Method and sample-related problems in the determination of AOX in effluents

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ABSTRACT

The effects of various analytical parameters including shaking time, number of adsorptions, quantities of granular activated carbon and nitrate, and the total volume of water used during adsorption of C- stage effluents on shaker AOX results were investigated. The authors conducted column and shaker AOX analyses of low and high molecular weight AOX fractions in C-stage and E-stage effluents and on several model compounds. Results show that the shaker method poorly recovers low molecular weight AOX but quantitatively recovers high molecular weight AOX. Considerably better recoveries of low molecular weight AOX were obtained using the column method.

Application:

Improvement of AOX determination in effluents is possible with selection of proper analytical technique, storage conditions, and preservation techniques.

Several recent studies have demonstrated that Adsorbable Organic Halogens (AOX) present in bleached kraft mill effluent (BKME) correlates poorly with acute or chronic toxicity to aquatic organisms *(1)*. In addition, AOX is a poor indicator of the bioaccumulable potential or persistence of the organochlorine compounds that comprise AOX *(2)*. Despite these findings, governments in many countries including Canada, the United States, Scandinavia, and Germany have imposed or are likely to impose limits on the amount of AOX discharged from kraft mills into receiving waters *(2–5)*. It therefore is very probable that the AOX assay will continue to be used for monitoring organochlorine levels in the effluents from mills using chlorine compounds for bleaching.

The last decade has seen the development of several methods and instruments for determining AOX present in water and wastewaters *(6–12)*. All AOX methods advocate the use of the shaker or batch procedure or the column procedure. For example, the German and Scandinavian standard methods *(7, 8)* specify the use of the shaker method exclusively. The CPPA and Environment Canada methods *(11, 12)* allow the use of either shaker or column method for AOX analysis.

In an earlier report *(13)*, we showed that shaker AOX results for C-stage effluents from four kraft mills were on average approximately 22% lower than the corresponding column method results. In contrast, AOX results for E-stage and final mill effluents obtained by both AOX methods were in good agreement. LaFleur *et al. (14)* reported similar trends, but they gave no explanation for the discrepancy. We have also observed significant differences between shaker and column AOX results for sulfite mill effluents. AOX values by both methods decreased with increasing amounts of sample used for adsorption.

Investigators have reported several interlaboratory comparisons of AOX methodologies in North America *(15, 16)* and in Europe *(7, 17, 18)*. These studies varied widely in scope. In some studies, "stabilized" final mill effluents were examined, while in others, "stabilized" chlorination and both treated and untreated effluents were used. The results indicate that the reproducibility of the AOX methods can vary considerably *(7, 15, 16)*. It is likely, however, that some of the variability may have been due to method and sample-related factors not recognized at the time. In addition, all the official methods specify several sample treatments including pH adjustment, refrigeration, freezing, and addition of sulfite. These aim to stabilize AOX during storage. Because of the limited number of studies reported to date on the effectiveness of such preservation techniques *(17–19)*, however, there is still considerable uncertainty about which conditions are most appropriate for storing effluents to minimize AOX loss.

Suspended solids contribute to the total AOX in the effluent. Some methods such as the American Public Health Association (APHA) standard specify filtration of samples before analysis. This can cause a significant decrease in AOX results *(16)*.

In this work, we have examined the effect of several analytical parameters on the shaker AOX results. We performed AOX analyses by both methods on original effluents and on low (AOX<1000) and high (AOX> 1000) molecular weight fractions and on model organochlorine compounds to determine whether the AOX methods poorly recover certain classes of compounds. Our work also assessed the effect of storage conditions and preservation techniques on AOX stability. We provide several recommendations based on these results for maintaining the integrity

of samples and reducing the variability in AOX measurements.

EXPERIMENTAL

Sample collection

The AOX studies included samples from five eastern Canadian fully bleached kraft mills. Table I summarizes specific information regarding mill operating conditions. For studies on AOX methodology, we collected grab samples of approximately 4 L of first bleaching stage. Samples were designated in the text by the terms chlorination stage or C-stage regardless of the ClO_2 substitution used in bleaching and extraction stage (E-1) effluents from mills A and B. Samples were stored in polyethylene containers at 4°C and at ambient pH in the dark for the duration of the investigation. For AOX stability studies, we collected approximately 4-L grab samples of C_1 and E_1 effluents and final BKME from mills C, D, and E. In addition, we used a sample of unbleached kraft pulp from mill A in laboratory scale bleaching experiments.

