Record #
245976
400-401

Shaughnessy No.: 056502
Date Out of EFGWB: JUN 29 1989

To: H. Toma
Product Manager PM #21
Registration Division (H7505C)

From: Emil Regelman, Supervisory Chemist
Environmental Chemistry Review Section #2
Environmental Fate & Ground Water Branch/EFED (H7507C)

Thru: Henry Jacoby, Acting Chief
Environmental Fate & Ground Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of...

Reg./File # : 000400-401

Chemical Name: PCNB

Type Product : fungicide

Product Name : TERRACLOR

Company Name : Uniroyal Chemical Co.

Purpose : Review photodegradation in water study submitted in response to the 1987 Registration Standard.

Action Code: 660 EFGWB #(s): 90612

Date Received: 5/10/89 Total Reviewing Time: 3 days

Date Completed: 6/27/89

Deferrals to: ___ Ecological Effects Branch

___ Dietary Exposure Branch

___ Non-Dietary Exposure Branch

___ Toxicology Branch I

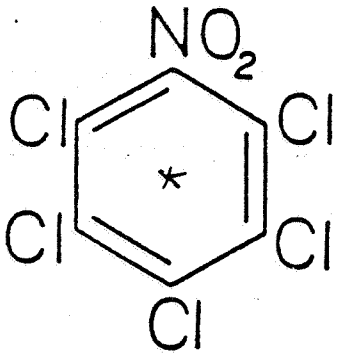
___ Toxicology Branch II

1. CHEMICAL:

chemical name: pentachloronitrobenzene

common name: PCNB

structure:




2. TEST MATERIAL:

$^{14}$C-PCNB, 99.3% pure, specific activity: 8.9 mCi/mmole

3. STUDY/ACTION TYPE:

Review a Photodegradation in Water study submitted in response to the January 1987 PCNB Registration Standard.

4. STUDY IDENTIFICATION:

Bowman, Brian R. "Determination of the Photolysis Rate of $^{14}$C-PCNB in pH 5 Aqueous Solution." Performed by ABC Laboratories for Uniroyal Chemical Company. Received by EPA on May 10, 1989. MRID #410907-01.

5. REVIEWED BY:

Dana Spatz
Chemist, ECRS #2
EFGWB/EFED/OPP

Date: JUN 27 1989

6. APPROVED BY:

Emil Regelman
Supervisory Chemist, ECRS #2
EFGWB/EFED/OPP

Date: JUN 29 1989

7. CONCLUSIONS:

PCNB, exposed to a Xenon Arc light system, photodegrades in water buffered at pH 5 with a half-life of 4 days. By day 7 in the exposed samples, 32% of the $^{14}C$-activity was PCNB and 68% was unidentified material. The dark control degraded with a half-life of 54.6 days. In the sensitized system, half-lives were 0.94 days and 27.4 days for the exposed and dark control, respectively.

This study is unacceptable for fulfilling the data requirements for the following reasons:

a. Degradates were not identified. Although an attempt was made to isolate and identify the degradates using HPLC, the retention times observed did not correlate with any of the known degradates. No attempt was made to identify the volatiles.

b. Recoveries from the gas traps were very poor: 20.7% and 28.1% for the nonsensitized exposed and dark control, respectively.

In addition, it was not specified if the Xenon light source was filtered below 290 nm and storage stability data was not provided. Also, it was stated that "data from sample day 3.72 was not used because of a sampling error." An adequate explanation was not given for eliminating this data, except that the "Q" test was used. The "raw" data were not provided.

It should be noted that on September 21, 1987, EAB agreed to a three month extension for submitting this study. Thus, this study was due to the Agency by February 3, 1988. It was not, however, received until May 10, 1989.

8. RECOMMENDATIONS:

This study must be repeated. EFGWB agrees with ABC Labs, the contract lab that performed the study, that "an attempt to produce sufficient quantity of the unknowns for identification by GC/MS or other techniques be undertaken."

9. BACKGROUND:

The PCNB Registration Standard was sent to Uniroyal in January 1987 and was received by them on February 3, 1987. The Photodegradation in Water study was required by the Registration Standard.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

See attached DER.

