Institute of Paper Science and Technology
Atlanta, Georgia

IPST TECHNICAL PAPER SERIES

NUMBER 476

PRE- AND POST-TREATMENTS OF PULPS TO ELIMINATE DIOXINS

D.R. DIMMEL, L.B. SONNENBERG, K.B. RIGGS,
G. PITTS, J. WHITE, AND S. LUCAS

MARCH 1993

Pre- and Post-treatments of Pulps to Eliminate Dioxins

D.R. Dimmel, L.B. Sonnenberg, K.B. Riggs, G. Pitts, J. White, and S. Lucas

Submitted to
Tappi Journal

Copyright© 1993 by the Institute of Paper Science and Technology

For Members Only

NOTICE AND DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

PRE- AND POST-TREATMENTS OF PULPS TO ELIMINATE DIOXINS

Donald R. Dimmel[1] and Lucinda B. Sonnenberg
The Institute of Paper Science and Technology
500 10th Street, Atlanta, Georgia 30318

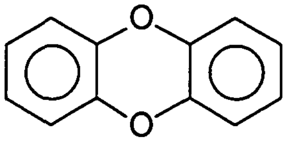
Karen B. Riggs, Gerry Pitts, Jon White, and Samuel Lucas[2]
Battelle
505 King Avenue, Columbus, Ohio 43201-2693

ABSTRACT

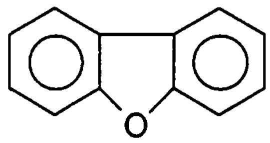
Experiments have been conducted to evaluate the effectiveness of pre- and post-treatments of chlorinated pulps, and a model pulp system, to reduce polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) levels. The model consisted of dibenzo-*p*-dioxin (DBD) and dibenzofuran (DBF) adsorbed on to cotton linters; DBD and DBF are known precursors of dioxins. Nitrogen dioxide treatment of DBD/F spiked cotton linters effectively reduced PCDD/F levels observed after chlorination of the linters. A similar O_3 treatment was ineffective, probably because the linters were too dry. A DBD/F spiked wet pulp gave extremely low levels of PCDD/F when pretreated with ozone prior to chlorination; an NO_2 pretreatment, followed by chlorination, gave a modest PCDD/F reduction. Post treatments of PCDD/F-containing pulps with ozone, hydrogen peroxide, and oxygen led to about 50% reductions in PCDD/F.

INTRODUCTION

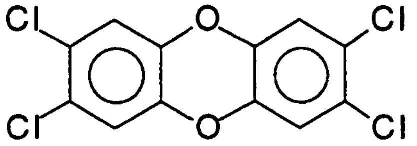
Previous studies have indicated that dibenzo-*p*-dioxin (DBD) and dibenzofuran (DBF) are important precursors to the production of polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) when wood pulp is bleached with high levels of chlorine.[3] The structures of DBD/F and the most toxic PCDD/F, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and furan (2378-TCDD and 2378-TCDF), are shown below:



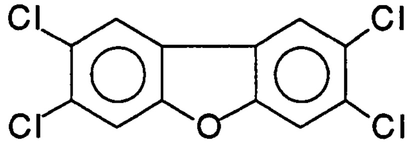
DBD



DBF



2378-TCDD



2378-TCDF

The question we wished to answer was whether DBD/F components could be selectively destroyed prior to chlorine bleaching, and thereby reduce or eliminate PCDD/F formation. To answer this question, we first conducted an extensive study of the reactions of DBD/F spiked cotton linters with nitrogen dioxide, nitric acid, sulfuric acid, oxygen, hydrogen peroxide, and ozone to determine what type of reagents would react with DBD/F.[4] These reagents were chosen because of their low cost and possible commercial potential. Nitrogen dioxide and ozone performed the best and were the reagents selected for further testing. Of the two, ozone was singled out for studies to define the reactivity differences of DBD/F and the lignin in pulp.[5]

While they reacted well with the PCDD/F precursors, O_3 and NO_2 treatments of pulps may still not prevent PCDD/F formation upon chlorination because (1) the lignin in the pulp consumes all of the reagent or (2) the alteration of the precursor by the reagent may not be permanent. For example, if nitrogen dioxide selectively attacks DBD/F to give a nitrogen derivatized product, what will the latter do upon chlorination? It was, therefore, imperative that we conduct chlorinations of samples containing DBD/F that had been first treated with O_3 and NO_2. The results of these experiments are described here.