Laboratory bleaching and extraction of kraft pulp

The pulp from mill A was first washed thoroughly with deionized water to remove entrained weak black liquor followed by centrifuging and fluffing before kappa number measurement and bleaching. Approximately 125 g o.d. portions of washed pulp [kappa number 31.4 and cupriethylenediamine (cuene) viscosity of 29.7 mPa·s] were then bleached by simultaneous addition of various proportions of ClO_2 and Cl_2 (D_{100}; $D_{70} + C_{30}$; $D_{50} + C_{50}$; C_{100}) at 50°C and 3.5% consistency for 30 min. The total available chlorine charge used in each chlorination was based on a chlorine multiple of 0.22. All bleached pulps underwent extraction with NaOH (3.45% based on o.d. pulp) at 70°C and 10% consistency for 60 min. Chlorination and extraction liquors were isolated by filtering the pulp slurry through a 150-mesh stainless steel screen. Effluents were stored in polyethylene containers as described previously. We determined the stability of AOX in effluents from laboratory chlorinations using 50%, 70%, and 100% ClO_2 substitution within 30 min of generation unless specified otherwise and at regular intervals after that using the column AOX method *(11)*. Sample storage between analysis was at 4°C.

Mill	Wood furnish	Bleaching sequence	ClO_2 substitution, %	Effluent treatment*
A	Softwood	D Eop D E D	100	1° and 2°
B	Hardwood	Cd Eo H Dp	50	1° and 2°
C	Hardwood	Cd E D E D	45	1°
D	Softwood	Cd Eo D E D	50	1°
E	Hardwood	Cd Eo H D E D	10	1° and 2°

* Primary treated = 1° and secondary treated = 2°

I. Summary of mills sampled and their respective operating conditions

AOX stability studies

The effects of storage temperature (4°C and 25°C), time (1 h to 9 weeks), pH (ambient pH and pH 2), and residual Cl_2/ClO_2 (C-stage effluents only) on the stability of AOX in the various effluents from mills C, D, and E were studied. All samples were split into two equal portions at each mill after collection. One portion of each sample received no reagents. Table II outlines the various treatments of the remaining aliquot. Both sets of samples were then stored at 4°C and 25°C. All chlorination effluents were tested for residual Cl_2/ClO_2 at the same collection time using KI and starch indicator. Sufficient Na_2SO_3 was added to destroy residual Cl_2/ClO_2 in one portion of these samples. This gave a positive result with the iodine-starch test. Initial AOX adsorptions were performed on each sample in duplicate on site within one hour of sample collection using the column method. Samples and adsorbates were stored in the dark in sealed vials and transported to Paprican on the same or following day for storage and AOX analyses.

AOX analyses

For studies on AOX methodology, samples were analyzed by the column and shaker methods *(11)*. Samples used in AOX stability studies were analyzed exclusively using the column method. All samples were stirred continuously during sampling for AOX analysis. A Dohrmann TOX analyzer was used to quantify AOX. Granular activated carbon (GAC) and powdered activated carbon (PAC) were purchased from Rosemount Analytical Inc., Santa Clara, CA, and Euroglass BV, Delft, The Netherlands, respectively. All column and shaker AOX analyses used GAC unless specified otherwise.

Ultrafiltration

The ultrafiltration (UF) apparatus consisted of an Amicon model 8400 stirred cell of 400-mL capacity, concentration and dialysis valve (CDS 10), and reservoir (RS4). The AOX in 100-mL aliquots of C-stage and E-stage effluents were fractionated using an Amicon YM1 membrane (76-mm diameter, effective area of 41.8 cm^2, and apparent molecular weight cut-off of 1000 Daltons) at 276 kPa (N_2) and 4°C. Water contained in the RS4 reservoir was added continuously to the cell during UF so the volume of sample remained constant. The water used in UF studies was adjusted to pH 2 with HNO_3 for C-stage effluents to avoid alkaline hydrolysis of AOX or

Effluent	pH*		Temperature, °C		Residual** Cl_2/ClO_2	
	2	Ambient	4	25	With sulfite	Without sulfite
C-stage	–	√	√	√	√	√
E-stage	√	√	√	√	–	–
BKME***	√	√	√	√	–	–

* Samples adjusted to pH 2 with concentrated HNO_3
** Test for residual chlorine/chlorine dioxide performed using KI and starch
*** Effluent from outlet of primary or secondary treatment system

