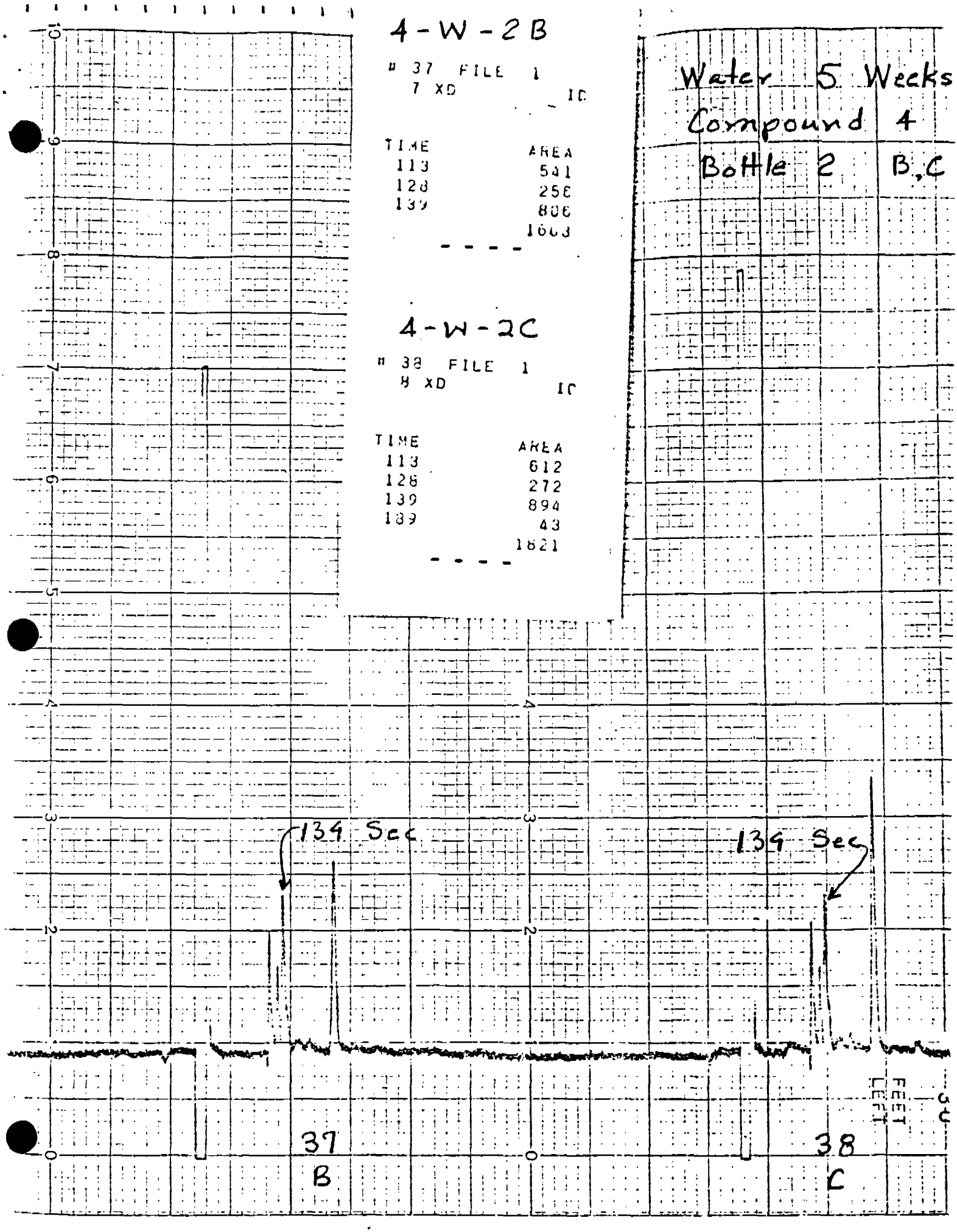
29 C

FEET

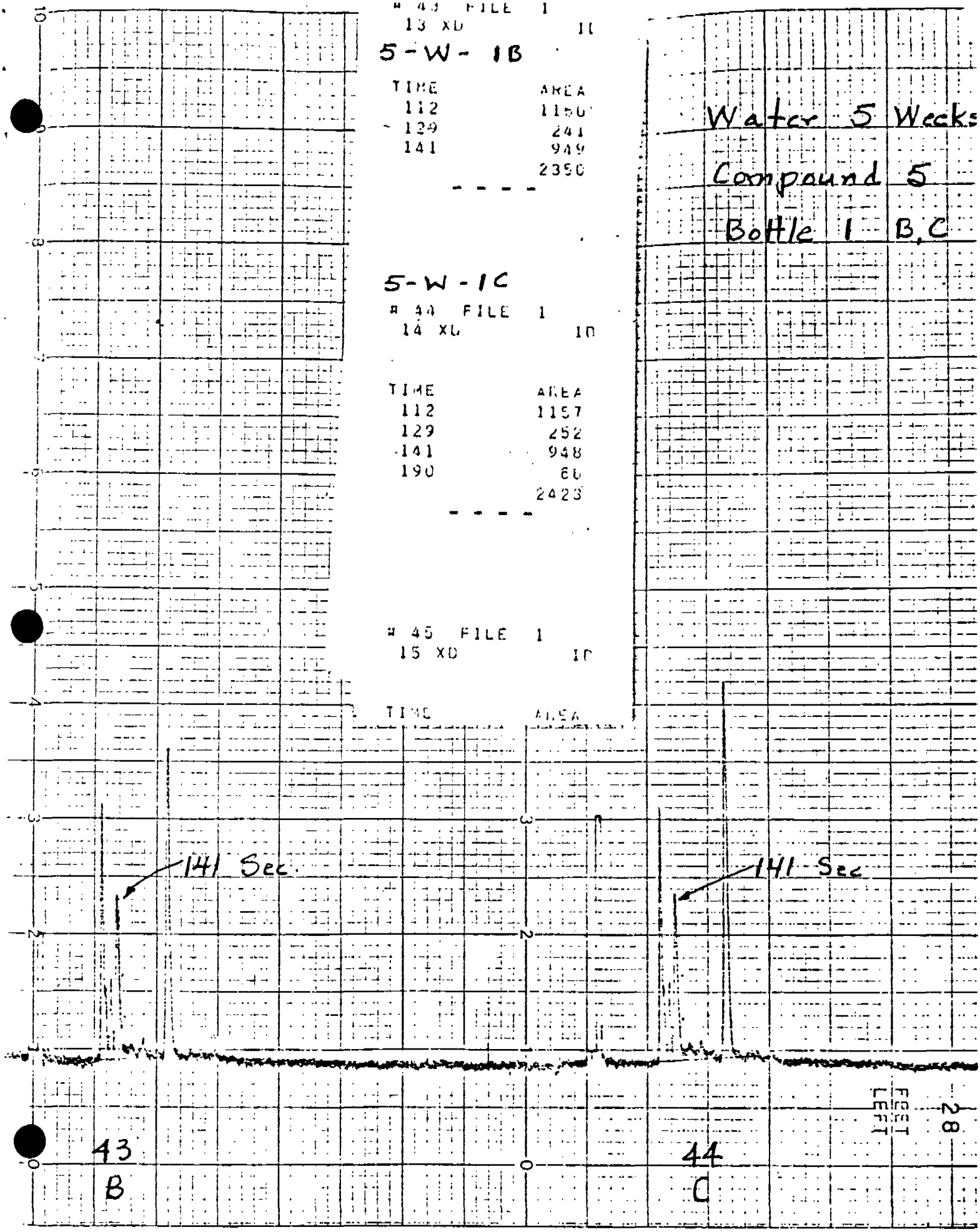
FEET

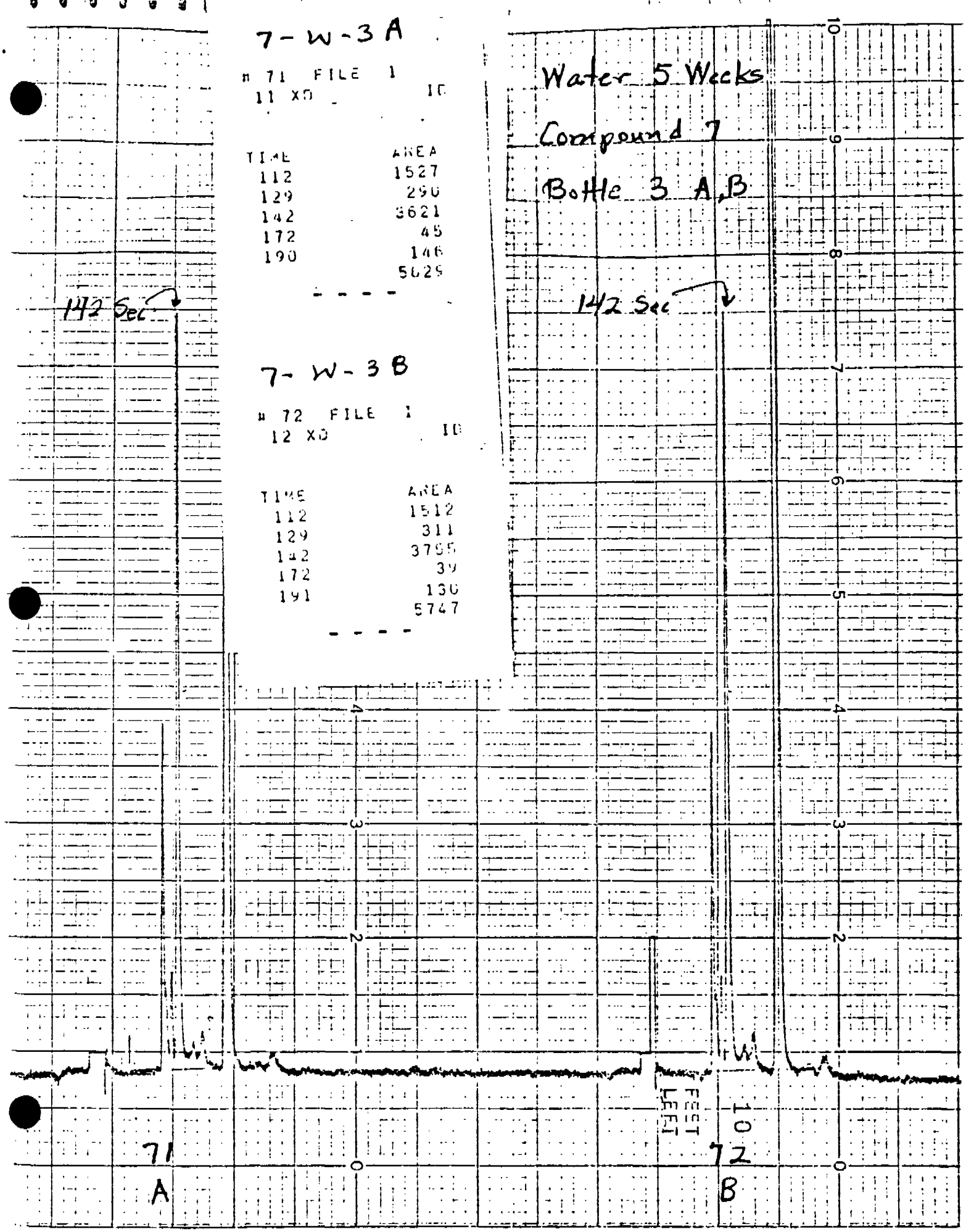
35

VC4082


4-W-2B
37 FILE 1
7 XD IC
TIME AREA
113 541
128 258
139 806
1603
4-W-2C
38 FILE 1
8 XD IC
TIME AREA
113 612
126 272
139 894
189 43
1821
Water 5 Weeks
Compound 4
Bottle 2 B,C
134 Sec
134 Sec
FEET
LEFT
37
B
38
C

VC4083


13 XD
5-W-1B
TIME AREA
112 1150
129 241
141 949
2350
Water 5 Weeks
Compound 5
Bottle 1 B,C
5-W-1C
44 FILE 1
14 XD
ID
TIME AREA
112 1157
129 252
141 948
190 66
2423
45 FILE 1
15 XD
ID
141 Sec.
141 Sec
43
B
44
C
FEET
28


7-W-3A
