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ANALYTICAL
(Type of Report)

REPORT NO.: NDA - 515

JOB/PROJECT NO.: 484.5010

DATE: 6 August 1984

PERIOD COVERED:

TITLE: ANALYSES OF BENCH SCALE DICHLOROANILINE BUP

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ABSTRACT: Samples of dichloraniline wastes and their bench-scale pyrolysis products were submitted by MIC for GC/MS analysis for specified organic compounds. The results of these analyses are shown in this report.

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TITLE: ANALYSES OF BENCH SCALE DICHLOROANILINE
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ACKNOWLEDGEMENT

Contributions of the following Dayton Laboratory personnel to this project are gratefully acknowledged:

Analyses: S. Berkadale
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R. Noble
R. Williams

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ANALYSES FOR: TETRACHLOROPHENAZINES

TETRACHLOROBENZIDINES/TETRACHLOROSEMIDINES

POLYCHLORINATED BIPHENYLS

MONS 220808

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1. INTRODUCTION

Samples of dichloroaniline wastes and their bench - scale pyrolysis products were submitted by MIC for GC/MS analyses for tetrachlorophenazines, tetrachlorobenzidines/tetrachlorosemidines, polychlorinated biphenyls (PCBs), tetrachlorodibenzo-p-dioxins (TCDDs), and tetrachlorodibenzofurans (TCDFs). The pyrolysis samples resulted from heating of dichloroaniline wastes at various temperatures, and varied in type from a product that resembled the original waste to one that was primarily a char or carbonaceous material. Because of this variation in the organic carbon content among the samples, as well as the variation in the levels of the analytes in the samples, a host of workup methods were required to prepare the samples for GC/MS analyses. This section of this report will deal with methods of analysis for tetrachlorophenazines, tetrachlorobenzidines/tetrachlorosemidines, and PCBs. While some common extractions done for PCBs, TCDDs, and TCDFs are described in this section, the further cleanup and analysis of these extracts for TCDDs and TCDFs are described in a later section.

II. SAMPLE PREPARATION METHODS

The analysis goal for this project was quantification of total isomers of each analyte type down to the 1 ppm level. This requirement necessitated much lower detection limits on a per isomer basis, since each compound class included from 22 to 650 isomers. Table 1 details the number of isomers for each compound class, and the per isomer detection limit required to achieve the 1 ppm total isomer content goal. It should be noted that analysis for tetrachlorosemidines was not specifically requested for this project, but since these compounds are not distinguishable by mass spectrometry under electron impact ionization from the isomeric tetrachlorobenzidines, they had to be included in the analysis, and this further complicated detection limit problems.

Sample preparation methods for low levels of PCBs, TCDDs, and TCDFs are used routinely in the Environmental Sciences Center at the Dayton Laboratory, but low-level methods for tetrachlorophenazines and tetrachlorobenzidines/tetrachlorosemidines in organic matrices had not yet been developed. A method was developed for the phenazine analysis for this project. This method involved modification of workup procedures normally applied for analysis of the stucturally similar dioxin. Method development for low-level analysis of the semidines/benzidines was predicted to be a sizeable undertaking and the decision was made by MIC to forego funding of such a project at this time.

The attempted workup methods for these samples followed an orderly sequence from easiest and least time-consuming to hardest. In general, a simple sample dilution or an extraction without solvent concentration was attempted first. If the analytes were not detected in this "extract", lower detection limits were obtained by using Soxhlet extraction (for samples low in organics) or by applying sample cleanup (for samples high in organics). Of course, cleanup techniques were not available for the benzidines/semidines, so the options were limited for this analysis.

A. METHODS FOR DICHLOROANILINE WASTE PYROLYSIS PRODUCTS

Methods 1-4 detailed below were applied to the bench scale burn products. Not all methods were applied to all samples; appropriate methods were chosen for each sample according to the overall concentrations of organics in the sample, as well as the analyte concentrations.

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METHOD 1. GENERAL EXTRACTION METHOD FOR TETRACHLOROPHENAZINES AND TETRACHLORO-BENZIDINES/TETRACHLOROSEMIDINES

1. Place about 0.5 g of sample in a 14 mL Pierce vial.

2. Spike with:
   a. Pyrene-d10 - 2.0 ug/g
   b. Chrysene-d12 - 2.0 ug/g

3. Add 5 mL of benzene.

4. Extract by ultrasound for 30 minutes.

METHOD 2. EXTRACTION METHOD FOR TETRACHLOROPHENAZINE SAMPLES REQUIRING SPECIAL CLEANUP FOR LOWER DETECTION LIMITS

1. Place about a one gram sample into a 40 mL Pierce vial.

2. Dry sample if needed by adding about 1 gram of sodium sulfate to vial.

3. Extract sample with three 15 mL aliquots of methylene chloride.

4. Combine extracts in a 125 mL seperatory funnel and add 40 mL of 10% hydrochloric acid, remove acid then add same amount of 1 N potassium hydroxide and remove base.

5. Add 10 mL of hexane.

6. Drain into a 50 mL centrifuge tube and reduce volume to 1 or 2 mL.

7. Quantitatively transfer sample to column containing 3 grams of silica gel and 1 centimeter of sodium sulfate on top.

8. Elute with 30 mL of hexane first and save.

9. Elute with 30 ml of methylene chloride/hexane and reduce to 1 mL.

10. Elute with 40 ml of 10% methylene acetate/hexane and save.

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METHOD 3. SOXHLET EXTRACTION METHOD FOR TETRACHLOROPHENAZINES, TETRACHLOROBENZIDINES/TETRACHLOROSEMIDINES, PCB'S, TCDD'S AND TCDF'S - USED FOR "CLEAN" SAMPLES

1. Place about 5.00 g of sample on four centimeters of sodium sulfate in a Soxhlet extraction apparatus (without thimble).

