WGK ANALYTICAL RESEARCH AND DEVELOPMENT REPORT No. 2161, June 16, 1972

OTHER LOCATIONS	GENERAL OFFICE	W. G. KRUMMRICH PLANT
		E. E. Stewart A. E. Leisy W. C. Engman G. A. Hippe File

COMPANY CONFIDENTIAL

TITLE:

PCB Reduction in Tank Car Wash Water - Dept. 246

PERSONNEL:

J. A. Gloeckner, K. L. Schutzenhofer (H. J. Horner)

PROBLEM:

Decanted aroclor tank car wash water contains PCB's in the ppm range, whereas solubility is believed to be about 300 ppb. A procedure must be devised to remove more PCB's from the wash water before sewering.

JUSTIFICATION:

Permit eventual control of PCB content in the sewer stream from the plant to 0.5 #/day.

SUMMARY:

Based on laboratory tests performed to date, it appears that the most effective procedure for removal of PCB's from the wash water is filtration with either lime or carbon.

K. L. Schutzenhofer

J. A. Gloeckner

dy

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WGK 277

DSW 345180

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Discussion of Results

The sample used for Tests #1 - #10 was thoroughly mixed before obtaining portions for each test. The sample solution was allowed to settle for two hours, after treatment, before decanting in the tests as indicated. The filter paper used in each test as indicated was 1-3 micron, glass fiber paper.

The sample used for test #11 was a turbid, light green-brown liquid with brown residue on the bottom and also floating on top. A portion of this sample was taken for analysis from the middle of the sample in an effort to exclude the residue.

Conclusions

A comparison of the as is analyses of the sample taken from the catch tank and the sample taken directly from the tank car is not a good one because the catch tank sample was thoroughly mixed and the tank car sample was allowed to settle before analyzing. It appears that the PCB content is directly proportional to the amount of solids present in the sample portions used for analysis.

The only decanting procedure that shows any promise is that made after lime treatment. Comparable results could probably have been achieved with carbon, also. Decanting procedures will require some settling time.

Reference

WGK Research Notebook, pp. 16026-16029, 16032-16033.

DSW 345181

STLCOPCB4083963

Details

Background

Facilities were installed at the Rip Track to permit the continuous decanting of wash water as part of the aroclor tank car washing procedure. It was hoped that after settling, the decanted wash water would oontain polychlorinated biphenyls at approximately the 300 ppb level. However, the sewered water has been found to contain PCB's in the ppm range.

The tank cars are ~~wash~~ washed with H_2O only. This water is collected in a catch tank that may contain residual detergent solutions from washes of other types of tank cars. The aroclor car washes are passed from this catch tank to a 6000 gallon settling tank. After a settling period the wash water is decanted from the top of the trailer. It is thought that an emulsion might be forming in the wash water, accounting for amounts above the 300 ppb level in the decanted water.

Procedure

A one gallon sample of aroclor wash water was taken from the catch tank. This material was tested for demulsifying and filtration.

Results

This sample was a turbid, yellow liquid with some residue on the bottom. The pH of the sample was 7.6.

Test No.	PCB's (ppm)	Type of Test
1	54.48	Sample as is (after mixing).
2	0.726	Mixed with filter aid and filtered thru filter paper.
3	1.58	Filtered thru filter paper, only.
4	0.007	Carbon treated and filtered thru filter paper.
5	0.074	NaCl treated and filtered thru filter paper.
6	22.93	NaCl treated and decanted. DSW 345182
7	0.466	CaO treated and decanted.
8	18.23	Acetone treated and decanted.
9	3.24	Filtered thru polypropylene bag filter, only (5-micron).
10	8.25	$AlCl_3$ treated and decanted.
11	2.82	New wash water sample taken directly from a tank car. This sample was allowed to settle and then decanted for analysis.

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FROM (NAME & LOCATION) K. L. Schutzenhofer - WGK

DATE March 25, 1974

SUBJECT PCB Analysis of Water Scrubber Samples

REFERENCE

TO : K. E. Boucher

CC L. H. Horcher
C. F. Buckley
G. A. Hippe
H. J. Horner

The following results were obtained on the analysis of the samples, as listed, for PCB content.

Bottle No.	Sample Time	PCB's (ppm)
1	3/20/74, 12.25 pm, 0 min.	44.6
4	' , 12.45 pm, 20 min.	8.92
6	' , 1.05 pm, 40 min.	3.73
7	' , 1.25 pm, 60 min.	2.75
9	' , 1.45 pm, 80 min.	3.11
10	' , 1.45 pm, 80 min.	20.2
11	' , 2.05 pm, 100 min.	3.87
14	' , 2.25 pm, 120 min.	2.96
16	' , 2.45 pm, 140 min.	1.73
17	' , 3.05 pm, 160 min.	3.05
19	' , 3.25 pm, 180 min.	1.61

The above results were obtained by WGK Method No. S-005, utilizing the Cary Spectrophotometer, and do not include 1109 aroclor content.