71 FILE 1
11 XD ID
TIME AREA
112 1527
129 290
142 3621
172 45
190 146
5629
142 Sec
7-W-3B
72 FILE 1
12 XD ID
TIME AREA
112 1512
129 311
142 3795
172 39
191 130
5747
Water 5 Weeks
Compound 7
Bottle 3 A,B
142 Sec
10 9 8 7 6 5 4 3 2 1 0
FEET
71
A
72
B

RETENTION TIME OF GAS STANDARDS

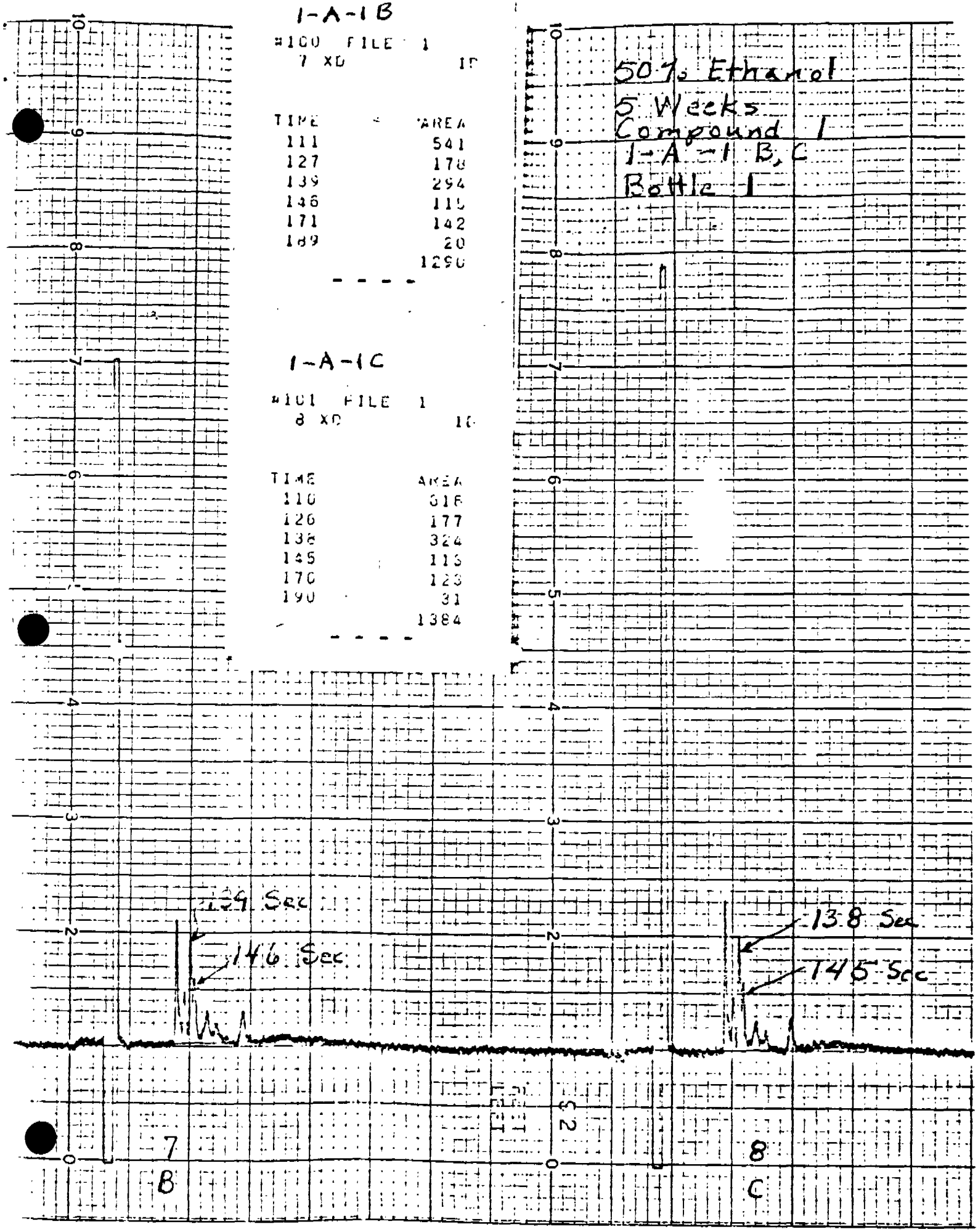
50% Aqueous Ethanol at Five Weeks

File No.	Retention Time, Sec.
1 - 5	139 - 141
45 - 49	142 - 144
74 - 78	146 - 148

RETENTION TIME OF GAS STANDARDS

50% Aqueous Ethanol at Five Weeks

File No.	Retention Time, Sec.
1 - 5	139 - 141
45 - 49	142 - 144
74 - 78	146 - 148