2. Spike with:
   a. Pyrene-d10 - 0.20 ug/g
   b. Chrysene-d12 - 0.20 ug/g
   c. 3,3',4,4'-Tetrachlorobiphenyl-d6 - 0.20 ug/g
   d. C13-TCDD - 5.39 ng/g
   e. C13-TCDF - 4.67 ng/g

3. Place four centimeters of sodium sulfate on top of the sample.

4. Add 300 mL of methylene chloride.

5. Extract for 48 hours.

6. Concentrate to 1 mL by using Kuderna-Danish apparatus followed by nitrogen blowdown.

METHOD 4. EXTRACTION METHOD FOR PCB'S, TCDD'S, AND TCDF'S - SAMPLES REQUIRING EXTENSIVE CLEAN UP

1. Place about 5.00 g of sample into a 40 mL Pierce vial.

2. Spike with:
   a. 3,3',4,4'-Tetrachlorobiphenyl-d6 - 0.2 ug/g
   b. C13-TCDD - 5.16 ng/g
   c. C13-TCDF - 5.03 ng/g

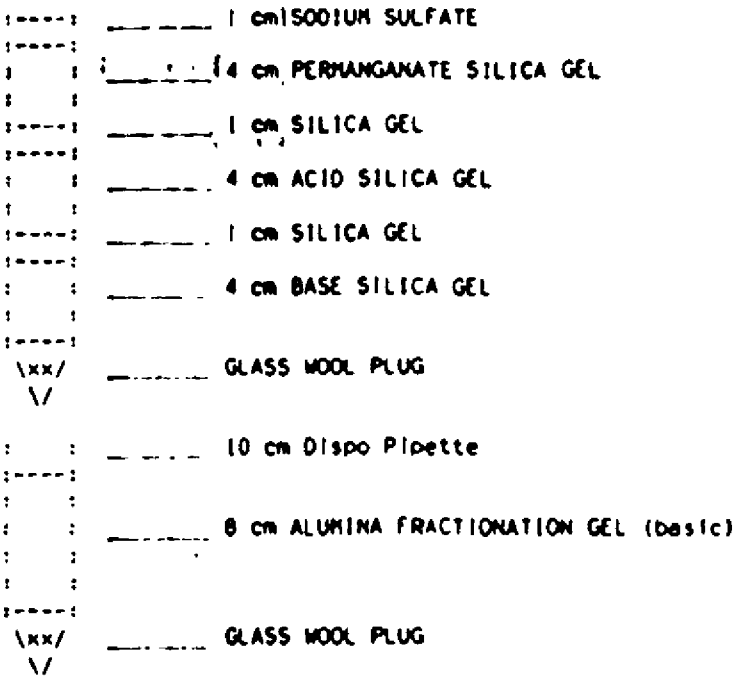
3. Extract by ultrasound with six 10 mL aliquots of benzene (15 minutes/extraction).

4. Elute extracts through a 10 mL dispo pipet with glass wool plug.

5. Rinse sample with 10 mL of methylene chloride and combine with benzene extracts.

6. Extract by ultrasound with four 10 mL aliquots of benzene (15 minutes/extraction).

7. Reduce extract volume to 10 mL and wash with 75% sulfuric acid.



8. Reduce extract volume to dryness, dilute with 10 mL of hexane, and quantitatively transfer to cleanup column.

9. Elute extract through both cleanup and alumina columns with 40 mL of hexane.

10. Elute alumina column with 15 mL of 5% methylene chloride/hexane.

11. Elute alumina column again with 20 mL of 50% methylene chloride/hexane.

12. Collect each eluent and concentrate to 1 mL using nitrogen blowdown.

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8. METHODS FOR DICHLOROANILINE WASTES

Methods 5-6 detailed below were applied to analysis of the dichloroaniline wastes used as starting materials in the pyrolysis studies. Method 5, essentially a sample dilution, was used for the tetrachlorophenazine and tetrachlorosemidine/benzidine analysis. Method 6 was the extraction and sample cleanup method employed for the PCB, TCDD, and TCDF analyses.