The strategy was to first test the value of the "pretreatments" with DBD/F spiked cotton linters. The use of spikes greatly simplifies the analysis and leads to greater accuracy. The pretreatments were then repeated with unbleached pulps to demonstrate their effectiveness in lowering PCDD/F levels in the presence of lignin.

A second area of study was to examine procedures for reducing PCDD/F levels in pulps. A bleached pulp which contains trace levels of PCDD/F was treated with ozone, peroxide, oxygen, and other possible commercial electrophilic reagents to test the stability of PCDD/F to various post-chlorine bleaching stages.

RESULTS

Effects of Pretreatments - Spiked Cotton Linters

Samples of NO_2-treated and O_3-treated DBD/F spiked cotton linters were chlorinated to produce the data presented in Table 1. The spike levels before NO_2 treatment were 19 ppb DBF and 17 ppb DBD. The NO_2 treatment of spiked cotton linters is known to reduce DBD levels almost completely and DBF by about one-third.[4] The present analysis showed a similar trend, nearly complete loss of DBD and partial loss of DBF (last column, Table 1) and substantially reduced PCDD/F levels, especially the TCDD type. *The DBD and DBF destroyed by the NO_2 treatments apparently are not converted back to chlorinated DBD/F products upon chlorination.*

The degradation of cotton linters absorbed DBD and DBF by ozone was much less than the NO_2 treatment (compare columns 5 and 6, Table 1) and, therefore, resulted in more chlorinated products after chlorination (column 2 vs. 3). The spiked DBD/F linters used in the O_3 experiment were prepared in a similar manner to the one used in the NO_2 experiment, however, there was insufficient sample available to confirm the exact loading levels. Quite obviously the O_3 treatment was not very effective. Yet, previous work established that ozone efficiently destroyed DBD and DBF spiked on to linters.[4] There was, however, a very important difference in two ozone treatments. The effective treatments were done in the presence of wet linters,

Table 1. Results for Cotton Linters Pretreatment Samples

	Unreacted, Chlorinated	O_3-reacted, Chlorinated	NO_2-reacted, Chlorinated	Process Blank	O_3-reacted, Non-Chlorinated	NO_2-reacted, Non-Chlorinated
Analyte Concentration (ng/g/linter)[a,b]						
DBF	5.0	5.0	3.7	15	27	7.6
DBD	0.28	0.071	0.010	0.10	12	0.050
Mono-CDF	0.088	0.041	0.026[c]	0.031	--	--
Mono-CDD	0.053	0.014	--	--	--	--
Di-CDF	7.9	5.0	3.1	--	--	--
Di-CDD	0.20	0.057	--	--	--	--
Tri-CDF	17	17	5.8	--	0.02[d]	--
Tri-CDD	6.4	1.6	0.013	--	0.01[d]	--
Tetra-CDF	2.7	4.3	0.98	--	--	--
Tetra-CDD	18	7.5	0.041	--	0.05[d]	--
Internal Standard Recoveries (%)[a]						
DBF-$^{13}C_{12}$	65	52	65	36	31	59
DBF-$^{13}C_{12}$	63	60	64	47	28	58
TCDF-$^{13}C_{12}$	46	52	61	43	41	59
TCDD-$^{13}C_{12}$	48	50	57	40	40	58

[a] Average of duplicate results. [b] "--" indicates analyte not detected above estimated method detection limit of 0.005 ng/g. [c] Single sample value - duplicate exhibited atypically high level of 0.484 ng/g. [d] Average of calculated detection limit in sample and slight presence in duplicate.

the ineffective one (shown in Table 1) was done on dry linters. The effectiveness of ozone was re-examined in the case of pulp, which is described next.

For this sample set, internal standard recoveries were generally acceptable (> 40%); the analytical precision was also good, agreement within 30-50% for most duplicates.

Effects of Pretreatment - Pulp

A pulp which had been spiked with 0.2 ppb DBD and 10 ppb DBF was treated with ozone in one case and nitrogen dioxide in another case. The treated pulps were then chlorinated. The level of Cl_2 used was based on the residual lignin left in the pulp, employing common commercial practices. The results are given in Table 2. Good precision was obtained between duplicate samples. Internal standard and cleanup standard recoveries were greater than 50 percent in all cases indicating efficient removal of TCDD/TCDF from the sample matrix.