VC4088

3-A-1 B

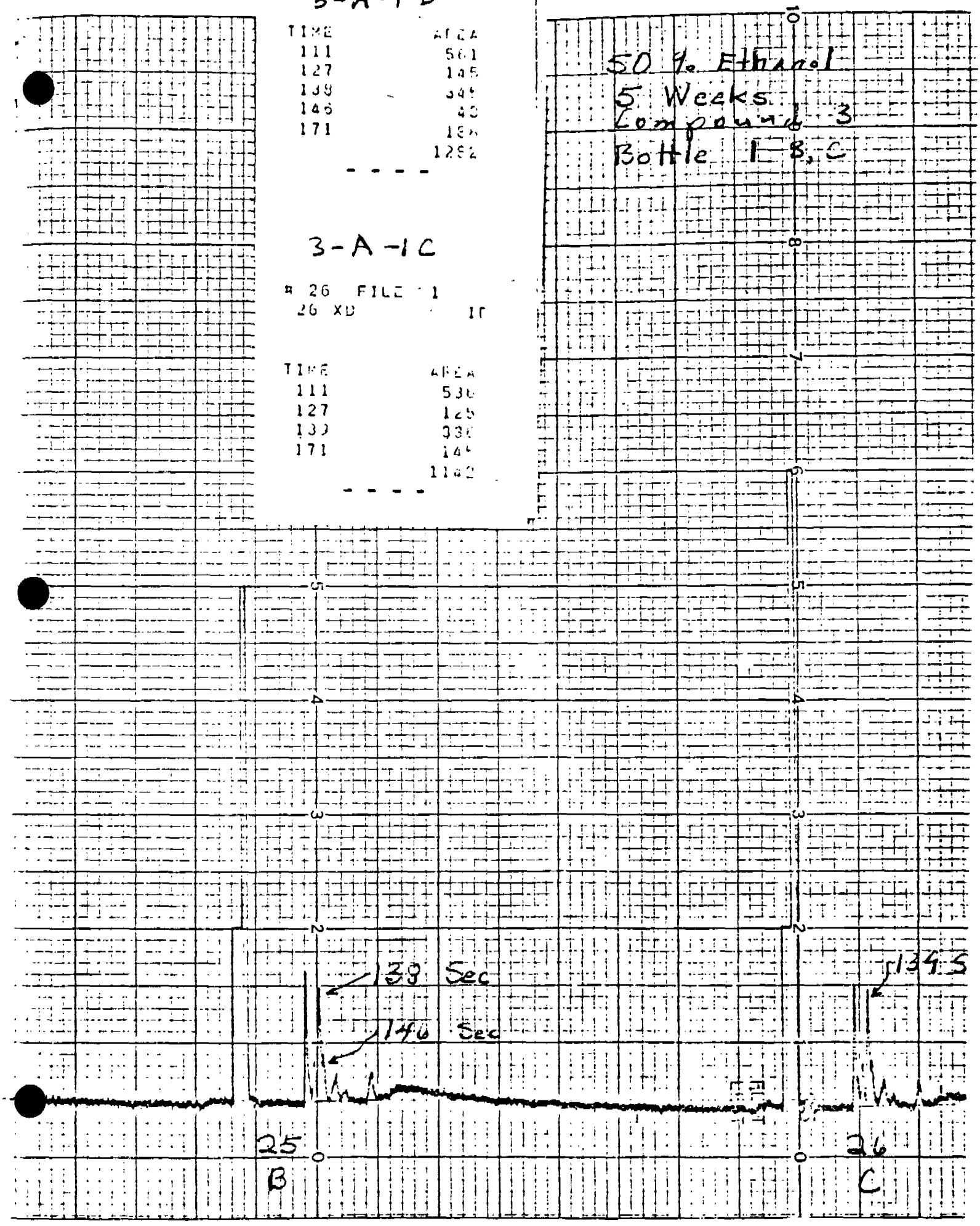
TIME	AREA
111	561
127	145
139	341
146	43
171	184
	1294

3-A-1 C

26 FILE 1
26 XD 11

TIME	AREA
111	536
127	125
139	336
171	145
	1142

50 % Ethanol
5 Weeks
Compound 3
Bottle 1 B, C



VC4089

4 XD

4-A-1B

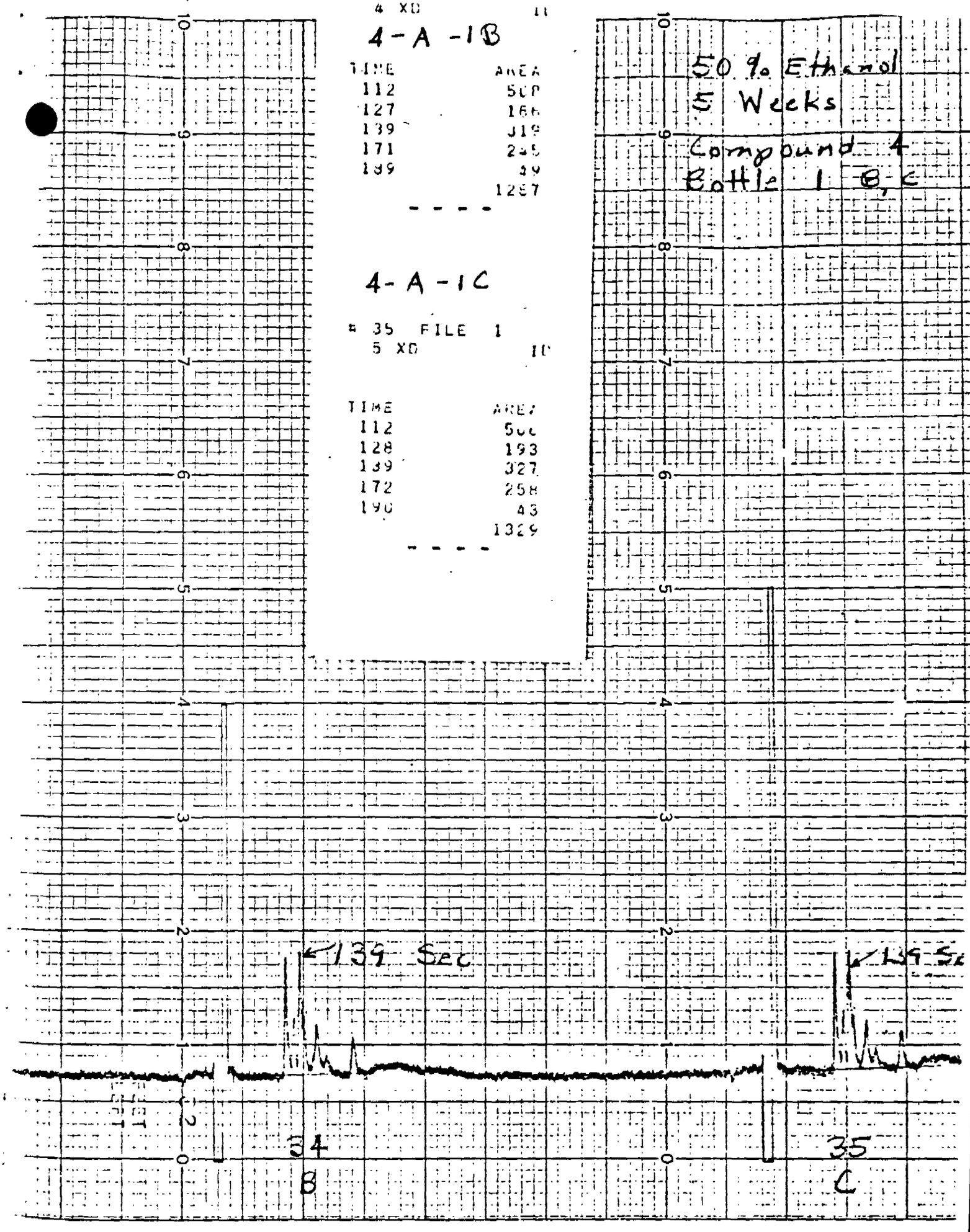
TIME	AREA
112	500
127	166
139	319
171	245
189	39
	1257