METHOD 5. SAMPLE PREPARATION FOR TETRACHLOROPHENAZINE AND TETRACHLORO-BENZIDINE/TETRACHLOROSEMIDINE ANALYSIS

1. Place about 0.1 g sample in a 14 mL Pierce vial.

2. Add 10 mL benzene and shake vigorously.

3. Dilute the resulting solution 1:10 in benzene.

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METHOD 6. EXTRACTION METHOD FOR PCB'S, TCDD'S AND TCDF'S

1. Place about 5.00 g of sample into a 40 mL Pierce vial.

2. Spike with:
   a. 3,3',4,4'-Tetrachlorobiphenyl-d6 - 0.2 ug/g
   b. C13-TCDD - 4.8 ng/g.
   c. C13-TCDF - 4.7 ng/g.

3. Extract by ultrasound for 30 minutes with 20 mL benzene.

4. Shake with 10 mL 5% sulfuric acid.

5. Quantitatively transfer sample with benzene to a 500 mL bottle.

6. Wash extract with 50 mL 50% sulfuric acid and remove acid.

7. Raise benzene level to 200-250 mL.

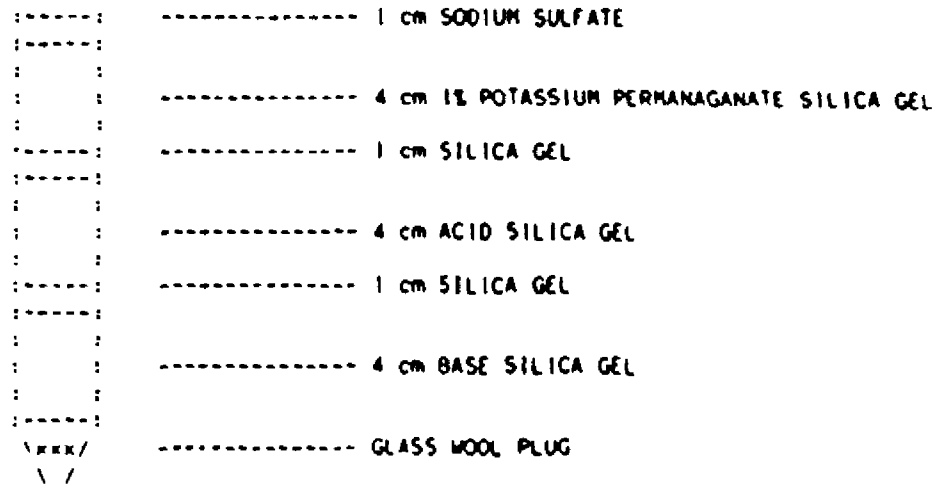
8. Wash with 80% sulfuric acid until clear (6-8 washes required).

9. Wash with 40 mL concentrated sulfuric acid.

10. Wash extract with 50 mL water followed by 20% KOH followed by 50 mL water and remove water completely.

11. Reduce volume with Kuderna-Danish to 3-5 mL.

12. Reduce extract volume to dryness, dilute with 10 mL of hexane, and quantitatively transfer to cleanup column.



13. Elute sample through cleanup column with 40 mL hexane and collect in 50-mL centrifuge tube.

14. Concentrate to 1.0 mL in warm sand bath under gentle stream of nitrogen.

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GC/MS ANALYSIS

Sample extracts were analyzed for tetrachlorophenazines, tetrachlorosemidines/ tetrachlorobenzidines, and PCBs using the instrument conditions outlined in Tables 2 and 3. For tetrachlorophenazines and tetrachlorobenzidines/ semidines, positives were identified by concurrence and correct ratio of the major ion peaks. Standards containing one isomer of tetrachlorophenazine and one isomer of tetrachlorobenzidine were used to calculate response factors based on the major ion areas for these compounds relative to the internal standard area. These response factors were used to calculate concentrations of all positives detected in the extracts. This approach assumes identical mass spectral response for all isomers, an assumption which gives accuracies within 30% for most compounds.

For the PCB analysis, a standard containing from one to three isomers for each chlorine class was analyzed to determine response factors for each class (mono- through deca-). The complexity of the PCB data (due to the large number of peaks present in many of the extracts) necessitated that the data reduction scheme be simpler than the peak-by-peak approach taken for the other analytes. As a result, an approach based on summing the total areas for PCBs of each chlorine class was adopted. Details of this procedure are given in Table 4.

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TABLE 1. NUMBER OF ISOMERS FOR EACH ANALYTE CLASS FOR BENCH SCALE DCA PYROLYSIS

COMPOUND	#ISOMERS	PER ISOMER REQUESTED DETECTION LIMIT (ug/g)
Tetrachlorophenazines	22	0.046
Tetrachlorobenzidines/semidines	650	0.0015
TCDDs	22	0.046
TCDFs	38	0.026
PCBs	209	0.0048

Breakdown of PCBs for each chlorine class:

COMPOUND	#ISOMERS
Monochlorobiphenyls	3
Dichlorobiphenyls	12
Trichlorobiphenyls	24
Tetrachlorobiphenyl	42
Pentachlorobiphenyl	46
Hexachlorobiphenyl	42
Heptachlorobiphenyl	24
Octachlorobiphenyl	12
Nonachlorobiphenyl	3
Decachlorobiphenyl	1
TOTAL	209

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TABLE 2. GC/MS CONDITIONS FOR BENCH SCALE BURN ANALYSES

Instrument:	HP 5985A GC/MS system with SIDS software and 7920 disc drive for data storage
Column:	30m fused silica capillary column coated with DB-5 liquid phase (J&W) - connected directly to source
Temperature program :	hold at 50 C for 4 min.; program at 8 C/min. to 300 C; hold for duration of run
Injector temperature:	250 C
Transfer line temperature:	250 C
Injection mode:	splitless
Ion source temperature:	200 C
Mass spectrometer mode:	selected ion monitoring
Ions monitored:	tetrachlorophenazine: 316,318,320,283 tetrachlorobenzidine/semidine: 320,322, 250,252 PCBs: see Table 3
Internal standard:	anthracene-d10

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TABLE 3. IONS MONITORED FOR PCB ANALYSIS

Chlorine Class	Major Ions
Monochlorobiphenyl	186.188
Dichlorobiphenyl	222.224
Trichlorobiphenyl	255.9,257.9
Tetrachlorobiphenyl	289.8,291.8
Pentachlorobiphenyl	323 8,325.8
Hexachlorobiphenyl	357.8,359.8
Heptachlorobiphenyl	391.7,393.7
Octachlorobiphenyl	427.7,429.7
Nonachlorobiphenyl	461.6,463.6
Decachlorobiphenyl	497.6,499.6