II. Summary of sample treatments used in the AOX stability study

Sample origin	ClO_2 used in chlorination stage, %	Ratio of shaker to column AOX
	C-stage effluents	
Mill A	100	0.82
Mill B	50	0.82
Mill B[1)]	NA	0.67
Mill D[1)]	NA	0.77
Laboratory	100	0.84
Laboratory	50	0.80
Laboratory	0	0.85
Interlaboratory AOX study[2)]	NA	0.66
	E-stage effluents	
Mill A	100	0.93
Mill B	50	0.93
Mill B[1)]	NA	0.94
Laboratory	100	0.91
Laboratory	50	0.96
	BKME	
Mill B	50	1.03
Mill B[1)]	NA	1.01
Interlaboratory AOX study[2)]	NA	1.01
Interlaboratory AOX study[2)]	NA	0.92

1) Samples from reference 13
2) Source of interlaboratory samples is confidential
NA = not available

III. Comparison of AOX results obtained for laboratory and mill-generated C-stage, E-stage, and final mill effluents using standard shaker and column AOX methods

to the pH of the E-stage sample using 0.1*M* NaOH. All UF proceeded until a total of 600 mL of filtrate had been collected. Retentates (AOX > 1000) and permeates (AOX < 1000) were stored at ambient pH and 4°C until AOX analyses were performed.

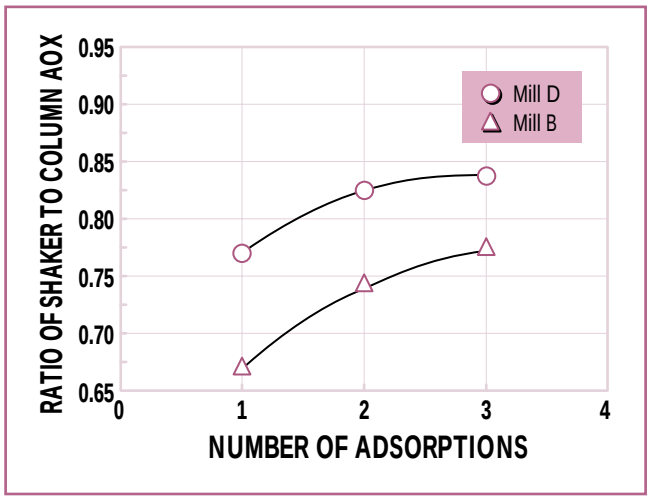
Model compounds used in AOX recovery experiments

The following chlorinated organic compounds were used in AOX spike-recovery experiments: Monochloroacetic, dichloroacetic, and tricholoroacetic acids; 1-chloroacetone, 1,3-dichloroacetone, and 1,1,3,3-tetrachloroacetone; and 2-chlorophenol and 2,4,6-trichlorophenol. All reagents were more than 99% pure and came from Aldrich, Milwaukee, WI. Stock solutions of each compound were prepared in methanol to give a total chlorine concentration of 10 g/L. An aliquot of each stock solution was then further diluted with methanol to obtain a 1 µg/µL solution for use in the spike-recovery experiments. The recovery of each model compound was assessed by spiking 50-mL aliquots of deionized water with 10 µL (10 µg Cl) of each solution followed by AOX analyses of the spiked samples using the column and shaker methods.

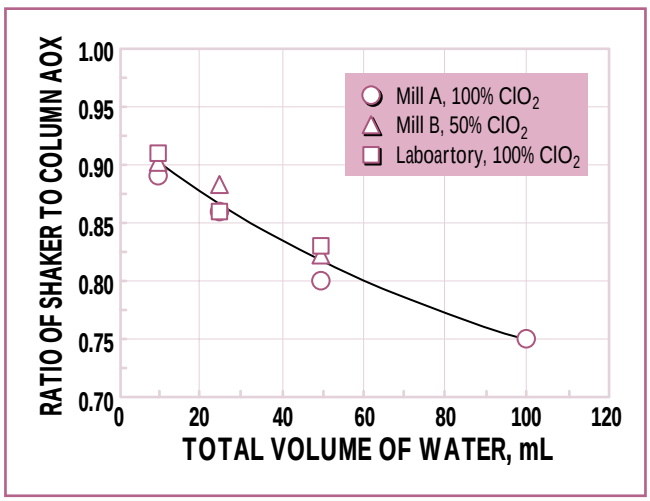
RESULTS AND DISCUSSION

Comparison of shaker and column methods

Table III shows a comparison of AOX results for several types of samples using the shaker and column methods *(11)*. As indicated, the discrepancy between the two methods is greatest for C-stage effluents and least significant for BKME samples. The extent of the discrepancy for C-