The data in the table indicate that *O_3-treatment is very effective in producing a pulp with low TCDD/F levels.* The values observed for TCDF and TCDD (4 ppt and non detect, respectively) should be compared to the levels of TCDD/F expected from a chlorinated, non alkali-extracted DBD/F spiked pulp which had not been pretreated. Such a pulp was not analyzed, but can be estimated to be >3600 ppt TCDF and >22 ppt TCDD. The estimate comes from TCDD/F analyses of the combined pulp and aqueous phases from an oxygen/alkali treatment of spiked chlorinated pulp (Table 5). To the extent that the oxygen treatment destroyed TCDD/F, the values present in the untreated pulp will be greater than that observed after treatment. Part of the TCDD/F lowering observed with O_3-treatment may be related to the lower level of Cl_2 employed with this pulp which contained less residual lignin.

The NO_2-pretreatment was effective at lowering TCDD/F levels, but was not nearly as effective as ozone. The observed dioxins levels of 600 ppt TCDF and 1.5 ppt TCDD were still well below the levels which could have been produced from a pulp spiked with 10,000 ppt DBF and 200 ppt DBD.

Table 2. Results for Pretreated Pulp Samples

	O_3-Cl_2 Pulp		NO_2-Cl_2 Pulp		Spiked Pulp Control	
	Rep 1, 2	Avg	Rep 1, 2	Avg	Rep 1, 2	Laboratory Method Blank
Concentration (pg/g)[a]						
2378-TCDF	3.0, 3.0	3.0	399, 409	404	--, --	--
Total TCDF	4.9, 3.0	4.0	590, 606	598		
2378-TCDD	--, --	--	--, 3.0	1.5	--, --	--
Total TCDD	--, --	--	--, 3.0	1.5	--, --	--
Recoveries (%)						
2378-TCDD-$^{13}C_{12}$	69, 66		62, 64		86, 84	86
2378-TCDF-$^{13}C_{12}$	62, 56		54, 53		72, 80	70
2378-TCDD-$^{37}Cl_4$	98, 89		95, 95		97, 99	93

a. "--" indicates analyte not detected.

Post-treatment of Pulps Containing Dioxins

The DBD/F spiked pulp described above was chlorinated and extracted with base. The resulting pulp, which should contain enriched levels of PCDD/F, was then treated with three oxygen-based bleaching chemicals (O_2/NaOH, H_2O_2, and O_3). The chlorinated pulp and treated pulps were analyzed for TCDD and TCDF to determine if these commercial electrophilic reagents were capable of destroying TCDD/F. The specific results are presented in Table 3.

The untreated E-stage pulp had a TCDF concentration of ~83 ppt. This relatively low value probably means that significant amounts of TCDF were partitioned from the pulp to the E-stage extract; the spiked pulp began with 10,000 ppt DBF. The TCDF concentration in the O_2/NaOH treated pulp was reduced by approximately 95%, while the reduction in the O_3 and H_2O_2 cases was about 50%. The concentration of TCDD in the untreated E-stage pulp was ~2 ppt; TCDD was not present in the any of the treated pulps at levels above the analytical detection limit of 0.8 ppt. In all samples, the 2,3,7,8-substituted TCDD/TCDF isomers were the major contributors to the total TCDD/TCDF concentrations. Approximately five additional isomers were detected for TCDF; only one additional isomer was present for TCDD.

Table 3. TCDD/F Levels for Post-treatment of Chlorinated Pulp Samples

	Concentration (pg/g)[a,b]				
Sample	Total TCDF	2,3,7,8-TCDF	Total TCDD	2,3,7,8-TCDD	Percent Moisture
Untreated E Stage	84	52	1.1	0.5	81
Untreated E Stage	81	51	2.4	1.1	
O_2/NaOH Treated	3.3	2.1	--	--	85
O_2/NaOH Treated	6.0	4.6	--	--	
O_3 Treated	45	28	--	--	79
O_3 Treated	42	26	--	--	
H_2O_2 Treated	32	20	--	--	79
H_2O_2 Treated	45	27	--	--	
Method Blank	--	--	--	--	NA

a. values are on a wet weight basis
b. "--" indicates analyte not detected above estimated detection limit of 0.8 ppt.

Tetrachlorodioxins and furans were not detected in the method blank processed with these pulp samples, indicating that the samples were not exposed to contamination sources during sample preparation and analysis. Internal standard recoveries for these analyses are presented in Table 4. Recoveries were 79% or greater which indicates efficient extraction of TCDF/TCDD from the pulp matrix and minimal loss of TCDF/TCDD through extract cleanup procedures. Most duplicate results were relatively consistent indicating acceptable analytical precision.