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TABLE 4. DATA REDUCTION PROCEDURE FOR PCB ANALYSIS

1. Obtain total ion area and mass spectrum for each major peak in the extract.

2. Examine each mass spectrum and determine whether it is a PCB or an interferent.

3. If the mass spectrum is a PCB, determine which chlorine class (mono-,di-,tri-,etc).

4. Add total ion areas of PCBs of each chlorine class (e.g. total trichlorobiphenyl area).

5. Divide total area by response factor for that chlorine class to obtain concentration in extract.

6. Calculate sample concentration.

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RESULTS AND DISCUSSION

A. PYROLYSIS PRODUCTS

Results for tetrachlorophenazine and benzidine/semidines in the OCA pyrolysis products are presented in Tables 5 - 7. Table 5 gives results obtained using the Method 1 (simple screening extraction) workup procedure. Despite the high detection limits inherent in this method, a number of samples were analyzable using this procedure. In cases where the phenazine and benzidine/semidine were not detected in this analysis, two courses of action were available. If the particular sample was low in organic content, as indicated by a relatively clear colorless extract, the sample was subjected to Soxhlet extraction (Method 3). This was the method of choice because it permitted simultaneous extraction of all analytes required for this study, including PCBs, TCDDs, and TCDFs, and because this method permitted the lowest detection limits. Results from this extraction are given in Table 7. If the sample was high in organic content, as indicated by a highly colored extract from Method 1, the extract was cleaned up using Method 2. This allowed lower detection limits to be achieved for the tetrachlorophenazines, but did not permit analysis of the terachlorobenzidines/semidines. Due to financial considerations, development of cleanup procedures for these compounds was not desired by MIC at this time. Results stemming from the Method 2 cleanup are given in Table 6.

PCB results for the OCA pyrolysis products are tabulated by chlorine class in Table 8. These results were obtained using extracts resulting from Method 3 (samples low in organics) or Method 4 (samples high in organics). It should be noted that the final alumina column fractionation in Method 4 was designed to separate the PCBs (5% CH2CL2/hexane eluant) from the nonretained organics (hexane eluant) and the TCDDs/TCDFs (50% CH2Cl2/hexane eluant). While this procedure sucessfully isolated the TCDDs/TCDFs in the 50% CH2Cl2/hexane fraction, the PCBs were found to be spread across all three fractions. Hence, all three were analyzed and their results summed to give the concentrations in Table 8. The method was subsequently modified for the OCA waste extractions.

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B. DICHLOROANILINE WASTES

Because all the dichloroaniline wastes were similar in organic content, sample preparation procedures were more uniform than was the case with the pyrolysis products. Results of these analyses are given in Tables 9-11. Table 9 lists results of the analyses of Method 5 extracts for tetrachlorophenazines and tetrachlorobenzidines/semidines. Table 10 gives results of analysis of Method 6 extracts for PCBs, and Table 11 provides recoveries of native spikes for the PCB analysis. Note that while not requested, the Midland-Ross DCA waste sample was included in the PCB analysis for comparison purposes.

Detection limits given in these tables are generally higher than the requested 1 ppm total isomer content limit. This is due to limited sample size, cleanup limitations, and the large number of isomers analyzed. However, in most cases this proved to be irrelevant since analytes were detected in the samples above the requested level of detection.

TABLE 3. TETRACHLORODIBENZIDINE AND TETRACHLORODIBENZIDINE/TETRACHLORODIBENZIDINE RESULTS FOR BENCH-SCALE PYROLYSIS SAMPLES PREPARED USING GENERAL EXTRACTION METHOD (METHOD 1)

SAMPLE IDENTIFICATION	SAMPLE WT (g)	FINAL EXTRACT VOLUME (mL)	DILUTION FACTOR	TOTAL CONCENTRATION OF ISOMERS (ng/g)		% RECOVERY	
				TETRACHLORODIBENZIDINE	TETRACHLORODIBENZIDINE/ TETRACHLORODIBENZODIOXIDINE	PYRENE-d10	CHRYSENE-d10
Batch 15	0.491	5.0	1:10	21.2	ND[a]	89.9	87.1
Batch 4,5,6 composite	0.512	5.0	-	0.87	ND[b]	66.5	58.9
Batch 13, 14 composite	0.105	5.0	1:10	1.4×10^4	3.3×10^3	124	272
Batch 10	0.652	5.0	1:10	262	ND[a]	60.4	53.9
Batch 8, 9 composite	0.470	5.0	1:10	ND (See Table 6)	ND[a]	121	107
Batch 19 PCA	0.495	5.0	-	ND (See Table 6)	ND[b]	117	131
Batch 17, 18 composite PCA	0.147	5.0	1:100 (phenazine) 1:10 (benzidine)	1.7×10^4	2.3×10^3	91.5	165
Batch 20 PCA	0.550	5.0	-	ND (See Table 7)	ND (See Table 7)	93.4	97.0
Batch 20 PCA duplicate	0.547	5.0	-	ND (See Table 7)	ND (See Table 7)	88.2	99.4
Batch 21 PCA	0.507	5.0	-	ND (See Table 7)	ND (See Table 7)	79.0	89.0
Method Blank	-	5.0	-	ND	ND	114	119

[a]ND = not detected. Detection limit was 100 ng/g for each isomer, or 65 mg/g for the approximately 650 isomers.

