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TO: Chief Chemists (See Distribution)

FROM: J. W. Born Brecksville R&D Center, D/8506 11/18/82

SUBJECT: Report of Results of the "One-Time" Vinyl Chloride Cross-Check

RETENTION CODE 801-001

PROJECT REPORT

Summary

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During the past two-year cross-check study of vinyl chloride analyses at BFG plants, the BRDC Environmental Laboratory provided the samples for analysis. The Environmental Lab cleaned the Bendix Flasher tubes (PMCC's) and then loaded each with approximately 5 or 10 micrograms of vinyl chloride monomer (VCM). The recoveries of VCM averaged above 90 percent with 95 percent confidence limits of ± 35 percent or better each time. The question arose lately whether results would be as good if we used Flasher tubes which each plant cleaned. We made this study to answer the question.

The average percent recovery was essentially the same for both sets of cleaned tubes. The BRDC-cleaned tubes gave 91 percent average recovery of VCM. The plant-cleaned tubes averaged 92 percent recovery. However, the 95 percent confidence limits were ± 22 percent for the BRDC-cleaned tubes compared with ± 34 percent for the plant-cleaned tubes. Thus, the accuracy of analysis averaged the same. But the precision of measurement was much better for the samples in the BRDC-cleaned Flasher tubes.

Experiment

The Environmental Lab cleaned five Bendix Flasher tubes (PMCC's) for each of the 13 BFG plants named in Table I. The tubes were cleaned by thermal desorption, one by one, in the Bendix Flasher. We repeated the cleaning of each tube until no significant VCM peak appeared in the subsequent GC chromatogram. We then loaded each Flasher tube (PMCC) with approximately 5 micrograms of VCM. The loadings involved flowing a standard commercial 10.0 ppm VCM-air mixture through each tube for 4.0 minutes at about 49 cc per minute. We mailed five Flasher tubes to each plant for GC analysis. The plant labs reported the analytical results shown in Appendices A and B and Table I.

The Environmental Lab also asked eight of the labs to clean five Flasher tubes per plant in the usual way and send them to us. We loaded them with approximately the same amount of VCM and in the same way as before without further cleaning. The five loaded tubes were returned to the plant lab for analysis in each case. Appendix B and Table I give the results.

The Plaquemine plant customarily uses SKC charcoal tubes instead of Flasher tubes. We loaded five SKC tubes for the Plaquemine plant and five more for the Brecksville Research & Development Center. They were loaded just as the Flasher tubes were. The two labs analyzed the samples. Their results appear in Table II.

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TABLE I

A Summary of the Analytical Results of the Cross-Check

<u>Identification of Plant</u>	<u>Percent Recovery of VCM</u>	
	<u>BRDC-Cleaned Tubes</u>	<u>Plant-Cleaned Tubes</u>
Avon Lake General Chemical Plant	79.2 ($\sigma = 8.5$)	67.2 ($\sigma = 6.2$)
Avon Lake Technical Center	88.3 ($\sigma = 5.9$)	---
Brecksville R&D Center	115.0 ($\sigma = 9.2$)	---
Calvert City	98.4 ($\sigma = 10.8$)	124.0 ($\sigma = 18.3$)
Deer Park	93.4 ($\sigma = 1.9$)	94.3 ($\sigma = 14.6$)
Henry	89.6 ($\sigma = 10.4$)	89.2 ($\sigma = 5.8$)
La Porte	93.1 ($\sigma = 18.2$)	108.0 ($\sigma = 15.8$)
Long Beach	93.7 ($\sigma = 3.7$)	86.8 ($\sigma = 1.7$)
Louisville	72.0 ($\sigma = 3.7$)	80.9 ($\sigma = 2.3$)
Niagara Falls	99.1 ($\sigma = 1.8$)	---
Pedricktown	91.2 ($\sigma = 1.5$)	---
Plaquemine	81.2 ($\sigma = 8.5$)	---
Shawinigan	162.0 ($\sigma = 11.1$) ^a	---
Overall Results:	91.2 ($\sigma = 11.0$)	92.5 ($\sigma = 17.2$)

^a This value is a statistical "outlier" according to the Table of Critical Values for T(One-Sided Test). As such, this value was omitted in computing the overall result.