4-A-1C

35 FILE 1
5 XD

TIME	AREA
112	500
128	193
139	327
172	258
190	43
	1329

50% Ethanol
5 Weeks
Compound 4
Bottle 1 B, C



5-A-2A

50 FILE 1
20 XD ID

TIME	AREA
111	511
127	126
140	662
165	16
171	44
	1361

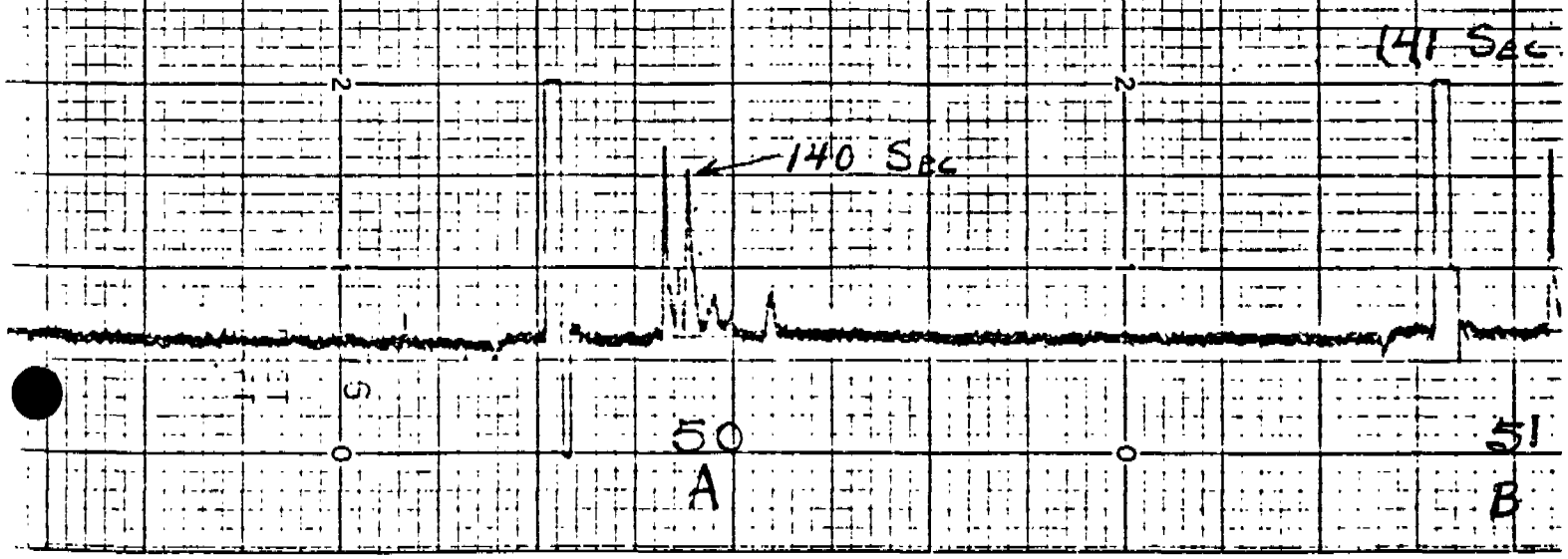
5-A-2B

51 FILE 1
21 XD ID

TIME	AREA
112	466
128	118
141	644
167	14
172	59
	1301

---

50 % Ethanol
5 Weeks
Compound 5
Bottle 2 A, B



VC4091

50 FILE 1
50 XD II

6-A-2B

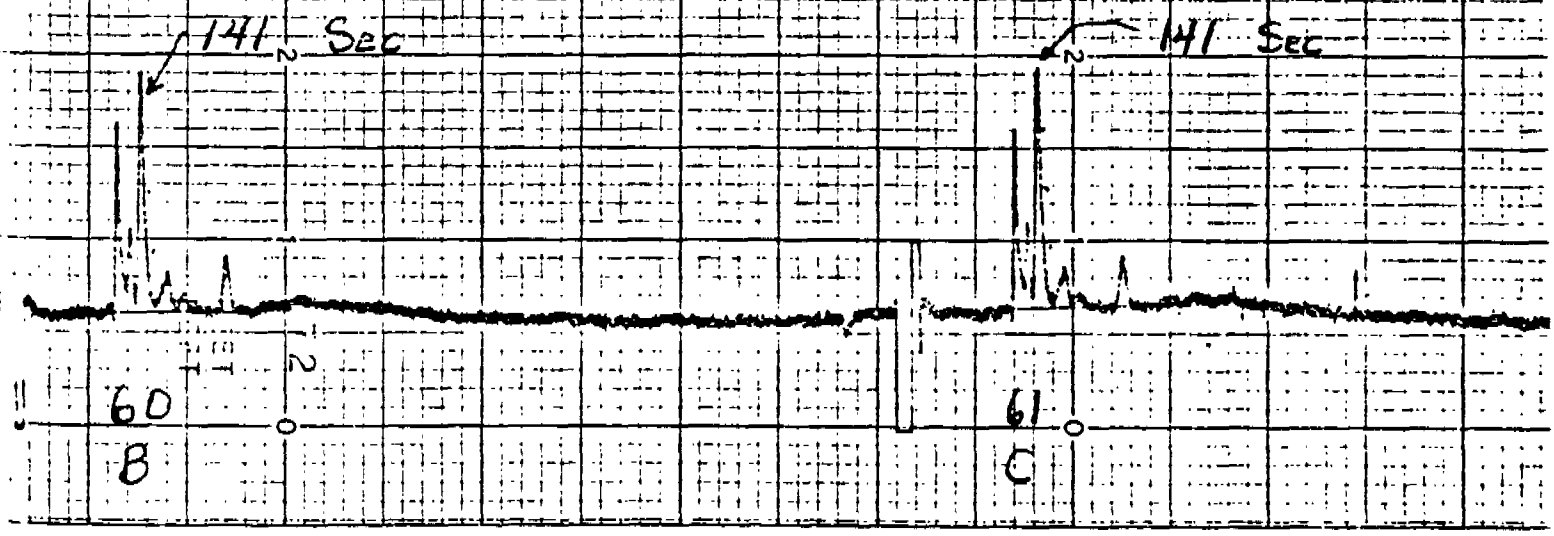
TIME	AREA
112	490
127	156
141	905
166	4
171	42
	1601

6-A-2C

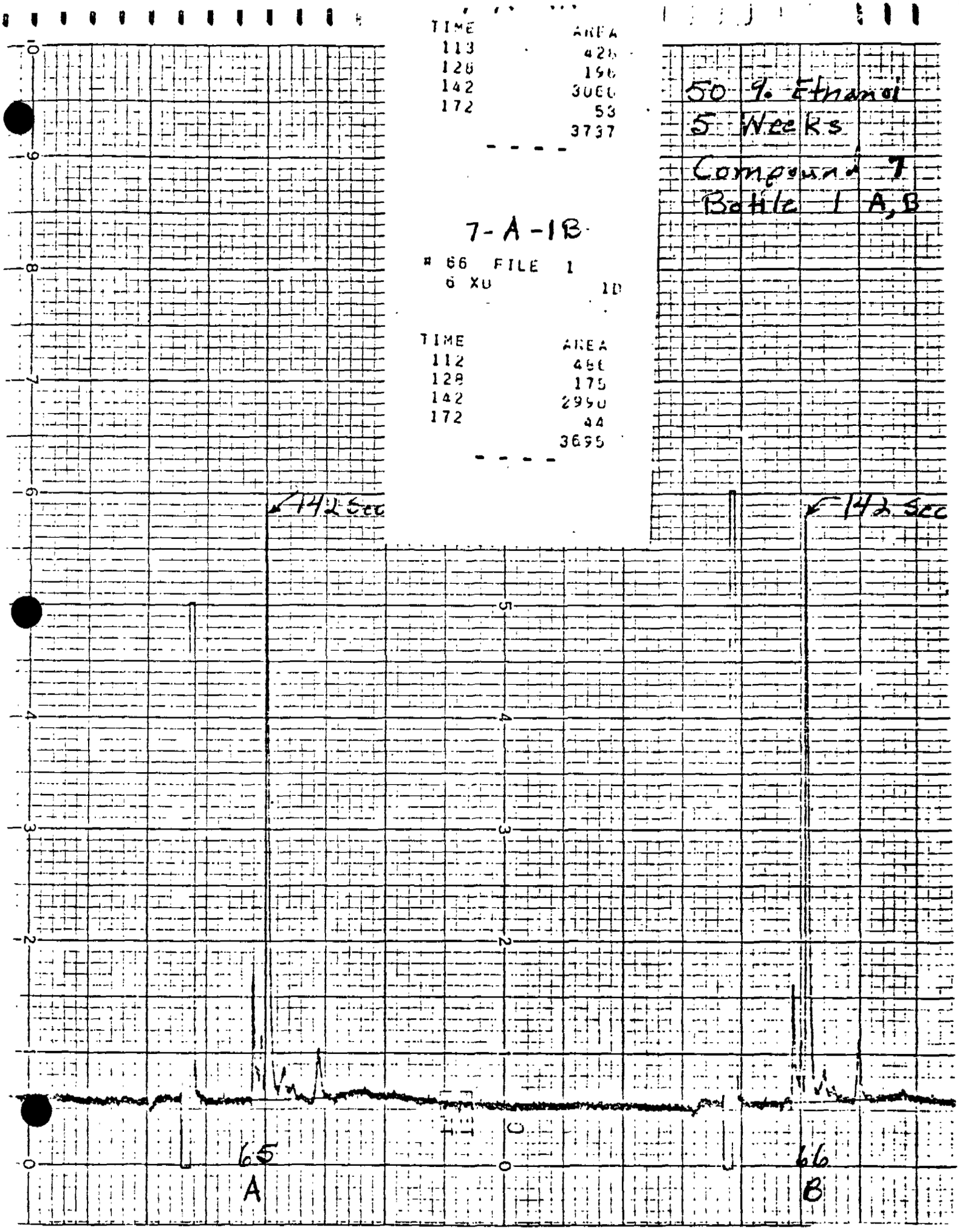
51 FILE 1
1 XD 1C

TIME	AREA
112	481
128	155
141	851
167	12
171	44
	1543

50% Ethanol
5 Weeks
Compound 6
Battle 2 B, C



VC4092


TIME AREA
113 42
128 19
142 3060
172 53
3737
7-A-1B
66 FILE 1
6 XU 1D
TIME AREA
112 46
128 17
142 2950
172 44
3695
50 % Ethanol
5 Weeks
Compound 7
Bottle 1 A, B
142 Sec
142 Sec
65
A
66
B