1. Effect of the number of adsorptions used in the shaker AOX method on the recovery of organic halogen from mill C-stage effluents obtained from an earlier study **(13)**



2. Effect of the volume of water used during adsorption on the shaker to column AOX ratio

stage effluents appears unrelated to the level of chlorine dioxide substitution.We initially considered several factors to explain this discrepancy, including:

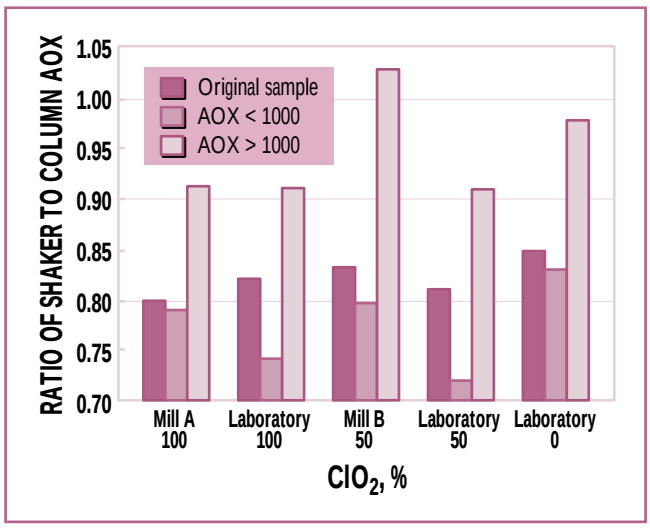
- Desorption of shaker AOX from GAC during the nitrate washing step
- Elevated column AOX results resulting from incomplete removal of inorganic halide during the nitrate wash step
- Incomplete recovery of specific compounds during shaker adsorption.

Effluent	ClO_2 used in the chlorination stage, %	Percent of total AOX AOX <1000	AOX >1000	Recovery of AOX from UF step, %
		C-stage effluents		
Mill A	100	88	13	101
Laboratory	100	87	13	100
Mill B	50	77	22	98
Laboratory	50	78	23	97
Laboratory	0	77	23	100
		E-stage effluents		
Mill A	100	68	32	100
Mill B	50	54	46	97

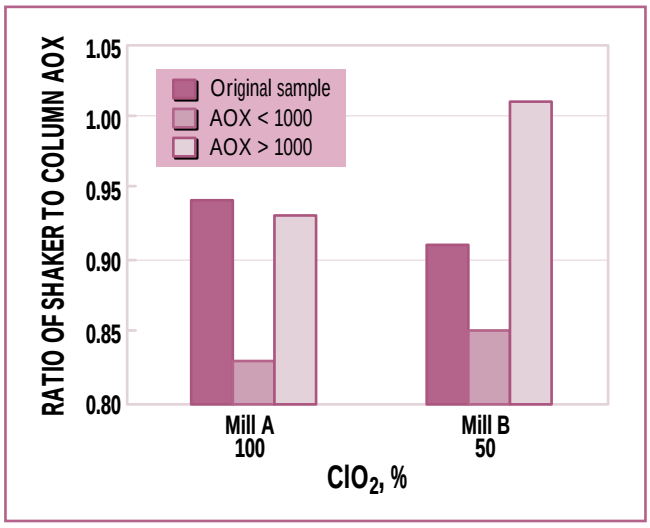
IV. Molecular weight distribution of AOX in mill and laboratory-generated C-stage and E-stage effluents

It is unlikely, however, that the first two factors play a significant role, since AOX results obtained for E-stage and BKME samples using both methods agree well. It appeared therefore that incomplete recovery of specific compounds or classes of compounds was the most likely cause for the low AOX results obtained by the shaker method. To test this hypothesis, we determined the effect of various analytical parameters on the shaker AOX results including amount of nitrate, shaking time and successive adsorptions, volume of water used during adsorption, and quantity and type of GAC or PAC. Varying both the shaking time from 15 min to 2 h and the quantity of nitrate used in the adsorption step from 0.2–1.0 g/g GAC produced no significant effect on AOX recovery. In contrast, parameters such as the number of adsorptions and the quantity of GAC had a significant impact.