The first group of 75 samples was sent on October 1, 1982. We mailed the second group of 40 samples on October 15, 1982. The last plant report reached the Environmental Lab on November 5, 1982. The dates on which the labs analyzed the samples and the elapsed times appear in Appendix C.

Results

NIOSH advises that analyses of gas concentrations in air should have 95 percent confidence limits of ± 35 percent of the true value between 0.5 TLV and 1.0 TLV and ± 50 percent below 0.5 TLV. For VCM in air, 0.5 ppm equals 1.28 mg per cubic meter (at 25°C and 760 mm Hg). Six hours' sampling at 10.0 cc per minute gives a sample volume of 0.0036 m³. On that basis 100 percent recovery at 0.5 ppm would give a 4.6 μ g VCM sample. Thus, measurements of 4.6 μ g to 9.6 μ g VCM per charcoal tube should have 95 percent confidence limits of ± 35 percent of the true value. In this study we define "true value" as the weight of VCM loaded per tube. Measurements below 4.6 μ g per tube should have 95 percent confidence limits of ± 50 percent of the true value. In this study the 95 percent confidence limits are $\pm 2 \sigma$ (twice the standard deviation for the set of measurements). Only two sets of measurements in Table I exceed the 95 percent confidence limits of ± 35 percent of the true value. The Calvert City value of 149 percent recovery (Appendix B) accounts for the one case. In the Shawinigan case all five values

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TABLE II

A Two-Plant VCM Cross-Check Using SKC Charcoal Tubes

Identification of Plant Sample	Weight (μ g) of VCM per SKC Tube		Percent Recovery
	Recovered	Loaded	
Plaquemine:			
1	2.92	5.30	55.1
2	3.05	5.39	56.6
3	2.74	5.53	49.5
4	3.12	5.69	54.8
5	2.12	5.30	40.0 ^a
Average:			51.2 (σ = 6.8)
Brecksville R&D Center:			
1	--- ^b	4.84	---
2	5.68	4.42	128.
3	8.04	5.12	157. ^a
4	6.51	5.16	126.
5	7.53	6.14	128.
Average:			134.0 (σ = 15.8)

^a Although this value appears to be quite different from the other values in the set, it is not an "outlier" according to the Table of Critical Values for T(One-Sided Test).

^b The sample was spilled during preparation for analysis.

in the set exceed the +35 percent limit. While a single value beyond the limits in a set is not disturbing, having all five values beyond calls for investigating the cause. Figure 1 presents a graphic comparison of the results in Table I.

The overall average VCM recoveries were 91.2 percent for the BRDC-cleaned Flasher tube samples and 92.5 percent for the plant-cleaned Flasher tube samples. See Table I. The overall standard deviations were 11.0 percent in the former study and 17.2 percent in the latter study. These standard deviations represent 95 percent confidence limits of ± 22 percent and ± 34 percent the true values, respectively. Thus, in both studies the overall results were in compliance.

The results of the SKC tube study were both surprising and disappointing. The BRDC average recovery of 134 percent barely complied with the NIOSH limit of ± 35 percent of the true value for 95 percent confidence. See Table II. Again, an investigation of the cause for the high BRDC values is indicated. All five of the Plaquemine values did not meet the NIOSH requirement.

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There are at least four possible causes for recoveries very much above 100 percent. One is inaccurate loading of the sample tubes. A second is incomplete cleaning of the Flasher tubes before loading. A third is poor integration of the area under the VCM peak in the GC curve. And a fourth possible cause is assignment of the wrong retention time to the VCM adsorption peak.