Table 4. Internal Standard Recoveries for Post-treated Chlorinated Pulp Samples

Sample	TCDF-$^{13}C_{12}$	TCDD-$^{13}C_{12}$
Untreated E Stage	102	108
Untreated E Stag	79	85
O_2/NaOH Treated	92	97
O_2/NaOH Treated	98	101
O_3 Treated	113	127
O_3 Treated	110	111
H_2O_2 Treated	95	105
H_2O_2 Treated	88	86
Method Blank	122	139

The results were surprising in that the oxygen treatment appeared to be so much better than ozone. The O_2/NaOH experiment was, therefore, repeated; only this time the starting material was a spiked pulp which had been chlorinated, but not alkali extracted. The results are given in Table 5. The internal standard recoveries for the pulp samples were above 50 percent, indicating efficient removal of the TCDD/TCDF from the pulp matrix. Precision between duplicate results was good. The internal standard recoveries for the effluent sample were low (ca. 10%), while recovery of the cleanup standard was 100 percent. These results suggest that TCDD/TCDF were not efficiently removed from the effluent sample prior to extract cleanup, since analyte losses did not occur in the extract cleanup. The analyte concentrations were corrected for these low recoveries.

The levels found in the repeat were about 45 ppt TCDF and nondetect for TCDD in the pulp (Table 5). These values are similar to what was previously found for ozone and for peroxide. There is a fundamental difference between the level of water present in the ozone, peroxide, and oxygen experiments. For ozone, there was no separation of the reacted pulp from water solvent since there was no solvent. The hydrogen peroxide experiments were done in the presence of 2% NaOH and at 12%

consistency (12% pulp, 88% water); at the conclusion of the experiment, the treated pulp was squeezed to remove moisture (for the determination of residual pH and peroxide) and was also washed with water. The oxygen experiment contains large amounts of 2% NaOH and is equivalent to an extraction of the pulp, meaning that you get an E-stage type pulp. In the repeat experiment, the effluent from the O_2-treatment was also analyzed; 3600 ppt of TCDF and 22 ppt TCDD were observed. The hydrogen peroxide treatment may also have had TCDF and TCDD in its effluent; an analysis was not performed.

Table 5. TCDD/F Levels for Post-treatment of Chlorinated Pulp with O_2/NaOH (Repeat Experiment)

	Cl_2-O_2 Pulp				
	Rep 1	Rep 2	Avg	Effluent	Laboratory Method Blank
Concentration (pg/g)[a,b]					
2378-TCDF	28	34	31	2400	--
Total TCDF	40	49	45	3600	--
2378-TCDD	--	--	--	22	--
Total TCDD	--	--	--	22	--
Recoveries (%)					
2378-TCDD-$^{13}C_{12}$	73	71		6.4	86
2378-TCDF-$^{13}C_{12}$	63	59		9.3	70
2378-TCDD-$^{37}Cl_4$	92	86		100	93

a. values are on a wet weight basis
b. "--" indicates analyte not detected.

The data from this experimental set suggests that post-treatments of pulps containing TCDD/F can lower the PCDD/F pulp contents by about 50% and 100%, respectively. However, some of the TCDD/F is transferred to the effluents, suggesting that a post treatment may not be very effective in destroying PCDD/F.

SUMMARY

Nitrogen dioxide pretreatment of DBD/F spiked cotton linters effectively reduced PCDD/F levels observed after chlorination of the linters; in contrast, O_3 appeared ineffective. However, the O_3 treatment was performed on completely dry linters and was probably ineffective because solvent (water) may be required for efficient transportation of O_3 to reactive sites.

A DBD/F spiked pulp gave extremely low levels of TCDD/F when pretreated with ozone prior to chlorination; an NO_2 pretreatment, followed by chlorination, gave a modest TCDD/F reduction. The result suggests that an ozone bleaching stage before a chlorine/chlorine dioxide bleaching stage may successfully reduce PCDD/F to nondetectable levels.

Post treatments of dioxin-containing pulps with ozone, hydrogen peroxide, and oxygen led to about 50% reductions in TCDD/F. The TCDD/F reduction in the pulp was highest for the oxygen treatment; however, TCDD/F were found in the effluent, and thus it is uncertain whether the treatment destroyed TCDD/F or just redistributed the TCDD/F components.

These research results should provide guidance to the paper industry as changes are made in bleaching technologies to address governmental regulations surrounding the dioxin issue.