11. COMPLETION OF ONE-LINER:

Not applicable.

12. CBI APPENDIX:

Not applicable.

DATA EVALUATION RECORD

CASE GS -- PCNB STUDY 1

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CHEM 056502 PCNB

BRANCH EFGWB

FORMULATION 00 - ACTIVE INGREDIENT

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Bowman, Brian R. "Determination of the Photolysis Rate of $^{14}C$-PCNB in pH 5 Aqueous Solution." Performed by ABC Laboratories for Uniroyal Chemical Company. Received by EPA on May 10, 1989. MRID #410907-01.

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DIRECT RVW TIME = 3

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REVIEWED BY: D. Spatz
TITLE: Chemist
ORG: EFGWB/EFED/OPP

JUN 27 1989

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5

## MATERIALS AND METHODS:

### Preliminary Study

A preliminary study was conducted to determine if compound sorption to the test containers occurred. It was determined, in fact, that $^{14}C$-activity would be lost due to sorption of PCNB to glass. After 96 hours, an average of 10.7% of the applied activity was lost due to sorption to test containers in silanized tubes and 7.9% was lost in the non-silanized containers.

A second preliminary study was conducted with $^{14}C$-PCNB to determine an approximate degradation rate so a sample collection schedule could be set for the definitive study. The estimated photodegradation rate was 0.00916/hours with a half-life of 75.7 hours (3.15 days).

### Definitive Study

Primary stock (1065 ug/ml) $^{14}C$-PCNB was prepared in acetonitrile. Specific activity of the $^{14}C$-PCNB standard was 8.9 mCi/mmole and was 99.3% pure. Analytical grade standards included 2,3,4,5 TCNB, PCA, PCTA, 2,3,5,6-TCNB, HCB and PCB.

A Xenon Arc light system was used to expose the study samples. This system is approximately 1/2 the intensity of the sun so the samples were exposed 24 hours/day; which equaled 12 hours of natural sunlight.

All solutions were prepared using reagent grade chemicals and distilled deionized water, autoclaved for 45 minutes and filtered through a 0.22 micron filter to ensure sterile conditions.

pH of the buffer was measured to be 5.03. The buffer was then autoclaved for 45 minutes at 250$^{o}$F and 15 psi.

The test solutions for the study were prepared by placing a 395 ul aliquot of $^{14}C$-PCNB primary stock solution (1061 ug/ml in acetonitrile) into an Erlenmeyer flask. The test solution solvent was 1385 ml pH-5 buffered water along with 10.4 ml of acetonitrile as a cosolvent.

Acetone (5.25 ml) was added to 700 ml of the test solution as a photosensitizer. The remaining solution was used as the non-sensitized test solution.

Approximately 10 ml aliquots were placed into 40 sterile borosilicate culture tubes. The tubes were filled as completely as possible to minimize head space and reduce interactions with air. 100 ml of the test solutions were placed into 2 sweep bottles for the evaluation of the volatility of $^{14}C$-PCNB.

20 of the samples from each test solution were wrapped in foil, placed in a closed box, then placed in the photolysis chamber.

The sampling schedule was 0, 0.825, 1.73, 2.73, 3.72, 4.72, 5.84, and 6.72 days.

The exposed and dark samples were removed in duplicate and taken for analysis by LSC. Single 100 ul aliquots of the samples were analyzed by HPLC for parent compound concentration.

To evaluate volatility of the test compound and its degradation products, the test solutions were placed in 4 separate gas washing bottles fitted to sweep the solution surface. The four gas traps were ethylene glycol, 1N $H_2SO_4$, 1N KOH, and a second 1N KOH trap. The trapping solutions were changed using the same sample schedule as the collection of test samples. Duplicate 5 ml samples of each trapping solution were assayed for $^{14}C$-activity by LSC.