RETENTION TIME OF GAS STANDARDS

Water at 58 Days

File No.	Retention Time, Sec.
121 - 123	142 - 143*
151 - 153	148 - 149
181 - 183	142 - 143
208 - 210	143 - 144

* No. 121 is 146 seconds. This is the first sample of a run.

8-W-1 A

TIME	AREA
112	1352
129	613
140	293
192	136
	2394

8-W-1 B

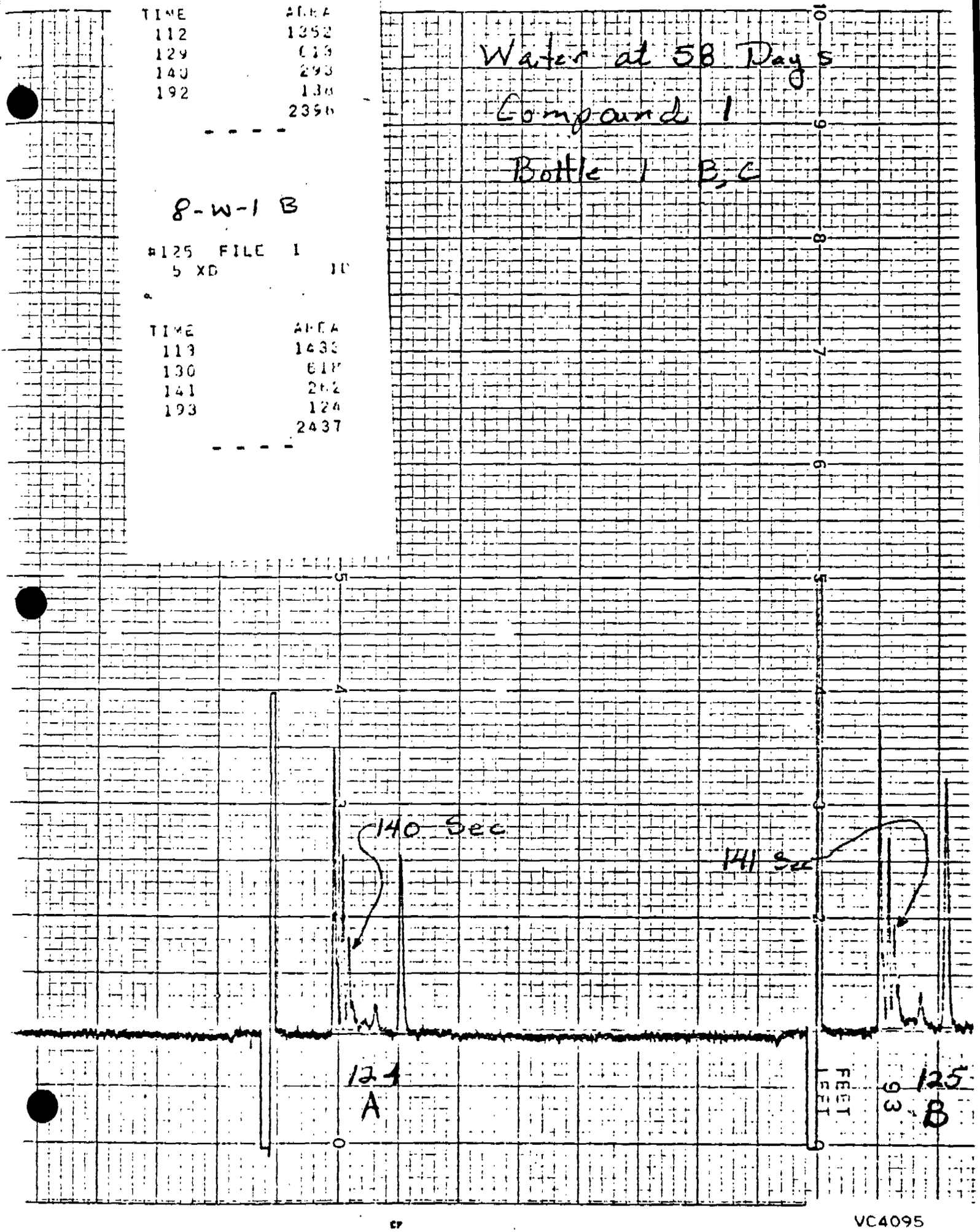
#125 FILE 1
5 XD

TIME	AREA
113	1433
130	617
141	262
193	124
	2437

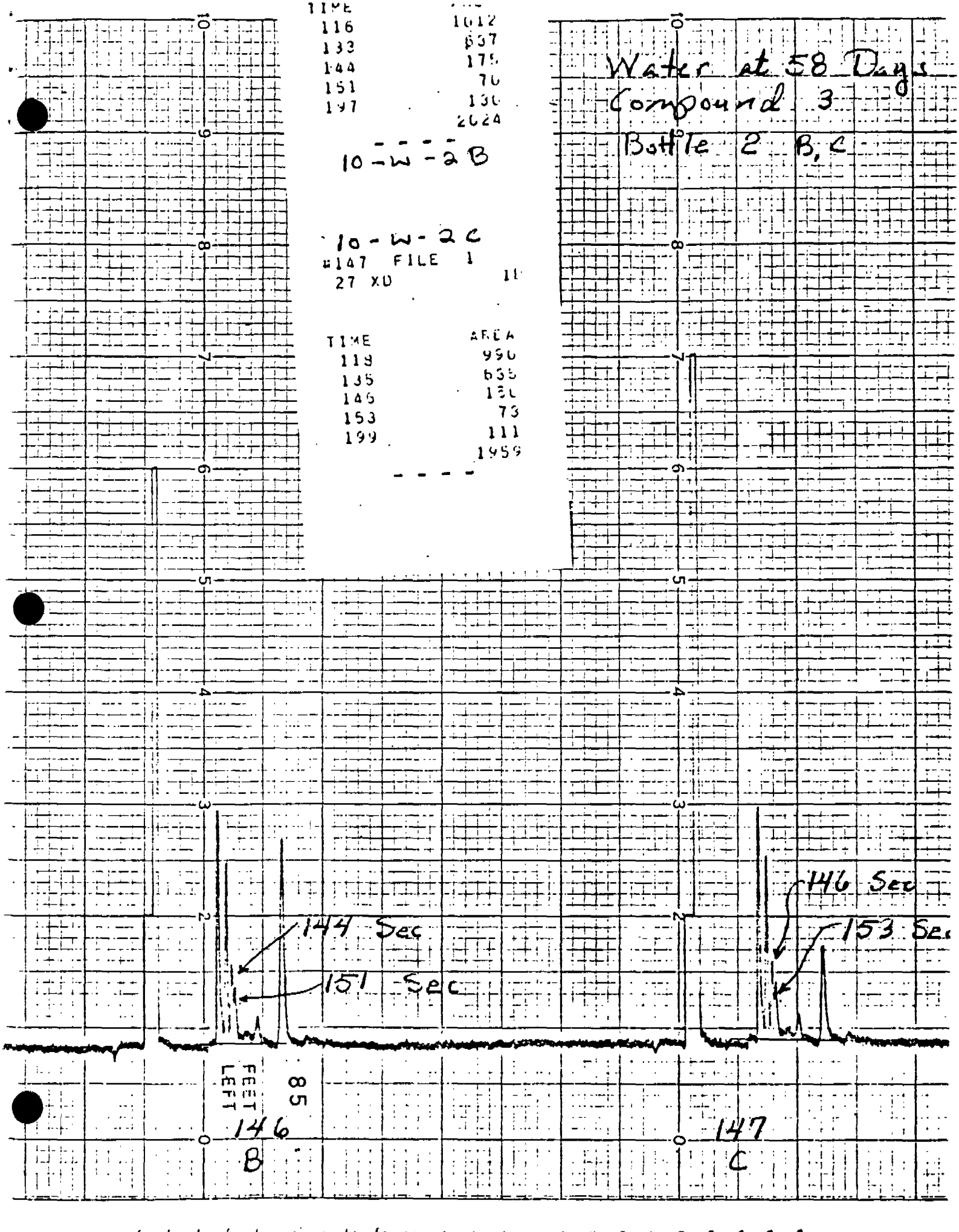
Water at 58 Days

Compound 1

Bottle 1 B, C



VC4095


TIME
116
133
144
151
197
1612
837
175
70
130
2624
10-W-2B
10-W-2C
#147 FILE 1
27 XD
TIME
118
135
146
153
199
AREA
990
635
131
73
111
1959
Water at 58 Days
Compound 3
Bottle 2 B, C
144 Sec
151 Sec
146 Sec
153 Sec
FEET
LEFT
85
146
B
147
C