EXPERIMENTAL

Ozone-Treatment of Spiked Cotton Linters. A blank was prepared by adding 50 mL of CH_2Cl_2 (Fisher Optima) to 5 g of the linters in a 1 L round-bottom flask. The mixture was evaporated to apparent dryness on a rotary evaporator. The flask was rotated as a stream of nitrogen containing ozone was introduced. The amount of ozone corresponded to 2% of the weight of the pulp. After addition of the ozone, the flask was purged for a few minutes with nitrogen to remove the excess ozone. The treated linters were then placed in an acid-washed, solvent-rinsed jar.

Approximately 23 g of cotton linters and 200 mL of CH_2Cl_2, which contained a fresh dose of 1.4 uL of ≈1 ug/uL stock solution of DBD and DBF in hexane, were placed into a 2000 mL RB. The flask was stoppered and shaken. The slurry was allowed to sit for 2 hours and frequently shaken. The linters were evaporated to apparent dryness on a rotary evaporator and the flask was tightly stoppered. [Confirmation of spike levels by gas chromatographic analysis was not conducted, since there was insufficient sample available; typically half of the spike is lost in this procedure.] Approximately 15 g of spiked linters was ozonated (2% charge) and handled similar to the blank sample.

Nitrogen Dioxide-Treatment of Spiked Cotton Linters. Extracted, dry cotton linters were spiked, as above, with approximately 60 ppb of DBD/DBF. Actual spike levels after solvent evaporation were determined by GC to be 19 ppb of DBF and 17 ppb of DBD for linters. [Dry linters were used in order to optimize the reaction since water will react with NO_2 competitively.] The dry, spiked linters were placed in a flask and brought under vacuum (~25" Hg). Approximately 0.2 g of cold NO_2 was placed in a double stopcock pipette which was connected to a modified rotary evaporator.[4] The NO_2 was expanded, over a 2 min period, into the linters by slowly opening two valves in the apparatus and allowing the vacuum to pull most of the NO_2 into the flask. After 5 min of treatment, the valves were opened to pull in small amounts of air so that the remaining NO_2 would be pulled into the flask and to convert any NO present to NO_2. After 10 minutes of reaction time at room temperature, the excess NO_2 was removed by repeated application of vacuum and N_2 purging. (The control sample also was subjected to the vacuum and N_2 purge sequence).

Chlorination of Spiked Cotton Linters Samples. Three 5 g samples of NO_2-treated linters, two 5 g samples of O_3-treated spiked linters,[4] and two untreated linters samples were chlorinated as before.[3] One spiked NO_2-treated linters (Process Blank) was not chlorinated. The method of chlorination, work up, internal standard spiking, concentration through alumina columns, and analysis was identical to that previously described for the other cotton linters reactions.[3]

Chlorination of NO_2-Treated Spiked Pulp. The DBD/F spiked pulp (30% consistency) was fluffed with nitrogen and 161.4 g (49.5 g oven dry basis) was placed in a 5 L round bottom flask attached to a rotatory evaporator. The pulp was treated with 1.0 g of NO_2, employing the procedure mentioned above. After 10 min reaction time, 664 mL of water was added to the flask and the flask was shaken for 1 min. The flask was emptied, along with 412 mL of rinse water. The pulp, now at 4% consistency was stirred, filtered (vacuum applied for 6 hours), fluffed, and sealed under nitrogen. The whole sample was chlorinated, using the same conditions as are described for the chlorination of DBD/F spiked pulp.[3]

Chlorination of O_3-Treated Spiked Pulp. The DBD/F spiked pulp (31% consistency) was fluffed with nitrogen and 160 g (50 g oven dry basis) was washed with acetic acid to pH 3 and placed in a round bottom flask attached to a rotatory evaporator. The pulp was treated for 12.5 min with an oxygen stream containing ozone. Based on the o. d. weight of pulp, 2.1% was applied, 1.8% was consumed. The final pH was 3.2 and the final kappa number was 5.9. The chlorination of 40 g of this pulp was performed as described below, except less chlorine was applied since the pulp contained less lignin. The chlorine level was 1.18% (0.2 kappa factor). The conditions were 30 min at 45°C at 3% consistency, with a final pH of 2.2.