The data in Appendix A and Table I indicate that the VCM loading of the tubes was accurate. Also, the tubes were loaded in the order shown in Appendix A. But the selection of the five samples for each plant was spread throughout the entire series at random. Thus, if there had been inaccuracies in loading the Shawinigan Flasher tubes, the data in Appendix B would have shown numerous other very high percent recoveries.

Incomplete cleaning of the Flasher tubes can cause one or both of two problems in analysis. Tailing of adjacent GC peaks can add to the net area under the VCM peak. Also, incomplete cleaning of the Flasher tube can lead to interference of contaminant GC peaks with the VCM peak.

Third, a contaminant peak can merge with the VCM peak to give poor resolution and poor integration.

Fourth, aging can cause migration of the adsorbed VCM throughout the charcoal bed of the Flasher tube. A significant change in VCM retention time can result. Failure to recognize the time shift can lead to selection of the wrong peak. Refrigeration of the Flasher tubes until analysis retards the VCM migration.

Conclusions

The loading of all the Flasher tubes with VCM was accurate. Except for only the Shawinigan results, all percent recoveries and standard deviations met the NIOSH requirements. The percent recoveries in this "one-time" study are consistent with the quarterly results of the two-year VCM cross-checks. With the exception of Calvert City, all plants cleaned their Flasher tubes well before the VCM loading occurred. The Shawinigan plant needs to determine why its analyses gave such consistently high results. The Niagara Falls lab deserves praise for its 99.1 percent average recovery with a standard deviation of only 1.8 percent. Those results show that it can be done.

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Recommendations

1. All BFG plants should periodically, at least once a year, make sure that their analyses of Flasher tube samples meet NIOSH requirements.
2. The Shawinigan lab should compare its analytical procedure with the Niagara Falls procedure in detail to improve its performance.
3. The BRDC lab should study the Niagara Falls procedure in an effort to avoid high percent VCM recoveries.