## REPORTED RESULTS:

Photodegradation of Pentachloronitrobenzene (PCNB)

Non-Sensitized System: Exposed Samples

| Sample Day | DPM/ml | ug/ml as PCNB | Percent as PCNB | ug/ml as PCNB | Percent of Time Zero | Natural log of % of T=0 |
|---|---|---|---|---|---|---|
| 0 | 10840 | 0.162 | 90.8 | 0.147 | 100 | 4.61 |
| 0.825 | 10300 | 0.154 | 92.6 | 0.143 | 96.9 | 4.57 |
| 1.73 | 9240 | 0.138 | 88.6 | 0.123 | 83.2 | 4.42 |
| 2.73 | 9700 | 0.145 | 70.0 | 0.102 | 69.0 | 4.23 |
| 3.72 | * | * | * | * | * | * |
| 4.72 | 9420 | 0.141 | 47.3 | 0.0667 | 45.3 | 3.81 |
| 5.85 | 9780 | 0.146 | 41.0 | 0.0600 | 40.7 | 3.71 |
| 6.72 | 10250 | 0.153 | 32.0 | 0.0491 | 33.3 | 3.51 |

Regression Output:

| | |
|---|---|
| Constant | 4.67 |
| R Squared | 0.989 |
| No. of Observations | 8 |
| Degrees of Freedom | 5 |
| Rate Constant | 0.171 $Day^{-1}$ |
| Half-Life | 4.05 Days ✓ |

*Data not used because of sampling error.

Photodegradation of Pentachloronitrobenzene (PCNB)

Non-Sensitized System: Dark Samples

| Sample Day | DPM/ml | ug/ml as PCNB | Percent as PCNB | ug/ml as PCNB | Percent of Time Zero | Natural log of % of T=0 |
|---|---|---|---|---|---|---|
| 0 | 10840 | 0.162 | 90.8 | 0.147 | 100 | 4.61 |
| 0.825 | 10810 | 0.162 | 100 | 0.162 | 110 | 4.70 |
| 1.73 | 9240 | 0.138 | 78.4 | 0.108 | 73.6 | 4.30 |
| 2.73 | 8850 | 0.132 | 98.6 | 0.131 | 88.7 | 4.48 |
| 3.72 | * | * | * | * | * | * |
| 4.72 | 8580 | 0.128 | 100 | 0.128 | 87.2 | 4.47 |
| 5.85 | 9660 | 0.145 | 100 | 0.145 | 98.1 | 4.59 |
| 6.72 | 8580 | 0.128 | 98.6 | 0.127 | 86.0 | 4.45 |

Regression Output:

| | |
|---|---|
| Constant | 4.56 |
| R Squared | 0.0632 |
| No. of Observations | 7 |
| Degrees of Freedom | 5 |
| Rate Constant | 0.0127 $Day^{-1}$ |
| Half-Life | 54.6 Days |

*Data not used because of sampling error.

Photodegradation of Pentachloronitrobenzene (PCNB)

Sensitized System: Exposed Samples

| Sample Day | DPM/ml | µg/ml as PCNB | Percent as PCNB | µg/ml as PCNB | Percent of Time Zero | Natural log of % of T=0 |
|---|---|---|---|---|---|---|
| 0 | 10980 | 0.164 | 88.5 | 0.145 | 100 | 4.61 |
| 0.825 | 10920 | 0.163 | 89.3 | 0.146 | 100 | 4.61 |
| 1.73 | 10560 | 0.158 | 80.0 | 0.126 | 86.9 | 4.47 |
| 2.73 | 9040 | 0.135 | 68.5 | 0.0927 | 63.7 | 4.15 |
| 3.72 | * | * | * | * | * | * |
| 4.72 | 10180 | 0.152 | nd | nd | nd | nd |
| 5.85 | 9270 | 0.139 | 1.70 | 0.0023 | 1.621746 | 0.484 |
| 6.72 | 10120 | 0.151 | nd | nd | nd | nd |

Regression Output:

| | |
|---|---|
| Constant | 5.30 |
| R Squared | 0.869 |
| No. of Observations | 4 |
| Degrees of Freedom | 2 |
| Rate Constant | 0.735 $Day^{-1}$ |
| Half-Life | 0.94 Days |

nd = none detected.

*Data not used because of sampling error.