Effect of successive adsorptions. The effect of repetitive adsorptions on the shaker AOX result for C-stage effluents was assessed with samples from mills B and D obtained during an earlier study *(13)*. Initial shaker AOX analyses were carried out in the usual way. The filtrates from the initial adsorptions were then collected in flasks containing additional GAC—equivalent to the amount used in the initial adsorptions. The flasks were then agitated for 1 h. At the end of the second adsorption period, the GAC was filtered off and combusted while any remaining organic halide in the filtrates was adsorbed a final time as described



3. Variation in the ratio of shaker to column AOX with fractions obtained from the UF of laboratory and mill-generated C-stage effluents



4. Variation in the ratio of shaker to column AOX with fractions obtained from the UF of mill-generated E-stage effluents

Compound	Recovery of chlorine, %		Ratio of shaker to column AOX
	Shaker method	Column method	
Chloroacetic acid	33.5	93.5	0.36
Dichloroacetic acid	67.1	96.4	0.70
Trichloroacetic acid	84.6	96.1	0.88
1-Chloroacetone	36.8	95.6	0.39
1,3-Dichloroacetone	91.5	96.6	0.95
1,1,3,3-Tetrachloroacetone	91.6	96.5	0.95
2-Chlorophenol	100	98.8	1.01
2,4,6-Trichlorophenol	91.8	96.7	0.95

V. Recovery of model organohalogens from water using standard shaker and column AOX methods

above. Using this sequential adsorption scheme, three adsorptions were carried out on each sample and the blank. Each sample was also analyzed using the column method.

As Fig. 1 shows, the recovery of organic halogen by the shaker method expressed as the ratio of shaker to column AOX increased with increasing number of adsorptions for both samples. It reached an approximately constant value after three adsorptions. Even after three adsorptions, however, the shaker results for mills B and D were about 25% and 15% lower, respectively, than those obtained using the column method. These results strongly suggest that a certain portion of the organic halogen in C-stage effluents has a relatively low affinity for the GAC. It therefore is not possible to recover it using the standard shaker method.

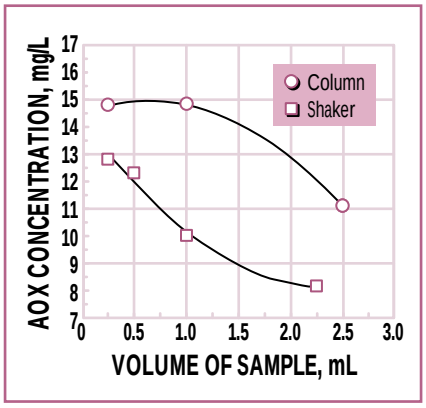
Effects of the water to GAC ratio on shaker AOX results for C-stage effluents. We assessed the effect of the ratio of water to GAC used during the shaker adsorption step using laboratory and mill C-stage effluents from mills A and B. The water to carbon ratio varied from 10 to 100 mL per 40 mg GAC for each sample by the addition of appropriate volumes of pH 2 water. In each case, adsorptions were performed using a fixed volume of dilute sample with a constant volume of nitrate solution and a fixed mixing time. As Fig. 2 indicates, the volume of water present during the shaker adsorption step has a significant impact on the shaker AOX result. For example, decreasing the total volume of water from 100 mL to 10 mL for the mill A sample increased the shaker to column ratio from 0.76 to 0.89. There were similar trends for the other two samples.

Standard AOX methods specify diluting samples to a final volume of 50 to 100 mL before the adsorption step. From our findings, this could lead to low recoveries and could partially explain the variability in AOX results observed in interlaboratory studies. As the total volume of water decreases, a closer agreement with column results occurs. It also appears that the level of ClO_2 substitution has little effect on the extent of agreement between the methods. These results suggest that reducing the volume of water used in the

Storage time, days	AOX conc., mg/L		Storage time, days	AOX conc., mg/L	
	With sulfite	Without sulfite		With sulfite	Without sulfite
	4°C			25°C	
0	129	126	0	129	126
2	118	121	1	120	119
7	118	119	4	ND	120
15	117	119	8	117	122
22	120	120	17	110	119
29	120	117	23	108	114
37	122	119	30	106	112
			38	104	108
			65	99	102

ND = not determined

VI. Effects of sodium sulfite, storage temperature, and time on AOX in C-stage effluent from mill C



5. Effect of sample loading on the AOX results for a Canadian bleached sulfite mill effluent using the standard column and shaker AOX methods

adsorption step can shift the equilibrium between the poorly adsorbed organic halogen in the aqueous and carbon phases toward carbon. We also studied the effect of carrying out a standard shaker adsorption under pressurized conditions (276 kPa using N_2) using the same three samples. These conditions closely approximate the pressure applied during column adsorptions. This approach produced no improvement in shaker AOX results, however.