VC4096

199 115
1622

Water at 58 Days
Compound 4
Bottle 2 B & C

11-W-2 B

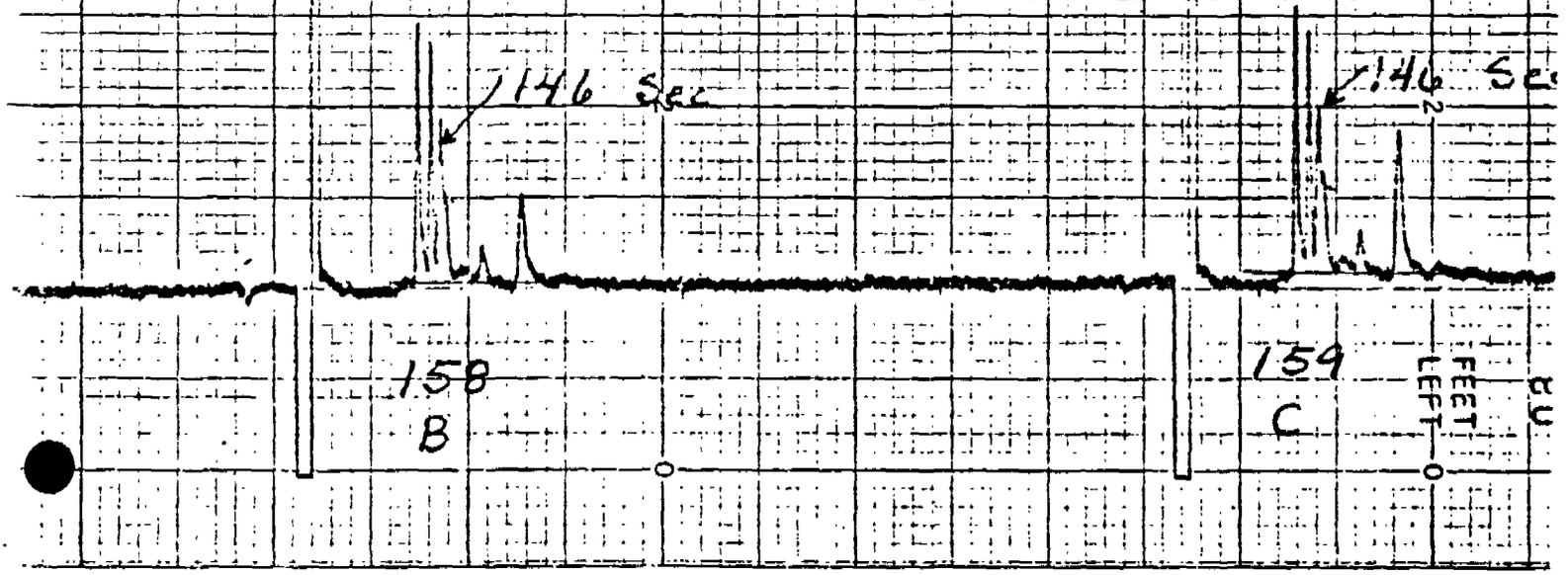
#158 FILL 1
A XD II

TIME	AREA
116	680
135	515
146	643
198	101
	1945

11-W-2 C

#159 FILE 1
9 XD II

TIME	AREA
118	694
134	529
146	263
198	85
	1571



0222

VC4097

12-W-1 A

#163 FILE 1
13 XD 10

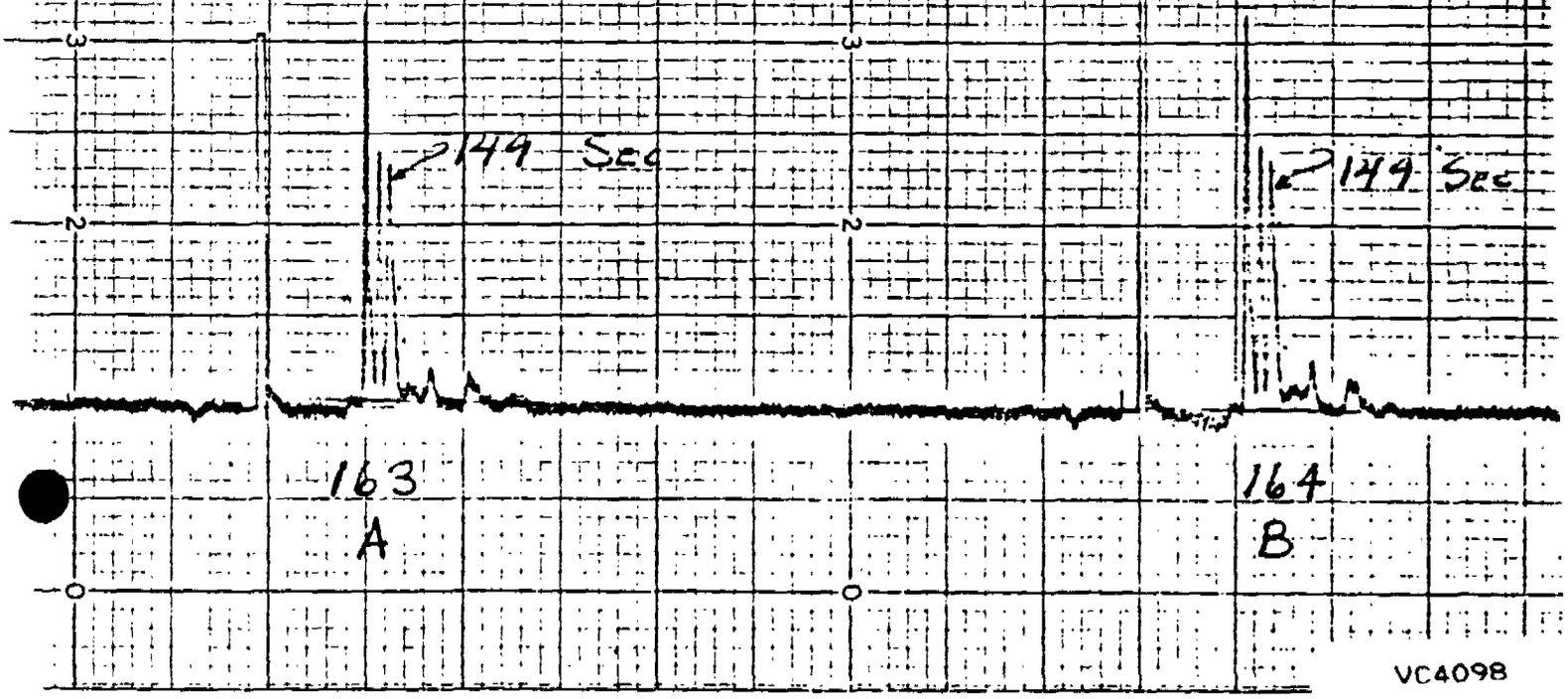
TIME	AREA
119	1132
136	544
149	893
199	96
	2665