[b]ND = not detected. Detection limit was 10 ng/g for each isomer, or 6.5 mg/g for the approximately 650 isomers.

TABLE 6. TETRACHLOROPHENAZINE RESULTS FOR BENCH-SCALE PYROLYSIS SAMPLES REQUIRING SPECIALIZED CLEAN-UP FOR LOWER DETECTION LIMITS (METHOD 3)

SAMPLE IDENTIFICATION	WT (g)	FINAL EXTRACT VOLUME (mL)	DILUTION FACTOR	TOTAL CONC OF ISOMERS TETRACHLOROPHENAZINE (µg/g)	% RECOVERY TETRACHLOROPHENAZINE
Batch 8, 9 composite	1.0361	1.0	-	ND[a]	-
Batch 8, 9 composite + low spike[b]	1.0718	1.0	-	0.93	93.5
Batch 19	1.1458	1.0	-	ND[a]	-
Batch 19 duplicate	1.1457	1.0	-	ND[a]	-

[a]ND = not detected. Detection limit was 1 µg/g for each isomer, or a total of 22 µg/g for the sum of the 22 possible isomers.

[b]low spike = 1.04 µg/g 1,2,6,7-tetrachlorophenazine

TABLE 7. TETRACHLOROPHENANTHRENE AND TETRACHLORODIBENZOFURAN/TETRACHLOROTHIOPHENE RESULTS FOR BENCH-SCALE PYROLYSIS SAMPLES PREPARED USING SOXHLET EXTRACTION FOR LOWER DETECTION LIMITS (METHOD 3)

SAMPLE IDENTIFICATION	SAMPLE WT (g)	FINAL EXTRACT VOLUME (mL)	DILUTION FACTOR	TOTAL CONCENTRATION OF ISOMERS (ng/g)		% RECOVERY	
				TETRACHLOROPHENANTHRENE	TETRACHLORODIBENZOFURAN/ TETRACHLOROTHIOPHENE	PYRENE-d10	CHRYSENE-d10
Batch 20	4.6298	1.0	-	0.34	ND[a]	113	221
Batch 21	5.0083	1.0	-	0.073	ND[a]	122	164
Batch 21 duplicate	5.0157	1.0	-	0.066	ND[a]	76.8	98.1

[a]ND = not detected. Detection limit was 0.06 ng/g per isomer, or 39 ng/g for the approximately 650 isomers

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TABLE 8 RESULTS OF GC/MS ANALYSES OF BENCH-SCALE DICHLOROANILINE PYROLYSIS PRODUCTS FOR POLYCHLORINATED BIPHENYLS (PCBs) (METHOD 3 and METHOD 4)

	TOTAL CONCENTRATION (µg/g)							
COMPOUND	BATCH 4,5,6	BATCH 8,9	BATCH 13,14	BATCH 15	BATCH 17,18	BATCH 19	BATCH 20	BATCH 21
Cl_1-biphenyls	0 007	0.14	0 13	0 08	0.01	0 06	0 45	0 03
Cl_2-biphenyls	0.02	0 96	3 56	1 50	0 89	0 52	0 03	0 01
Cl_3-biphenyls	0 04	0.93	5 00	8 76	0.41	0 24	ND	ND
Cl_4-biphenyls	0 05	1.60	6 03	8.31	1 09	0 02	ND[b]	
Cl_5-biphenyls	0 01	0 19	9 09	11 63	ND	ND	ND	0 01
Cl_6-biphenyls	ND	ND	1 50	ND	ND	ND	ND	ND
Cl_7-biphenyls	ND	ND	ND	ND	ND	ND	ND	ND
Cl_8 -biphenyls	ND	ND	ND	ND	ND	ND	ND	ND
Cl_9 -biphenyls	ND	ND	ND	ND	ND	ND	ND	ND
Cl_{10}-biphenyls	ND	ND	ND	ND	ND	ND	ND	ND
Total PCBs	0 12	3.82	24.13	30.28	2.40	0 84	0 48	0 07
% Recovery 3,3',4,4'-tetra chlorobiphenyl-d_6	122.6	114.9	420.1[a]	340 5[a]	104.0[a]	74.1	101 8	96 1

[a]Apparent high recovery was result of interference at retention time of deuterated spike compound.

[b]ND = not detected, with a detection limit of 0.01 µg/g per PCB isomer for samples containing less than 5 µg/g total PCBs and 0.1 µg/g per PCB isomer for samples containing more than 5 µg/g total PCBs. To determine the detection limit for each chlorine class, multiply the per isomer detection limit by the number of isomers in that class (see Table 1).

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TABLE 9 RESULTS OF GC/MS ANALYSIS OF DICHLOROANILINE WASTES FOR TETRACHLOROPHENAZINES AND TETRACHLOROBENZIDINES/TETRACHLOROSEMIDINES (METHOD 5)

	TOTAL CONCENTRATION OF ISOMERS (mg/g)	
SAMPLE IDENTIFICATION	TETRACHLOROPHENAZINE	TETRACHLOROBENZIDINE/ TETRACHLOROSEMIDINE
PCA Residue	6.7	0.91
DCA Heads	ND[a]	ND
DCA Residue - A	4.7	28.0
DCA Residue - B	4.4	35 0
DCA Residue - B (dup)	4.7	40.0
Blank	ND	ND

[a] ND = not detected, with a detection limit of 1 mg/g per isomer, or 22 mg/g for the 22 tetrachlorophenazine isomers and 650 mg/g for the approximately 650 tetrachlorobenzidine/semidine isomers.