Reference. WGK Laboratory Notebook, pp.17871-72.

K. L. Schutzenhofer

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DSW 345183

IN - 10 REV. 1-72

STLCOPCB4083965

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FROM (NAME & LOCATION) K. L. Schutzenhofer

DATE March 19, 1974

SUBJECT PCB Analysis of Water Scrubber Samples

REFERENCE

cc C. F. Buckley
G. A. Hippe
H. J. Horner

TO : K. E. Boucher

The following results were obtained on the analysis of the samples, as listed, for PCB content.

Bottle No.	Sample Time	PCB's (ppm)
1	3/12/74,12.30 p.m. 0 min.	1.77
3	3/12/74, 12.45 p.m.,15 min.	0.85
6	3/12/74, 1.00 p.m.,30 min.	0.40
8	3/12/74, 1.15 p.m.,45 min.	1.06
9	3/12/74, 1.30 p.m,60 min.	0.69
11	3/12/74, 1.45 p.m.,75 min.	1.21
13	3/12/74,2.00 p.m.,90 min.	0.61
15	3/12/74, 2.15 p.m.,105 min.	0.67
18	3/12/74, 2.30 p.m.,120 min.	0.55

Ref. WGK Laboratory Notebook pp.17868-69.

K. L. Schutzenhofer

K. L. Schutzenhofer

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DSW 345184

IN - 10 REV. 1 72

STLCOPCB4083966

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FROM (NAME & LOCATION): K. L. Schutzenhofer

DATE: February 25, 1974

SUBJECT: PCB Analysis of Scrubber Water Samples

REFERENCE:

cc: C. F. Buckley
G. A. Hippe
H. J. Horner

TO: K. E. Boucher

The following results were obtained on the analysis of the samples, as listed, for PCB content.

	Sample Identification	PCB's (ppm)
1.	2/11/74, 12:10 p.m. Continuous Chlorinator-75%, no batch chlorinators	1.62
2.	2/11/74, 3:45 p.m. Continuous chlorinator - 65%, one batch chlorinator	12.7
3.	2/12/74, 4:15 a.m. Continuous chlorinator -75%, two batch chlorinators	4.00
4.	2/12/74, 8:00 a.m. Continuous chlorinator - 70%, no batch chlorinators	0.67
5.	2/13/74, 8:00 a.m. Continuous chlorinator - 75%, no batch chlorinators	0.87
6.	2/14/74, 9:00 a.m. Continuous chlorinator - 75%, one batch chlorinator	0.67
7.	2/14/74, 4:30 p.m. Biphenyl feed - unknown, no batch chlorinators	0.68
8.	2/15/74, 7:45 a.m. Biphenyl feed- unknown, batch chlorinators unknown	0.65
9.	2/15/74, 4:30 p.m. Biphenyl feed - 75%, no batch chlorinators	1.35

Reference: WGK Lab Notebook pp 17853-54.

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FROM (NAME & LOCATION) K. L. Schutzenhofer - WGK

DATE April 4, 1974

cc C. F. Buckley
G. A. Hippe
H. J. Horner

SUBJECT PCB Analysis of water Scrubber Samples

REFERENCE

TO : K. E. Boucher

The following results were obtained on the analysis of the samples, as listed, for PCB content. The results were obtained by WGK Method S-Q05, utilizing the Cary Spectrophotometer.

Set No. 4 (3/29/74 samples)

Bottle No.	Sample Time	PCB's (ppm)
0	before start-up	1.31
2	1.00 pm, 0 min.	12.2
4	1.15 pm, 15 min.	5.88
6	1.30 pm, 30 min.	3.45
7	1.45 pm, 45 min.	5.13
10	2.00 pm,60 min.	3.68
12	2.15 pm, 75 min	3.16
14	2.30 pm, 90 min.	1.68
16	2.45 pm, 105 min.	1.40
17	3.00 pm, 120 min.	0.84

Set No. 5 (4/2/74 samples)

Bottle No.	Sample Time	PCB's (ppm)
1	11.00 am, 0 min.	2.47
3	11.15 am, 15 min.	2.42
5	11.30 am, 30 min	2.37
7	11.45 am, 45 min.	2.19
9	12.00 noon, 60 min.	1.96
11	12.15 pm, 75 min.	1.66
13	12.30 pm, 90 min.	1.48
15	12.45 pm, 105 min.	1.47
18	1.00 pm, 120 min.	1.56