12-W-1 B

#164 FILE 1
14 XD 10

TIME	AREA
119	1132
136	544
149	953
200	101
	2730

Water at 58 Days
Compound 5
Bottle 1 A, B



VC4098

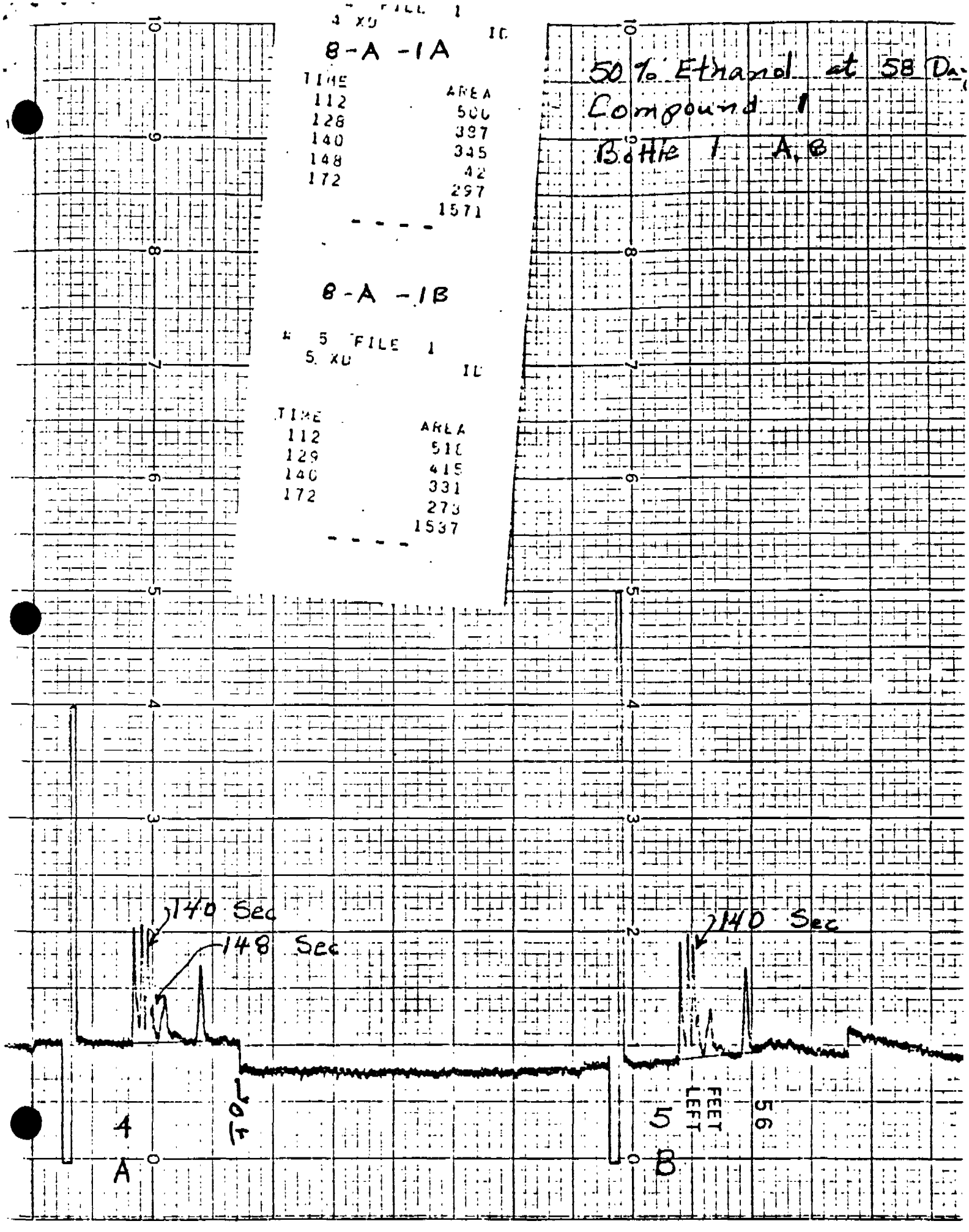
RETENTION TIME OF GAS STANDARDS

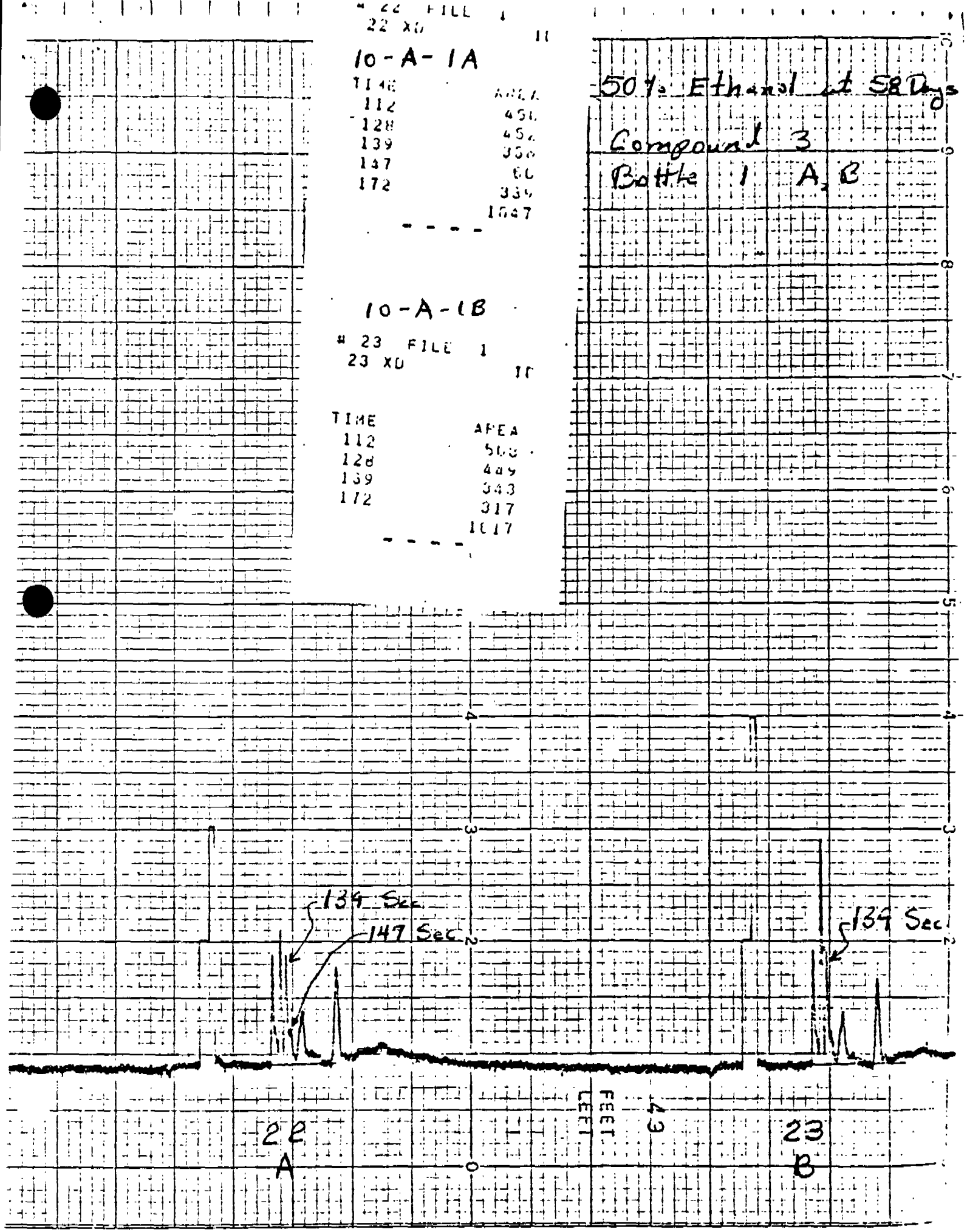
50% Aqueous Ethanol at 58 Days

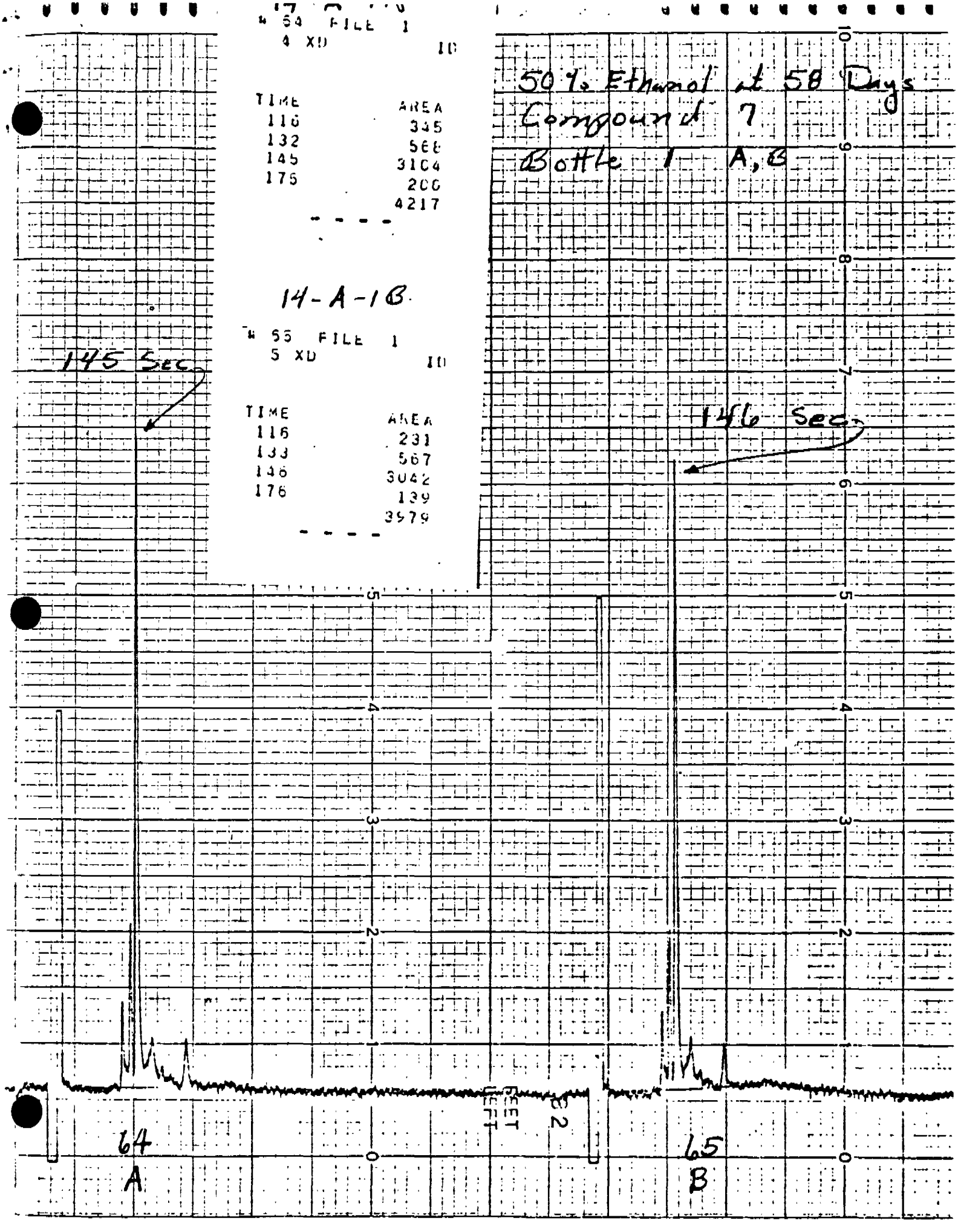
File No.	Retention Time, Sec.
1 - 3	142 - 143*
31 - 33	141 - 142
61 - 63	145 - 146
88 - 90	147

* No. 1 has 136-second retention time. First analysis of a run.

VC4099


50% Ethanol at 58 Da
Compound 1
Bottle 1 A, B
B-A-1A
TIME AREA
112 500
128 387
140 345
148 42
172 297
1571
B-A-1B
TIME AREA
112 510
129 415
140 331
172 273
1537
140 Sec
148 Sec
140 Sec
A
B
FEET LEFT
56


22 XD
10-A-1A
TIME AREA
112 45
128 45
139 35
147 60
172 33
1047
50% Ethanol at 58 Days
Compound 3
Bottle 1 A, B
10-A-1B
23 FILE 1
23 XD
TIME AREA
112 50
128 48
139 34
172 31
1017
139 Sec
147 Sec
139 Sec
22
A
FEET
43
23
B


54 FILE 1
4 XD
ID
TIME AREA
116 345
132 566
145 3104
175 200
4217
14-A-1B
55 FILE 1
5 XD
ID
TIME AREA
116 231
133 567
146 3042
176 139
3979
145 Sec.
146 Sec.