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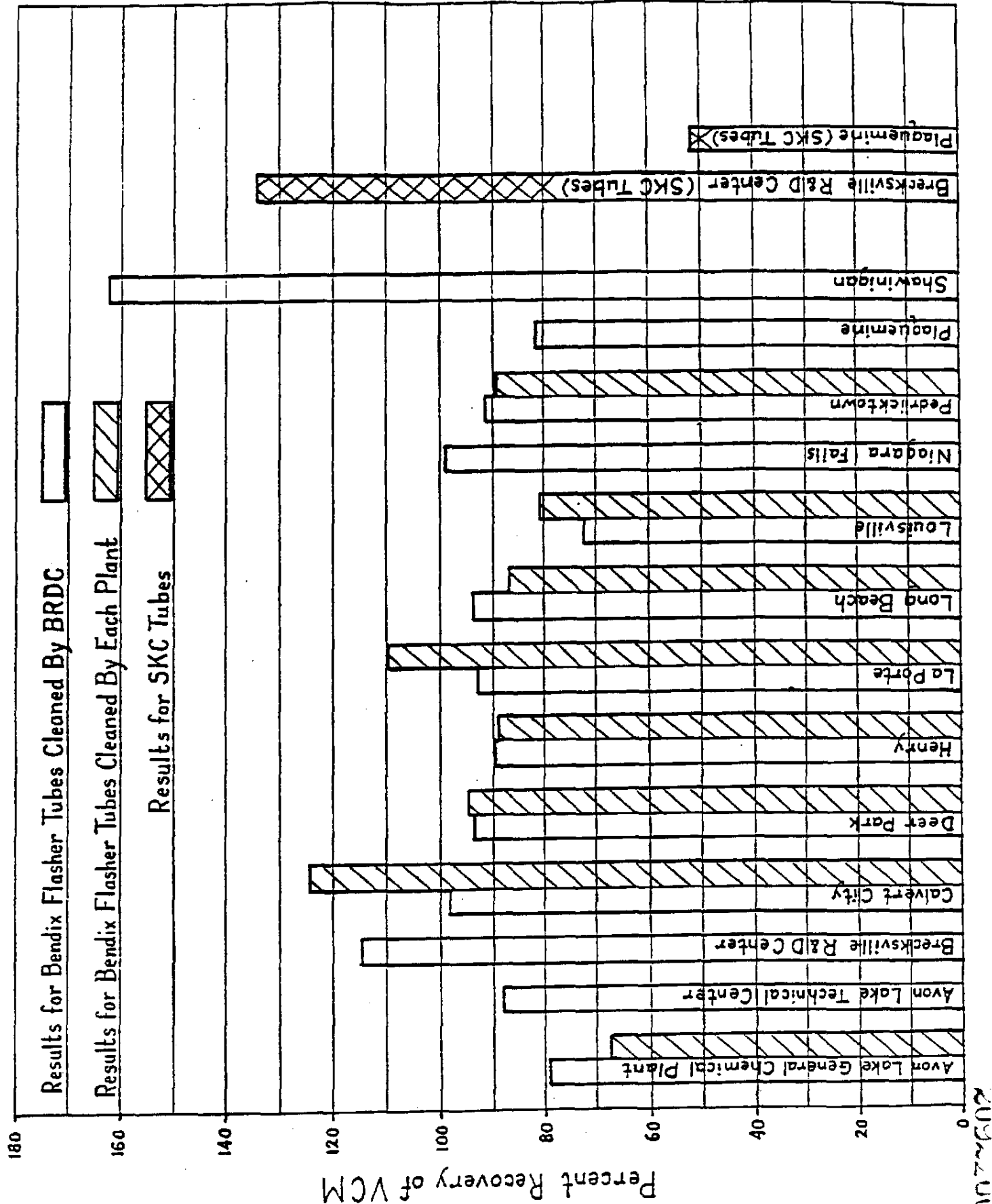
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FIGURE 1. Average Results of the "One-Time" VCM Cross-Check



APPENDIX A

Analytical Results for VCM Samples
in BRDC-Cleaned Tubes

<u>Identification of Samples</u>	<u>Weight of VCM (µg) per Flasher Tube</u>		<u>Percent Recovery</u>
	<u>Loaded</u>	<u>Recovered</u>	
C-1	5.16	4.96	96.1
C-2	4.92	4.74	96.3
C-3	5.91	5.20	88.0
C-4	4.69	5.60	119.
C-5	5.59	6.15	110.
C-6	5.48	3.71	67.7 ^a
C-7	5.96	5.11	85.7
C-8	5.04	1.87	37.1 ^a
C-9	5.59	4.00	71.6
C-10	5.25	4.50	85.7
C-11	5.69	3.81	67.0
C-12	6.02	5.66	94.0
C-14	6.27	7.26	116.
C-16	4.88	3.79	77.7
C-17	4.62	4.91	106.
C-19	5.25	4.44	84.6
C-21	5.49	4.78	87.1
C-23	5.74	4.89	85.2
C-24	5.74	5.73	99.8
C-25	5.39	5.03	93.3
C-26	4.88	2.63	53.9 ^a
C-27	4.88	3.48	71.3
C-28	5.25	4.55	86.7
C-30	4.39	4.12	93.8
C-31	4.88	4.83	99.0
C-32	5.00	4.65	93.0
C-35	5.12	4.65	90.8
C-36	5.59	4.57	81.8
C-38	5.00	3.48	69.6
C-39	6.21	6.20	99.8
C-41	6.08	4.14	68.1
C-42	5.44	6.83	126.
C-43	4.88	4.45	91.2
C-45	4.69	3.98	84.9
C-47	5.39	5.68	105.
C-49	5.49	5.35	97.4
C-50	5.39	4.48	83.1
C-51	5.12	4.77	93.2
C-52	5.30	5.37	101.
C-53	5.39	5.90	109.
C-54	5.08	4.82	94.9
C-55	5.34	4.96	92.9
C-57	5.74	3.96	69.0
C-59	5.30	5.83	110.