Chlorination of DBD/F Spiked Pulp. A solution of methanol, containing known small amounts of DBD and DBF, was slowly dripped in a stirred slurry of unbleached commercial softwood kraft (kappa number of 27.9) in a large volume of water (low consistency conditions); the ratio of water to methanol was high. The pulp was allowed to stand for a couple of hours and then was filtered and washed with water. The pulp spike level was calculated be 0.2 ppb DBD and 10 ppb DBF, if all the DBD/F stayed with the pulp. The chlorination was performed for 30 min at 45°C on the equivalent of 110 g oven-dry pulp, at 3% consistency, with 5.6% chlorine (0.2 kappa factor). The final pH was 2.2 and no chlorine remained.

Oxygen Treatment of Chlorinated, DBD/F Spiked Pulp. An oxygen bleach of 220 g of the chlorinated pulp described above was performed under the following conditions: 12% consistency, 2% NaOH (added at 110°C), 30 min at 110°C, and 100 psi oxygen pressure. The reactor was cooled for 2.5 hours before releasing the pressure at 35°C; the final pH was 10.9. The pulp was filtered and washed. In one of two oxygen experiments performed, the aqueous filtrate was collected and roughly 50% (870 mL) was analyzed for TCDD/F. The pulp effluent was spiked with TCDD/TCDF-$^{13}C_{12}$ internal standards, transferred to a 1-L separatory funnel, and extracted with three 60-mL portions of CH_2Cl_2. The resulting extract was dried over anhydrous sodium sulfate and concentrated to approximately 5 mL using K-D techniques. The effluent extract was then processed through acid/base washing, acid/base silica column cleanup, alumina column cleanup, and carbon column cleanup in an identical manner as previous pulp sample extracts.[3] The pulp was analyzed for TCDD/F similar to the other pulp samples.

Ozone Treatment of Chlorinated Pulps. The ozone treatment of 30 g (o.d. basis) of acetic acid washed (to pH 3) DBD/F spiked chlorinated pulp was done at a 1% level (1.04% applied, 1.01% consumed) for 3.5 min using the conditions described for ozonation of the unchlorinated pulp. The final pH was 3.5.

Hydrogen Peroxide Treatment of Chlorinated Pulps. The DBD/F spiked chlorinated pulp and chemicals were mixed for 1 min and then sealed in a plastic bag and heated at 60°C for 90 min. The treatment was done at 12% consistency with 30 g of o.d. basis pulp, 2% H_2O_2, 2% NaOH, and 0.05% $MgSO_4$. The residuals were: 0.09% H_2O_2, 1.18% NaOH, and pH 11.5.

Analysis of Pulp Samples for Chlorinated DBD/F. Triplicate samples of each pulp were prepared for analysis. Approximately 10 g of pulp was removed from the bulk sample and transferred to a Soxhlet apparatus thimble along with 60 g of anhydrous $NaSO_4$. The pulp samples were spiked with the following internal standards: 2 ng of 2,3,7,8-TCDD-$^{13}C_{12}$ and 2 ng of 2,3,7,8-TCDF-$^{13}C_{12}$. The pulp samples were extracted for approximately 18 hours with benzene in Soxhlet apparatus. The resulting pulp extracts were concentrated to approximately 5 to 10 mL using K-D techniques. After the addition of 0.8 ng of 2,3,7,8-TCDD-$^{37}Cl_4$ cleanup standard, the samples underwent acid/base washing, acid/base silica, alumina, and carbon column cleanup. A recovery standard, 4 ng of 1,2,3,4-TCDD-$^{13}C_{12}$, was added immediately before analysis. Samples were analyzed by high resolution gas chromatography/ mass spectroscopy for 2,3,7,8-TCDD/F, total TCDD/F, and DBD/F-Cl_x ($x = 0$-4), using previously described procedures.[3]

ACKNOWLEDGEMENTS

Financial support was provided by the Chlorine Institute. We would like to thank the assistance of Amy Malcolm, Kyle Reed, and Alexander Shakhet at the Institute of Paper Science and Technology for performing the pulp bleaching reactions involving chlorine, oxygen, nitrogen dioxide, and hydrogen peroxide.

REFERENCES

1. Address correspondes to this author

2. Present address is Automotive Testing Laboratory, P.O. Box 289, East Liberty, OH 43319.

3. D. R. Dimmel, K. B. Riggs, G. Pitts, J. White, and S. Lucas , Envir. Sci. Technol., submitted, March 1993.

4. L. B. Sonnenberg and D. R. Dimmel, Envir. Sci. Technol., accepted, 1993.

5. L. B. Sonnenberg and D. R. Dimmel, Tappi J., submitted, March 1993.