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TABLE 10. RESULTS OF GC/MS ANALYSES OF DICHLOROANILINE WASTES FOR POLYCHLORINATED BIPHENYLS (PCBs) (METHOD 6)

COMPOUND	TOTAL CONCENTRATION (µg/g) A SAMPLE	B SAMPLE	B SAMPLE DUPLICATE	DCA HEADS	PCA RESIDUE	METHOD BLANK	MIDLAND MONS SAMPLE
Cl_4-biphenyls	0.20	ND[a]	ND	ND	0.48	ND	ND
Cl_5-biphenyls	2.79	1.12	0.59	0.69	2.81	ND	0.94
Cl_6-biphenyls	0.17	0.08	0.12	ND	0.11	ND	0.11
Cl_7-biphenyls	6.78	5.66	10.9	ND	1.56	ND	5.66
Cl_8-biphenyls	ND	ND	ND	ND	ND	ND	ND
Cl_9-biphenyls	ND	ND	ND	ND	ND	ND	ND
Cl_{10}-biphenyls	ND	ND	ND	ND	ND	ND	ND
Cl_{11}-biphenyls	ND	ND	ND	ND	ND	ND	ND
Cl_{12}-biphenyls	ND	ND	ND	ND	ND	ND	ND
Total PCBs	9.94	6.86	11.6	0.69	4.96	ND	6.71
% Recovery							
3,3',4,4'-tetrachlorobiphenyl d_6	67.5	60.5	125.1	42.4	58.6	20.9	58.2

[a] ND = not detected, with a detection limit of 0.01 µg/g per PCB isomer. To determine the detection limit for each chlorine class, multiply the per isomer detection limit by the number of isomers in that class (see Table 1).

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TABLE II. SPIKE RECOVERIES FOR NATIVE PCBS IN DICHLOROANILINE WASTE[a]

COMPOUND	% RECOVERY A SAMPLE LOW SPIKE (0.2 ug/g)	% RECOVERY A SAMPLE HIGH SPIKE (0.4 ug/g)
C11-biphenyls	55.7	19.0
	107.1	57.3
	67.1	35.7
C12-biphenyls	69.3	57.1
	120.6	120.7
C13-biphenyls	81.7	73.7
	89.7	77.6
	91.6	82.8
C14-biphenyls	85.0	87.5
	86.4	81.3
	89.2	95.4
C15-biphenyls	89.9	89.5
	88.6	91.1
	86.0	96.7
C16-biphenyls	92.5	92.6
	95.0	88.1
C17-biphenyls	93.4	85.2
C18-biphenyls	106.7	81.9
C19-biphenyls	102.7	86.6
C110-biphenyls	85.4	77.3
3,3',4,4'-Tetrachlorobiphenyls-d6	85.6	90.3

[a] Lists % recovery for each isomer spiked into the waste.

MONS 220830

M50117:SM

ANALYSES FOR: TCDDs

TCDFs

MDNS 220831

RESULTS FOR BENCH SCALE BURN PROJECT FOR TCDD's AND TCDF's

Following completion of the target compound analysis the samples were submitted for TCDD and TCDF analysis. The samples were subjected to further cleanup prior to their analysis by GC/MS. The samples had initially been spiked with 2,3,7,8-TCDD and 2,3,7,8-TCDF before the start of sample preparation. Initially the further cleanup involved a solvent exchange to hexane. The Batch 20 and Batch 21 samples were then subjected to successive washes with water, concentrated sulfuric acid (until the acid layer was clear), water, 20% potassium hydroxide and water.

The hexane from Batches 20 and 21 was then concentrated, dried and applied to the head of a mixed phase column consisting of (top to bottom) 2 g of silica, 4 g of silica plus 40% sulfuric acid, 1 g of silica, 2 g of silica plus 36% potassium hydroxide and 1 g of silica. The column was eluted with 50 mL of hexane and the eluent was collected and concentrated to 2 mL. The hexane was then applied to a column consisting of 2.5 g of Woelm Basic alumina. The alumina was eluted first with 10 mL of a 2% methylene chloride in hexane solution and this fraction was discarded. An additional elution was made with 15 mL of 50% methylene chloride to elute the TCDDs and TCDFs from the column. This fraction was then concentrated to less than 1 mL and subjected to further cleanup by the EPA Option D technique along with the remainder of the samples.

The Option D technique involves placing the sample on the head of a column containing 18% Carbopack C on Celite packed to a depth of 2 cm in a 1.0 cm I.D. pipet. The column was then eluted with 1 mL of hexane, 1 mL of a 1:1 cyclohexane: methylene chloride mixture, 1 mL of 75:20:5 methylene chloride: methanol: benzene and finally 2 mL of toluene. The toluene fraction had 50 uL of dodecane added to it and was concentrated for analysis.

The GC/MS analyses were conducted using a Hewlett/Packard 5987 GC/MS instrument. A 30 m DB-5 capillary column was used for the TCDD analyses. A 60 m SP2330 capillary column was used for the TCDF and 2,3,7,8-TCDF specific analyses. The mass spectrometer was operated in the selected ion monitoring mode analyzing for ions characteristic of native (unlabeled) TCDD (m/z 257, 320, 322), C-13 labeled 2,3,7,8-TCDD (m/z 334), native TCDF (m/z 241, 304, 306), C-13 labeled 2,3,7,8-TCDF (m/z 318), and pentachloro- and hexachloro diphenylethers (m/z 342, 376).