50% Ethanol at 58 Days
Compound 7
Bottle 1 A, B
64
A
65
B
FEET
0
1
2
3
4
5
6
7
8
9
10

34 FILE 1
4 XD IC

11-A-1A

TIME	AREA
112	477
128	493
140	390
172	519
	1879

- - - -

11-A-1B

35 FILE 1
5 XD IL

TIME	AREA
112	464
128	520
140	370
172	446
	1800

- - - -

50% Ethanol at 58 Deg
Compound 4
Bottle 1 A, B

140 Sec

140 Sec

34 A

FEET LEFT 45

35 B

VC4103

112	430
129	491
140	391
172	400
	1712

50% Ethanol at 58 Day
Compound 5
Bottle 1 A, B

12-A-1A

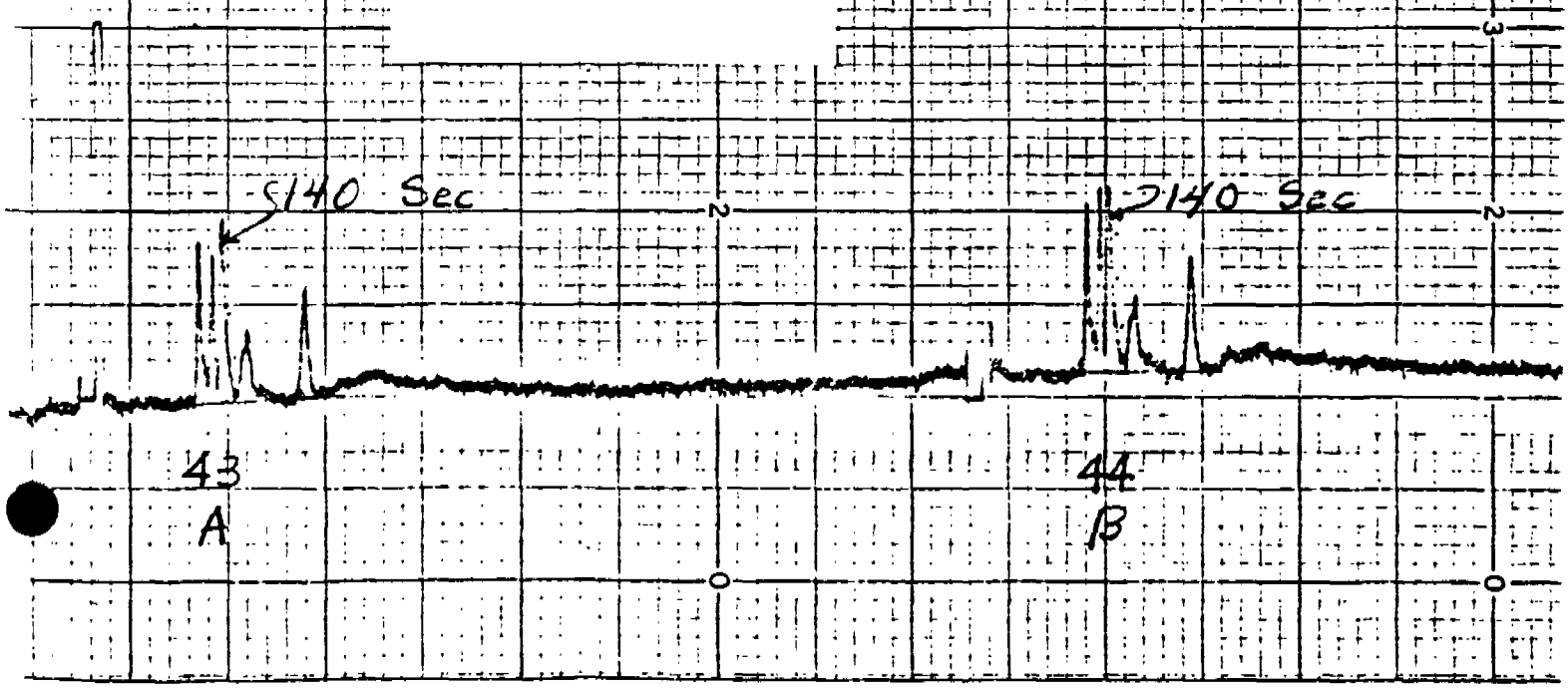
43 FILE 1
13-XD ID

TIME	AREA
112	403
129	304
140	643
172	279
	1624

12-A-1B

44 FILE 1
14 XD ID

TIME	AREA
112	430
129	307
140	618
171	326
	1741



VC4104

TIME	AREA
114	528
131	303
144	681
	1712

13-A-1 A

13-A-1 B

53 FILE 1

23 XD

TIME	AREA
114	340
130	291
144	860
169	29
174	56
	1797

50% Ethanol at 58 D
Compound 6
Bottle 1 A, B

144 Sec

144 Sec.

52
A

53
B

VC4105

64 FILE 1
4 XD 10

TIME	AREA
116	345
132	568
145	3104
175	200
	4217

14-A-16

65 FILE 1
5 XD 10

TIME	AREA
116	231
133	567
146	3042
176	139
	3979

145 Sec.

146 Sec.

50% Ethanol at 58 Days
Compound 7
Bottle 1 A, B