Reference. WGK Laboratory Notebook, pp.17879-82

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WGK ANALYTICAL RESEARCH AND DEVELOPMENT REPORT No. 2450, 4/24/74

OTHER LOCATIONS	GENERAL OFFICE	W. G. KRUMMRICH PLANT
	J. R. Savage - B2SL	K. E. Boucher W. C. Engman G. A. Hippe A. E. Leisy E. E. Stewart D. K. Lynch R. M. McCutchan J. R. Kuster File

COMPANY CONFIDENTIAL

TITLE: Dept. 246 - Aroclors. Start-up of HCl Off-Gas Scrubber

PERSONNEL:

PROBLEM: K. L. Schutzenhofer, L. H. Horcher (H. J. Horner)

JUSTIFICATION: The off-gas must be analyzed for PCB's to determine the efficiency, and the life of the scrubbing material. Methods of analysis must be developed and samples analyzed to facilitate start-up of this equipment.

For environmental reasons, the PCB losses to our sewers must be drastically reduced or eliminated.

SUMMARY:

A fifteen tray Aroclor scrubber was started up at the end of February using MCS 1016 bottoms to remove Biphenyl and PCB's from the off-gas before sewering or going to chlorosulfonic acid production. We developed a procedure and analyzed the scrubber liquor daily. The gas itself was not analyzed but the water used to drown the HCl gas was analyzed using both a routine GC procedure and a new ultra-violet method recently developed for another product.

References. WGK Notebook 17853-54, 17868-69, 17871-73, 17879-82, 17884-85, 18201-17, 18221, 18231-32.

L. H. Horcher

dy

DSW 345187

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Details

Background

The scrubber is based on work done by N. Thompson in the summer of 1972 to reduce the loss of PCB's in HCl off-gas to less than 2.5 lbs/day. A fifteen tray scrubber was designed on this basis using MCS 1016 bottoms as the scrubbing liquor. In order to start-up this equipment, a procedure to determine the mono- and lower dichlorobiphenyl build up in this liquor is required. The amount of PCB's in the gas after scrubbing also needs to be known.

Method Development

Scrubber Liquor

A procedure used to determine the higher boiling homologs in MCS 1016 was modified to analyze both the low boilers in MCS 1016 Bottoms, the Biphenyl, and PCB's scrubbed out of the gas by the liquor. The initial procedure using normal C_{18} as the internal standard required about ninety minutes per analysis. After the installation of a backflush valve, since we are interested in the low boilers, the analytical turnaround time was reduced to 45 minutes. An additional bonus is that reversal of gas flows should increase the life of a rather expensive column. The procedure is published as WGK Method No. T-2320 and is in routine use by the analytical section.

Data is attached in Appendix A.

HCl Drowning Water

An ultra-violet method (Method No. S-0055) developed for total PCB content in cooling water was used to analyze a series of water samples taken during the drowning of the HCl off-gas. This was to determine the efficiency of the scrubber (PCB losses to sewer in the gas). Data has been published in memos dated Feb. 25, Mar. 19, 25 and April 4, 1974 to K. E. Boucher from K. L. Schutzenhofer. We also used Method No. A-1009 to determine the type and amount of PCB's. Data is attached in Appendix B.

The above work allowed us to determine the mono-chlorinated and poly-chlorinated biphenyls but it gave us no information of the amount of biphenyl going to the sewer. A further concentration procedure of the extracts made for the other analyses was done and analyzed on a FID instrument. Our biphenyl levels ranged from 5 to 50 ppb but our total MCS 1109 from the FID analysis was lower than that by EC analysis. It is possible that the EC values are high due to resolution problems or the FID values are low due to losses occurring in the vigorous concentration techniques used.

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Conclusions

We were able to successfully monitor the start-up parameters without any undue delays. Procedures in standard form were published and the analytical personnel have been trained to use them on a routine basis. The scrubber liquor life is greater than the expected 7 to 10 days and the average losses to the sewer are at the level targeted by design. We, however, found the rate of build-up of biphenyl and mono-chlorobiphenyls was erratic and a better measure of scrubber life was the combined increase of the three dichloro-biphenyls. Evidently a trace of chlorine gas in the scrubber chlorinates to some extent the absorbed biphenyl and mono-chlorobiphenyls. The $FeCl_3$ level ranged from 0.017% after 24 hrs. to 0.045% and 0.065% after 2 and 3 weeks respectively.