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APPENDIX A (Continued)

Identification of Samples	Weight of VCM (μ g) per Flasher Tube		Percent Recovery
	Loaded	Recovered	
C-60	4.92	4.85	98.6
C-61	5.00	4.83	96.6
C-62	4.88	4.49	92.0
C-64	5.08	4.21	82.9
C-68	5.49	6.11	111.
C-70	5.91	4.30	72.8
C-72	5.91	5.45	92.2
C-74	5.49	8.16	149.0 ^a
C-75	6.14	9.36	152.
C-78	6.40	5.53	86.4
C-79	5.69	4.48	78.7
C-80	5.30	8.78	166.
C-81	5.00	8.69	174.
C-83	4.84	5.71	118.
C-87	4.76	8.10	170.
C-89	5.59	4.40	78.7
C-100	5.85	5.39	92.1
C-101	5.96	5.52	92.6
C-102	4.92	4.48	91.1
C-103	5.30	4.21	79.4 ^a
C-104	5.49	3.84	69.9
C-146	6.02	5.37	89.2

^a This value is a statistical "outlier according to the Table of Critical Values for T(One-Sided Test).

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APPENDIX B

Results of Analyses of VCM Samples Collected in PMCC's

A.) Results for BRDC-Cleaned PMCC's:

<u>Identification of Plant</u>	<u>Weight (µg) of VCM per PMCC</u>		<u>Percent Recovery</u>
	<u>Recovered</u>	<u>Loaded</u>	
Avon Lake General Chemical	5.11	5.96	85.7
	4.78	5.49	87.1
	3.48	4.88	71.3
	4.48	5.39	83.1
	3.96	5.74	69.0
Avon Lake Technical Center	1.87 ^a	5.04	37.1 ^a
	4.89	5.74	85.2
	4.57	5.59	81.8
	4.45	4.88	91.2
	4.82	5.08	94.9
Calvert City	3.71 ^a	5.48	67.7 ^a
	4.91	4.62	106.
	4.55	5.25	86.7
	5.90	5.39	109.
	4.49	4.88	92.0
Deer Park	4.96	5.16	96.1
	5.66	6.02	94.0
	4.65	5.12	90.8
	4.77	5.12	93.2
	4.96	5.34	92.9
Henry	4.50	5.25	85.7
	4.44	5.25	84.5
	2.63 ^a	4.88	53.9 ^a
	5.68	5.39	105.
	4.21	5.08	82.9
La Porte	6.15	5.59	110.
	3.81	5.69	67.0
	4.12	4.39	93.8
	3.98	4.69	84.9
	5.83	5.30	110.0
Long Beach	5.20	5.91	88.0
	5.03	5.39	93.3
	4.65	5.00	93.0
	5.35	5.49	97.4
	4.83	5.00	96.6

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APPENDIX B (Continued)

<u>Identification of Plant</u>	<u>Weight (μg) of VCM per PMCC</u>		<u>Percent Recovery</u>
	<u>Recovered</u>	<u>Loaded</u>	
Louisville	4.00	5.59	71.6
	3.79	4.88	77.7
	3.48	5.00	69.6
	4.14	6.08	68.1
	4.30	5.91	72.8
Niagara Falls	4.74	4.92	96.3
	5.73	5.74	99.8
	6.20	6.21	99.8
	5.37	5.30	101.
	4.85	4.92	98.6
Pedricktown	5.39	5.85	92.1
	5.52	5.96	92.6
	4.48	4.92	91.1
	4.21 ^a	5.30	79.4 ^a
	5.37	6.02	89.2
Plaquemine	5.45	5.91	92.2
	5.53	6.40	86.4
	4.48	5.69	78.7
	4.40	5.59	78.7
	3.84	5.49	69.9
Shawinigan	8.16	5.49	149.
	9.36	6.14	152.
	8.78	5.30	166.
	8.69	5.00	174.
	8.10	4.76	170.
Brecksville R & D Center	5.60	4.60	119.
	7.26	6.27	116.
	4.83	4.88	99.0
	6.83	5.44	126.
	6.11	5.49	111.
	5.71	4.84	118.