Effect of the quantity of GAC. Using the previous results, we thought that an increase in the quantity of GAC used for adsorption would have the same effect as reducing the volume of water. We therefore analyzed samples of C-stage effluents from mills A and B and laboratory scale bleaching using 100% ClO_2 by the standard shaker method except using two quantities of GAC (40 mg and 80 mg, respectively) and maintaining the total volume of water constant at 25 mL. Doubling the quantity of GAC from the recommended 40 mg to 80 mg approximates the total quantity of GAC used in the column method. As expected, the ratio of shaker to column AOX improved considerably from 0.82 to 0.84 (40 mg GAC) to 0.92 to 0.95 (80 mg GAC).

UF of effluents. Results so far suggest that certain compounds present in C-stage effluents have a poor affinity for the GAC. We thought that the low molecular weight material that is more abundant in C-stage effluents might be responsible for the low recovery of organic halogen. We assessed this hypothesis by fractionating laboratory generated and mill C-stage and E-stage effluents into low molecular weight (AOX < 1000) and high molecular weight (AOX > 1000) fractions. Then we determined the AOX content of the ultrafiltered samples by both column and shaker methods.

Table IV shows the molecular weight distribution of AOX in various effluents using the column method. As indicated, AOX in C-stage samples from both mill and laboratory scale bleaching using 100% ClO_2 substitution contains 87–88% of low molecular weight organohalogens. In contrast, samples generated by using 0% and 50% ClO_2 contain 77–78% low molecular weight organohalogens. The differences in the molecular weight distribution may arise from bleaching with high levels of ClO_2, which may produce more oxidized and consequently more polar and hydrophilic organic halogens. Note that the high percentage of AOX below 1000 in C-stage effluents is in marked contrast to the levels reported by Österberg and Lindström *(20)*. Jokela and Salkinoja-Salonen *(21)* have recently demonstrated, however, that the distribution of AOX in BKME strongly depends on the dilution of the wastewater at the time of filtration. They found that the percentage of AOX below 1000 increased from approximately 30% to nearly 60% simply by diluting the sample 1:1 and 1:100, respectively, with water before UF. The authors contend that the observed variability in the UF results may be due to the dissociation of organic complexes (disruption of micelles) upon sample dilution.

Under the conditions used in our UF studies, a gradual dilution of the original sample occurs. High molecular weight organic complexes may be dissociating upon dilution to form low molecular weight aggregates as described by Jokela and Salkinoja-Salonen *(21)*, which can then pass through the UF membrane.

The molecular weight distribution of AOX in E-stage effluents is quite different from C-stage effluents taken from the same mills. As Table IV shows, effluents derived from extracting pulps bleached with 50% and 100% ClO_2 contained 54% and

Time elapsed since sample generation	AOX Concentration, mg/L		
	50% ClO_2	70% ClO_2	100% ClO_2
Hours			
1	96.8	-	48.7
2	-	-	50.3
4	-	63.7	50.0
5	94.0	62.1	49.6
6	-	-	49.4
Days			
1	-	61.8	50.7
2	-	61.2	47.0
4	-	60.3	49.8
5	97.9	-	-
12	-	61.2	-
15	89.8	-	48.6
21	91.9	-	-
25	-	-	47.2
69	86.0	-	-
76	-	57.0	-
139	-	-	42.4