The results of the analyses are shown in Table 1. Table 1 also shows all pertinent QA/QC data. Please note that it is incorrect to calculate spike recoveries for internal standard calculated results as the internal standard corrects for recovery problems due to losses in workup.

Table 1: Results of Analysis for TCDDs and TCDFs

Sample	TCDD	2378-TCDD	added	TCDF	2378-TCDF	added
Batch 4,5,6 Composite	ND(7.9)	ND(7.9)	-	ND(7.8)	ND(0.1)	-
Batch 8,9 Composite	ND(4.8)	ND(4.8)	-	6.3	0.9	-
Batch 13,14 Composite	ND(0.5)	ND(0.5)	-	71	10.3	-
Batch 15	ND(1.2)	ND(1.2)	-	30	5.8	-
Batch 17,18 Composite	ND(1.4)	ND(1.4)	-	6.1	1.6	-
Batch 19	ND(1.1)	ND(1.1)	-	ND(0.8)	ND(0.1)	-
Composite spike 1 (Calculated Levels)	-	-	-	8.5	1.4	-
Composite spike 1	-	4.1	4.4	9.7	1.4	4.6
Composite spike 2 (Calculated levels)	-	-	-	9.0	1.4	-
Composite spike 2	-	7.8	4.5	17.3	1.8	4.6
Batch 20	ND(1.6)	ND(1.6)	-	ND(1.6)	ND(1.6)	-
Batch 20 High Spike	-	17	19	-	19.4	19
Batch 21	ND(1.8)	ND(1.8)	-	ND(0.5)	ND(0.5)	-
Batch 21 Low Spike	-	2.6	2.0	-	1.1	2.3
A-sample	ND(6.6)	ND(0.1)	-	20.8	9.2	-
A-sample Low Spike	-	3.7	4.2	-	13.1	4.3
A-sample High Spike	-	8.0	9.1	-	18.5	9.4
B-sample	ND(2.6)	ND(0.1)	-	20.4	8.8	-
B-sample Duplicate	ND(1.6)	ND(0.1)	-	20.0	8.7	-
DCA Heads	ND(2.3)	ND(0.1)	-	ND(0.6)	ND(0.1)	-
PCA Residue	ND(1.0)	ND(0.1)	-	11.8	1.6	-
Method Blank	ND(18)	ND(1.0)	-	ND(2.4)	ND(0.1)	-

ND( ) Not detected (detection limit)

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ESC/DAYTON (Department/Section)

ANALYTICAL (Type of Report)

REPORT NO.: MDA-515 (Addendum)

JOB/PROJECT NO.: 404.3010

DATE: August 1984

PERIOD COVERED:

TITLE: ANALYSIS OF OFFGAS FROM BENCH PYROLYSIS

AUTHORS: S. . Mazer/

ABSTRACT: The offgas from the bench-scale pyrolysis of [illegible] waste was analyzed for total tetrachlorodibenzenes. The results of these analyses are shown in this report.

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APPROVAL DATE: 8-16-84

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ACKNOWLEDGEMENT

Contributions of the following Dayton Laboratory personnel to this project are gratefully acknowledged:

Analyses: S. L. Mazer

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I. INTRODUCTION

The offgas from bench-scale pyrolysis of a dichloroaniline waste was collected by MIC personnel in a series of impingers, and the impinger contents and associated sampling apparatus were submitted to the Dayton Laboratory for GC/MS analyses for total tetrachlorophenazines. This report details methods for and results of these analyses.

II. SAMPLE PREPARATION METHODS

Table I lists the samples received and quality control samples prepared in conjunction with these analyses. The native spike samples were designed to demonstrate that the tetrachlorophenazines were recovered from each matrix, and the blanks were analyzed to show that the samples did not become contaminated during sample workup.

Samples for this study fell basically into three categories:

a. Water samples, including HCl and NaOH solutions.
b. Apparatus samples, including the gas washing bottles and Teflon tubing connector.
c. Crystals scraped from inside a pipe (Batch 22 scrapings).

The sample preparation methods designed for each category are described below.

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METHOD 1. EXTRACTION OF WATER SAMPLES

1. Place 250 mL sample into separatory funnel.
2. Spike with 1 ug 3,3',4,4'-tetrachlorobiphenyl-d6 surrogate spike compound.
3. Extract with one 90 and two 60-mL portions of methylene chloride.
4. Dry extract on sodium sulfate column.
5. Concentrate extract to 1 mL. Exception: HCl trap solution extract was concentrated to 15 ml.

METHOD 2. EXTRACTION OF GLASSWARE AND TUBING FROM SAMPLING APPARATUS

1. Spike apparatus with 1 ug 3,3',4,4'-tetrachlorobiphenyl-d6.
2. Rinse sample out of apparatus with 150 - 1000 mL methylene chloride. until crystals are entirely dissolved. Exception: Dissolving of crystals in HCl gas washing bottle was aided by addition of 200 - 300 mL distilled deionized water. This water was then extracted with methylene chloride.
3. If water was used in washing out crystals, dry extract with sodium sulfate.
4. Concentrate extract to 1.0 mL. Exception: Extract of HCl gas washing bottle was concentrated to 20 ml.