Photodegradation of Pentachloronitrobenzene (PCNB)

Sensitized System: Dark Samples

| Sample Day | DPM/ml | µg/ml as PCNB | Percent as PCNB | µg/ml as PCNB | Percent of Time Zero | Natural log of % of T=0 |
|---|---|---|---|---|---|---|
| 0 | 10980 | 0.164 | 88.5 | 0.145 | 100 | 4.61 |
| 0.825 | 11180 | 0.167 | 100 | 0.167 | 115 | 4.75 |
| 1.73 | 8620 | 0.129 | 96.4 | 0.124 | 85.5 | 4.45 |
| 2.73 | 10270 | 0.154 | 97.4 | 0.150 | 103 | 4.63 |
| 3.72 | * | * | * | * | * | * |
| 4.72 | 9000 | 0.135 | 100 | 0.135 | 92.6 | 4.53 |
| 5.85 | 8920 | 0.134 | 98.8 | 0.132 | 90.7 | 4.51 |
| 6.72 | 8540 | 0.128 | 98.8 | 0.126 | 86.8 | 4.46 |

Regression Output:

| | |
|---|---|
| Constant | 4.64 |
| R Squared | 0.372 |
| No. of Observations | 7 |
| Degrees of Freedom | 5 |
| Rate Constant | 0.0253 $Day^{-1}$ |
| Half-Life | 27.4 Days |

*Data not used because of sampling error.

Photodegradation of PCNB Mass Balance Table

| Sensitized System: Exposed Samples | | | Sensitized System: Dark Samples | | |
|---|---|---|---|---|---|
| Sample Day | DPM/ml | Percent of Time Zero | Sample Day | DPM/ml | Percent of Time Zero |
| 0 | 10980 | 100 | 0 | 10980 | 100 |
| 0.825 | 10920 | 99.5 | 0.825 | 11180 | 102 |
| 1.73 | 10560 | 96.2 | 1.73 | 8620 | 78.5 |
| 2.73 | 9040 | 82.3 | 2.73 | 10270 | 93.5 |
| 3.72 | * | * | 3.72 | * | * |
| 4.72 | 10180 | 92.7 | 4.72 | 9000 | 82.0 |
| 5.84 | 9270 | 84.4 | 5.84 | 8920 | 81.2 |
| 6.72 | 10120 | 92.2 | 6.72 | 8540 | 77.8 |
| Mean Accountability | | 92.5 | Mean Accountability | | 87.9 |

*Data not used because of sampling error.

Photodegradation of PCNB Mass Balance Table

| Non-Sensitized System: Exposed Samples | | | Non-Sensitized System: Dark Samples | | |
|---|---|---|---|---|---|
| Sample Day | DPM/ml | Percent of Time Zero | Sample Day | DPM/ml | Percent of Time Zero |
| 0 | 10840 | 100 | 0 | 10840 | 100 |
| 0.825 | 10300 | 95.0 | 0.825 | 10810 | 99.7 |
| 1.73 | 9240 | 85.2 | 1.73 | 9240 | 85.2 |
| 2.73 | 9700 | 89.5 | 2.73 | 8850 | 81.6 |
| 3.72 | * | * | 3.72 | * | * |
| 4.72 | 9420 | 86.9 | 4.72 | 8580 | 79.2 |
| 5.84 | 9780 | 90.2 | 5.84 | 9660 | 89.1 |
| 6.72 | 10250 | 94.4 | 6.72 | 8580 | 79.2 |
| Mean Accountability | | 91.6 | Mean Accountability | | 87.7 |

*Data not used because of sampling error.

Mass Accountability for the Volatile Trapping System[1]

| | Sensitized Exposed | Sensitized Dark | Non-Sensitized Exposed | Non-Sensitized Dark |
|---|---|---|---|---|
| Initial Dose | 15.4 | 15.4 | 16.5 | 16.5 |
| Ethylene Glycol | 0.0107 | 12.2 | 0.0513 | 4.43 |
| $H_2SO_4$ | 0.0122 | 0.0143 | 0.00417 | 0.0137 |
| KOH-1 | 0.402 | 0.0427 | 0.572 | 0.0674 |
| KOH-2 | 0.0680 | 0.0598 | 0.0600 | 0.0581 |
| Activity Remaining in Solution | 0.737 | 0.0763 | 2.42 | 0.0530 |
| Container Rinse | 0.837 | 0.0124 | 0.310 | 0.00521 |
| Sep-Pak Rinse | 0.00109 | 0.000881 | 0.000721 | 0.000256 |
| Total ug Recovered | 2.07 | 12.4 | 3.42 | 4.63 |
| Percent Recovered | 13.4 | 80.5 | 20.7 | 28.1 |

[1]This system is independent of the system used to determine rate constants.