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APPENDIX B (Continued)

B.) Results for Plant-Cleaned PMCC's:

<u>Identification of Sample</u>		<u>Weight (μg) of VCM per PMCC</u>		<u>Percent Recovery</u>
		<u>Recovered</u>	<u>Loaded</u>	
ALGCP	1	5.25	4.08	77.7
	2	5.12	3.39	66.2
	3	5.12	3.22	62.9
	4	5.59	3.73	66.7
	5	5.91	3.69	62.4
Calvert City	1	4.95	5.22	105.
	2	5.49	8.16	149 _b
	3	5.74	---	---
	4	6.14	7.41	121.
	5	6.47	7.86	121.
Deer Park	1	4.88	5.73	117.
	2	4.88	4.60	94.3
	3	4.92	4.01	81.5
	4	5.25	4.28	81.5
	5	5.69	5.53	97.2
Henry	1	5.74	4.70	81.9
	2	5.34	4.85	90.8
	3	5.64	4.77	84.6
	4	5.30	4.90	92.5
	5	5.00	4.81	96.2
La Porte	1	5.00	5.19	104.
	2	4.73	5.11	108.
	3	5.25	5.41	103. ^a
	4	5.25	7.04 ^a	134. ^a
	5	5.34	4.87	91.2
Long Beach	1	5.69	4.82	84.7
	2	5.54	4.78	86.3
	3	5.44	4.71	86.6
	4	5.34	4.64	86.9
	5	5.34	4.78	89.5
Louisville	1	6.01	4.78	79.5
	2	4.95	4.03	81.4
	3	5.04	3.97	78.8
	4	5.21	3.58 ^a	68.7 ^a
	5	5.25	4.41	84.0

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APPENDIX B (Continued)

		Weight (μ g) of VCM per PMCC		
<u>Identification of Sample</u>		<u>Recovered</u>	<u>Percent Loaded</u>	<u>Recovery</u>
Pedricktown	1	5.80	5.23	90.2
	2	5.64	5.28	93.6
	3	5.54	5.34	96.4
	4	5.39	5.03	85.4
	5	5.85	4.83	82.6

^a This value is a statistical "outlier" according to the Table of Critical Values for T(One-Sided Test).

^b The sample was lost during the thermal flashing step.

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APPENDIX C

Elapsed Time Between the VCM Loading and Analysis of the Samples

<u>Identification of Plant</u>	<u>Dates on Which the Samples Were--</u>		<u>Elapsed Time (Days)</u>
	<u>Loaded</u>	<u>Analyzed</u>	
Avon Lake General Chemical Plant	09/28/82	10/09/82	11
Avon Lake Technical Center		10/05/82	7
Brecksville R&D Center		10/05/82	7
Calvert City		10/26/82	28
Deer Park		10/12/82	14
Henry		10/13/82	15
La Porte		10/19/82	21
Long Beach		11/03/82	36
Louisville		10/13/82	15
Niagara Falls		10/19/82	21
Pedricktown		10/13/82	15
Plaquemine		10/20/82	22
Shawinigan	09/28/82	10/21/82	23
Avon Lake General Chemical Plant	10/14/82	10/19/82	5
Calvert City		10/27/82	13
Deer Park		10/27/82	13
Henry		10/19/82	5
La Porte		10/19/82	5
Long Beach		11/03/82	20
Louisville		10/21/82	7
Pedricktown	10/14/82	10/18/82	4

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