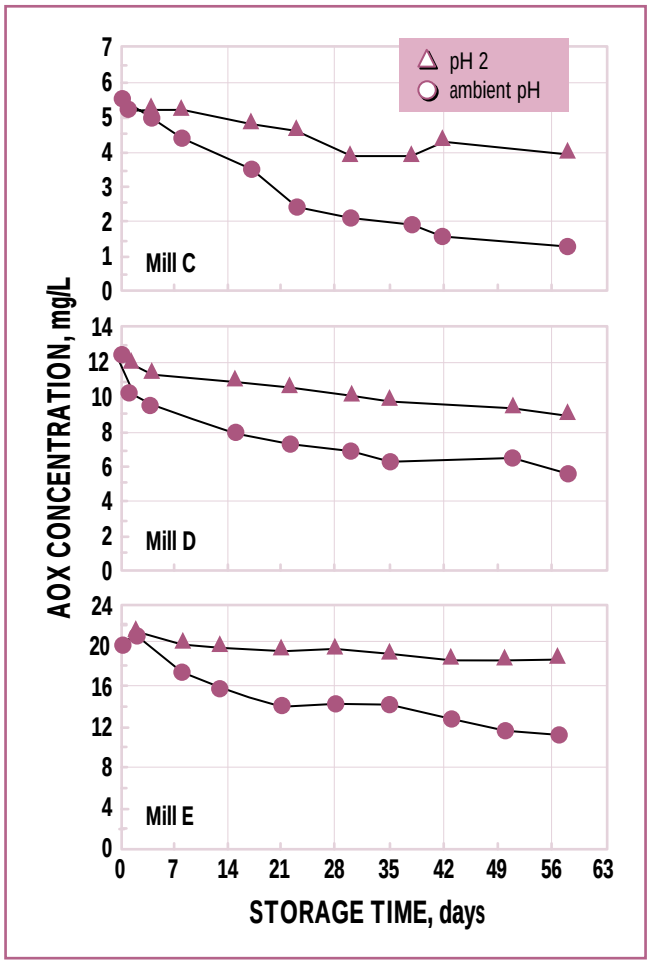
VII. Variation in AOX concentration of laboratory-generated chlorination effluents from bleaches using 50%, 70%, and 100% ClO_2 substitution

68% low molecular weight AOX, respectively. As in C-stage effluents, AOX below 1000 is more abundant in the 100% than in the 50% substitution sample. The last column in Table IV shows the recovery of AOX from each UF ranged between 97% and 101%. This indicates essentially quantitative recovery of the AOX present in the original sample.

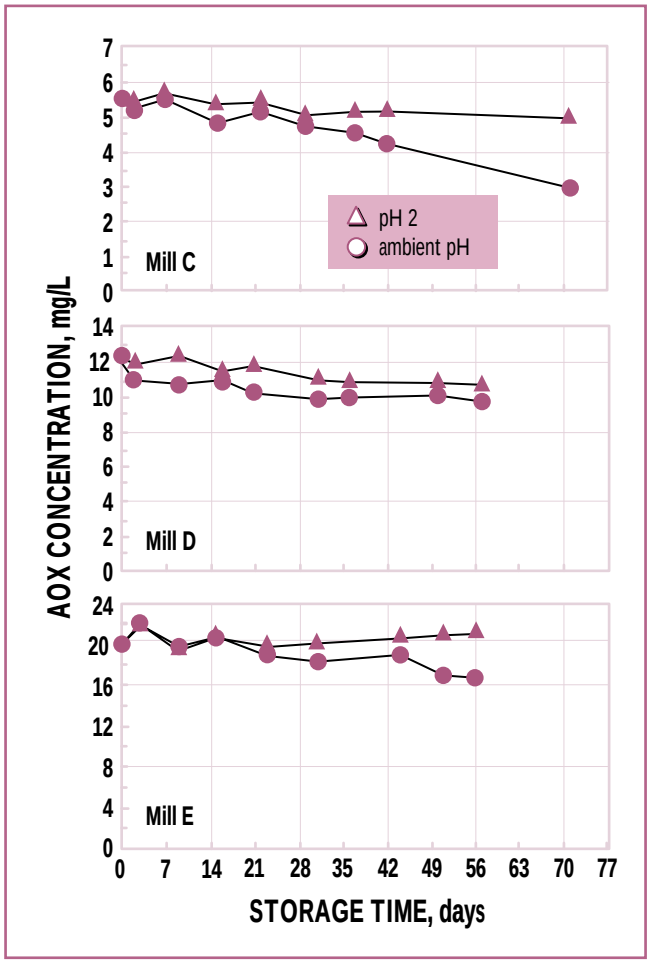
Effect of molecular weight on the recovery of organic halogen. We assessed the effect of molecular weight on the recovery of organic halogen by determining AOX in the original and fractionated samples of C-stage effluents listed in Table IV using both methods. As Fig. 3 indicates, the shaker to column AOX ratio is much closer to 1 for the AOX above 1000 fractions. As expected, the AOX below 1000 fractions have a lower ratio than the original sample. They range between 0.7–0.8. Similar results occurred with E-stage effluents as Fig. 4 shows. The ratio of shaker to column AOX ranged between 0.9 and 0.95 for the original samples but was much lower for AOX below 1000 fractions. The AOX ratio for AOX above 1000 fractions was equal to or better than that obtained for the original sample. These results suggest that low molecular weight AOX, regardless its origin, is poorly recovered during the shaker method.