Aqueous Photolysis of PCNB Non-Sensitized Samples

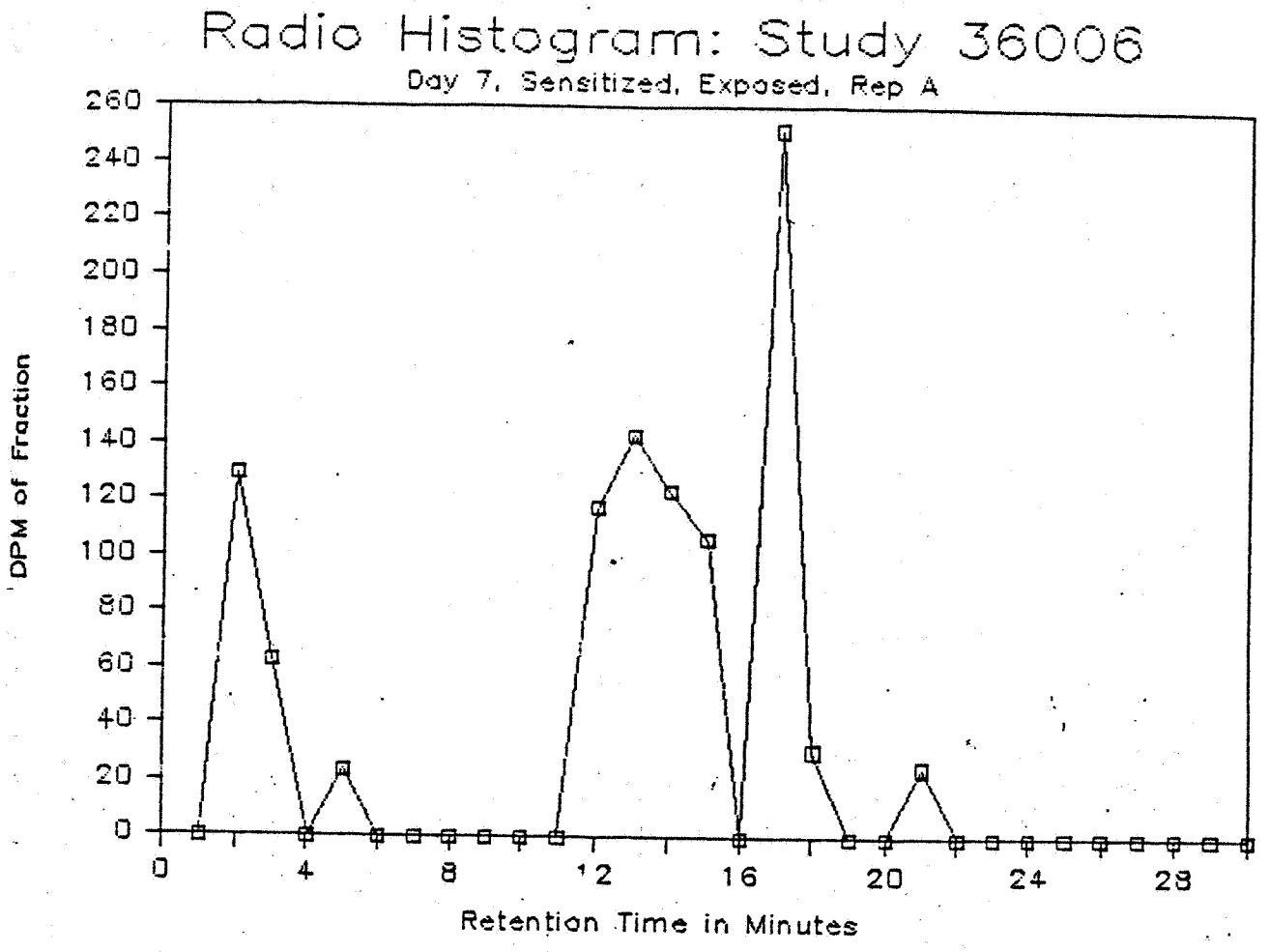
Distribution of $^{14}C$-Activity in the Study Samples Expressed as Percent of Recovered Activity