METHOD 3. SAMPLE PREPARATION METHOD FOR BATCH 22 SCRAPINGS

1. Weigh 0.1 g sample into 10 - mL volumetric flask.
2. Dilute to mark with methylene chloride.
3. Prepare a 1:10 dilution of the above solution in methylene chloride.

III. GC/MS ANALYSIS

Sample extracts were analyzed for tetrachlorophenazines using the instrument conditions outlined in Table 2. Positives were identified by concurrence and correct ratio of the major ion peaks. Standards of 1,2,6,7-tetrachlorophenazine were used to calibrate, and all responses were normalized to the internal standard. Recoveries of the deuterated spike and of the native tetrachlorophenazine were calculated relative to standards simulating 100% recovery.

IV. RESULTS AND DISCUSSION

Results of the GC/MS analyses, given in Table 3, show that the majority of the tetrachlorophenazine was found in the HCl gas washing bottle and its contents. Recoveries of the 3,3',4,4'-tetrachlorobiphenyl-d6 indicate that good extraction efficiences were maintained for the analysis in general, and recoveries of the native terachlorophenazine spiked into each sample matrix show that these compounds in particular were well recovered. The method blanks furthermore indicate that good laboratory techniques prevented sample cross-contamination. A summary of the offgas results is given in Table 4.

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TABLE 1. SAMPLES PREPARED AND ANALYZED FOR DCA PYROLYSIS OFFGAS STUDY

SAMPLE IDENTIFICATION	MIC SAMPLE	QC SAMPLE
4% HCl Trap Solution	•	
MIC 4% HCL Blank	•	
Dayton Lab 4% HCL Blank		•
Dayton Lab 4% HCL + 4 ug/L phenazine spike		•
10% NaOH Trap Solution	•	
MIC 10% NaOH Blank	•	
Dayton Lab 10% NaOH Blank		•
Dayton Lab 10% NaOH + 4 ug/L phenazine spike		•
Gas Washing Bottle	•	
NaOH Gas Washing Bottle	•	
Glassware Blank		•
Glassware + 1 ug phenazine spike		•
MIC Teflon Tubing	•	
Dayton Lab Teflon Tubing + 1 ug phenazine spike		•
Batch 22 Scrapings	•	
Batch 22 Scrapings (duplicate)	•	

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TABLE 2. GC/MS CONDITIONS FOR BENCH SCALE BURN ANALYSES

Instrument:	HP 5985A GC/MS system with SIDS software and 7920 disc drive for data storage
Column:	30m fused silica capillary column coated with DB-5 liquid phase (J&W) - connected directly to source
Temperature program :	hold at 50 C for 4 min.; program at 8 C/min. to 300 C; hold for duration of run.
Injector temperature:	250 C
Transfer line temperature:	250 C
lection mode:	splitless
Ion source temperature:	200 C
Mass spectrometer mode:	selected ion monitoring
Ions monitored:	tetrachlorophenazine: 316,318,320,283
Internal standard:	anthracene-d10

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TABLE 3. RESULTS OF GC/MS ANALYSIS OF OFFGAS SAMPLES FOR TETRACHLOROP[illegible]NES

	Total Tetrachlorophenazines (ug)	% RECOVERY 1,2,6,7 Tetrachlorophenazine	% RECOVERY 2,3',4,4'-TETRACHLOROBIPHENYL-d8
4% HCl Trap Solution	2.99 x 10⁴	NS[a]	NQ[b]
MIC 4% HCl Blank	ND[c]	NS	135.2
Dayton Lab 4% HCl Blank	ND	NS	140.6
Dayton Lab 4% HCl +4 ug/L phenazine spike	-	138.0	167.5
10% NaOH Trap Solution	18.0	NS	159.6
MIC 10% NaOH Blank	ND	NS	128.9
Dayton Lab 10% NaOH Blank	ND	NS	162.2
Dayton Lab 10% NaOH +4 ug/L phenazine spike	-	128.7	114.7
HCl Gas Washing Bottle	7.28 x 10⁴	NS	NQ
NaOH Gas Washing Bottle	11.2	NS	127.2
Glassware Blank	ND	NS	102.9
Glassware + 1 ug phenazine spike	-	86.0	84.7
MIC Teflon Tubing	1.35	NS	118.8
Dayton Lab Teflon Tubing +1 ug phenazine spike	-	89.8	96.4
Batch 22 Scrapings	634	NS	NA[b]
Batch 22 Scrapings (duplicate)	394	NS	NA

[a]NS = not spiked with native tetrachlorophenazine.

[b]NQ = not quantified. Sample was too high in organics to be concentrated to 1 mL, so spike could not be analyzed.

[c]ND = not detected, with a detection limit of 0.2 ug per tetrachlorphenazine isomer, or 4.4 ug for the total of the 22 isomers.

[b]NA = not applicable. Sample was diluted rather than extracted, so spiking was not necessary.

SAMPLE LOG NUMBERS

1-84-06 28-81, 1-84-07-03-04, 1-84-07-25-02

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TABLE 4. SUMMARY OF TETRACHLOROPHENAZINES DETECTED IN OFF-GAS SAMPLES

SAMPLE I.D.	TOTAL TETRACHLOROPHENAZINE (ug)
HCl Gas Washing Bottle	7.28×10^4
4% HCL Trap Solution	3.99×10^4
NaOH Gas Washing Bottle	11.2
10% NaOH Trap Solution	18.0
Teflon Tube Connector	1.35
Batch 22 Scrapings	414
TOTAL	11.31×10^4 ug
	= 113 mg

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