L. H. Horcher

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DSW 345189

Scrubber Liquor Analysis

Date	BiØ %	oClBiØ %	mClBiØ %	pClBiØ %	mono-ClBiØ %	Di-ClBiØ (1) %
2/27	0.005	-	-	-	0.025	-
2/28						
8.00 am	0.028	-	-	-	0.170	-
6.00 pm	0.010	-	-	-	0.221	-
12 Mid.	0.005	-	-	-	0.217	-
3/6	0.010	0.240	<0.100	0.020	0.260	-
8	0.033	0.323	<0.001	0.071	0.394	-
9	0.026	0.367	0.003	0.084	0.454	0.388
10	0.021	0.308	0.002	0.066	0.376	0.442
11	0.032	0.281	0.004	0.060	0.345	0.395
12	0.015	0.303	<0.001	0.057	0.360	0.458
13	0.018	0.315	<0.001	0.048	0.363	0.543
14	0.016	0.214	0.003	0.047	0.264	0.311
15						
16	0.004	0.243	<0.001	0.030	0.273	0.381
17	0.007	0.281	<0.001	0.022	0.303	0.425
18	0.010	0.251	<0.001	0.022	0.273	0.381
19	0.013	0.286	<0.001	0.029	0.315	0.396
20 8.00am	0.009	0.325	<0.001	0.046	0.371	0.400
1.00 pm	0.010	0.331	0.006	0.042	0.379	0.411
21	0.009	0.345	0.001	0.039	0.385	0.424
22	0.003	0.325	<0.001	0.027	0.352	0.425
23	0.005	0.332	0.001	0.033	0.366	0.450
24	0.004	0.281	0.002	0.020	0.304	0.491
25	0.003	0.221	<0.001	0.009	0.230	0.490
26	0.001	0.175	<0.001	0.002	0.177	0.483
27	0.004	0.184	<0.001	0.011	0.195	0.442
28	0.010	0.226	<0.001	0.027	0.253	0.502
29	0.016	0.262	<0.001	0.031	0.293	0.525
29	0.011	0.269	0.001	0.036	0.306	0.548
30	0.008	0.275	<0.001	0.014	0.289	0.584
31	0.009	0.268	<0.001	0.029	0.297	0.495
4/1 8.00am	0.011	0.372	<0.001	0.039	0.411	0.751
2.00pm	0.012	0.352	<0.001	0.041	0.393	0.622

(1) this includes on the first three DiClBiØ isomers.

DSW 345190

EC/GC Analysis of Off-Gas Drowning Water

Date of Test 3/12/74

Time	MCS-1221 thru 1254	MCS-1109
1.30 pm - 60 min.	0.69 ppm	0.69 ppm
2.00 pm - 90 min.	0.60 ppm	0.09 ppm
2.30 pm - 120 min.	0.69 ppm	0.10 ppm

Date of Test 3/20/74 Time	MCS-1221 thru 1254	MCS-1109
2.05 pm - 100 min.	3.44 ppm	0.23 ppm
2.45 pm - 140 min.	3.27 ppm	0.34 ppm
3.25 pm - 180 min.	3.04 ppm	0.47 ppm

Date of Test 3/29/74 Time	MCS-1242 - 1254 (1)	MCS-1109
2.00 pm - 60 min.	7.16 ppm	1.11 ppm
2.30 pm - 90 min.	3.11 ppm	0.55 ppm
3.00 pm - 120 min.	1.19 ppm	0.39 ppm

Date of Test 4/2/74 Time	MCS-1221 thru 1242 (2)	MCS-1109
12.00 noon - 60 min.	2.57 ppm	0.47 ppm
12.30 pm - 90 min.	1.47 ppm	0.90 ppm
1.00 pm - 120 min.	1.38 ppm	1.18 ppm

(1) No MCS-1221 present in these samples

(2) No MCS-1254 present in these samples

DSW 345191

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FROM (NAME & LOCATION) K. L. Schutzenhofer - WGK

DATE January 16, 1976

cc: H. J. Horner
J. A. Gloeckner

SUBJECT Analysis of Liquid from HCl High Line

REFERENCE

TO G. L. Johnson (Dept.246)

The following results were obtained on the analysis of the liquid sample taken from the HCl High Line at 10:15 am on 1/15/76.

Test	Result
H_2O	16.4%
pH (5%solution)	0.5
Chlorophenols	none detected
Iron	22.2% (as Fe) 64.6% (as $FeCl_3$)

The sample had to be diluted with water to a 5% solution before a pH measurement could be made. These analyses indicate that the material is essentially $FeCl_3$, HCl and H_2O.

Reference - WGK AR-D Notebook p.20828.

K. L. Schutzenhofer

K. L. Schutzenhofer

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DSW 345192

STLCOPCB4083974