| Exposed Samples | | | | | |
|---|---|---|---|---|---|
| Sample Day | Zone 1 | Zone 2 | Zone 3 | PCNB | Zone 4 |
| 0 | 0.0 | 3.4 | 1.2 | 90.9 | 2.9 |
| 0.875 | 3.4 | 1.2 | 2.9 | 94.8 | 0.0 |
| 1.73 | 3.6 | 0.0 | 6.5 | 88.7 | 0.0 |
| 2.73 | 22.7 | 2.5 | 2.8 | 69.2 | 3.0 |
| 3.72 | 50.4 | 1.6 | 4.9 | 41.4 | 1.8 |
| 4.72 | 49.5 | 0.0 | 3.3 | 47.3 | 0.0 |
| 5.85 | 57.5 | 1.7 | 0.0 | 41.0 | 0.0 |
| 6.72 | 55.9 | 7.7 | 4.6 | 32.0 | 0.0 |
| Dark Samples | | | | | |
| 0 | 0.0 | 3.4 | 1.2 | 90.9 | 2.9 |
| 0.875 | 0.0 | 0.0 | 0.0 | 100 | 0.0 |
| 1.73 | 20.3 | 0.0 | 1.4 | 78.4 | 0.0 |
| 2.73 | 0.0 | 0.0 | 0.0 | 98.7 | 1.4 |
| 3.72 | 0.0 | 0.0 | 0.0 | 100 | 0.0 |
| 4.72 | 0.0 | 0.0 | 0.0 | 100 | 0.0 |
| 5.85 | 0.0 | 0.0 | 0.0 | 100 | 0.0 |
| 6.72 | 0.0 | 0.0 | 1.4 | 98.6 | 0.0 |

Aqueous Photolysis of PCNB Sensitized Samples

Distribution of $^{14}C$-Activity in the Study Samples Expressed as Percent of Recovered Activity

| Exposed Samples | | | | | |
|---|---|---|---|---|---|
| Sample Day | Zone 1 | Zone 2 | Zone 3 | PCNB | Zone 4 |
| 0 | 1.0 | 1.4 | 2.4 | 88.5 | 5.5 |
| 0.875 | 9.7 | 0.0 | 1.1 | 89.3 | 0.0 |
| 1.73 | 17.1 | 0.0 | 1.3 | 80.0 | 1.6 |
| 2.73 | 22.9 | 3.2 | 4.0 | 68.5 | 1.6 |
| 3.72 | 28.4 | 60.8 | 0.0 | 9.5 | 1.4 |
| 4.72 | 42.6 | 43.7 | 9.6 | 4.3 | 0.0 |
| 5.85 | 34.2 | 57.1 | 7.1 | 1.7 | 0.0 |
| 6.72 | 22.7 | 45.8 | 21.7 | 1.3 | 0.0 |
| Dark Samples | | | | | |
| 0 | 1.0 | 1.4 | 2.4 | 88.5 | 5.5 |
| 0.875 | 0.0 | 0.0 | 0.0 | 100 | 0.0 |
| 1.73 | 0.0 | 2.5 | 1.2 | 96.4 | 0.0 |
| 2.73 | 0.0 | 0.0 | 0.0 | 97.4 | 2.6 |
| 3.72 | 0.0 | 0.0 | 0.0 | 98.2 | 1.8 |
| 4.72 | 0.0 | 0.0 | 0.0 | 100 | 0.0 |
| 5.85 | 0.0 | 0.0 | 0.0 | 98.8 | 1.2 |
| 6.72 | 0.0 | 0.0 | 0.0 | 98.8 | 0.0 |


Radio Histogram: Study 36006
Day 7, Sensitized, Exposed, Rep A
DPM of Fraction
260
240
220
200
180
160
140
120
100
80
60
40
20
0
0
4
8
12
16
20
24
28
Retention Time in Minutes