Recovery of model compounds. Since AOX below 1000 is so poorly recovered compared to AOX above 1000, we next investigated the extent to which we could recover several low molecular weight model organochlorine compounds known to exist in bleached pulp mill effluents *(22)* from aqueous solutions using both standard shaker and column AOX methods.

As Table V shows, we obtained greater than 93% recovery of chlorine for all compounds using standard column AOX conditions. In contrast, recoveries of the same compounds using standard shaker AOX conditions were much lower for monochloroacetic and dichloroacetic acids (approximately 34% and 67%, respectively) and chloroacetone (approximately 37%). We obtained recoveries of approximately 92% for the remaining compounds except trichloroacetic acid (85% recovery) and 2-chlorophenol (100% recovery) using the shaker method. These results indicate that polar, low molecular weight, relatively hydrophilic organic halogens are poorly recovered using the standard shaker AOX analysis conditions. This may partly explain the low recoveries of AOX below 1000 observed for both C-stage and E-stage samples. We expect that samples with the most abundant quantities of these compounds will exhibit the poorest agreement between shaker and column AOX results.



6. Effects of pH and storage time on AOX in samples of BKME from Mills C, D, and E stored in the dark at 25°C



7. Effects of pH and storage time on AOX in samples of BKME from Mills C, D, and E stored in the dark at 4°C

Sulfite mill effluents. AOX results for combined bleached kraft mill effluents obtained by column and shaker methods generally agree to within 5–10% of each other *(13–17)*. During our studies, however, we have found poor agreement between column and shaker AOX results for a combined mill effluent from a bleached sulfite mill. In addition, AOX results obtained by both methods decreased significantly with the amount of sample loaded onto the GAC.

As Fig. 5 illustrates, the AOX results for the effluent sample obtained by the shaker method at each level of sample loading were always lower than the corresponding column AOX result. For example, the ratio of shaker to column AOX varied from 0.85 with the 0.25-mL sample to approximately 0.67 for the 2.25-mL sample used for the analysis.

Using the column method, the percentage of total AOX recovered in the second column increased with increasing sample volume. The breakthrough of organic halogen into the second column was 5.8%, 21%, and 26% of the total for 0.25 mL, 1.00 mL, and 2.50 mL of sample, respectively. Less than 10% of the total AOX should ideally occur in the second column. The reasons for the discrepancy in AOX results may be partly due to the incomplete recovery of hydrophilic, low molecular weight AOX components such as chlorinated sulfonic acids, which may be quite abundant in sulfite effluents. The problem of breakthrough seems particularly severe for effluents from this type of process. To our knowledge, kraft mill effluents do not exhibit this problem. Further evidence for this conclusion recently came from examining the column AOX results of a nationwide survey of AOX in bleached pulp mill effluents from Canadian mills conducted by CPPA *(23)*. Average recovery of AOX in the second column was about twice as high for sulfite mill effluents as for kraft mill effluents. The high level of organic halogen found in the second

column may be due to overloading of the first column by nonchlorinated, relatively hydrophobic substances such as high molecular weight lignosulfonic acids that may have a higher affinity for the limited adsorption sites on the GAC.

Stability of AOX during sample storage

The effluents from the various bleaching streams of pulp and paper mills vary widely in the type and concentration of organohalogens present, pH, ionic strength, total organic carbon (TOC) content, and microbial populations. Some AOX in the various streams significantly degrades under alkaline conditions. A large portion of AOX is unstable in the presence of the indigenous and varied microbial populations present in the various mill effluents. There is little information about the rate and extent of degradation of AOX in the commonly tested effluents under ambient or other storage conditions, however. In this work, we monitored the AOX concentration in effluents from three bleached pulp mills stored under various conditions for up to 9 weeks. In addition, we followed the concentration of AOX in several laboratory generated effluents—50%, 70%, and 100% ClO_2 substitution—to evaluate the potential effects of high ClO_2 substitution on AOX stability.

Stability of AOX in mill and laboratory C-stage samples. Table VI summarizes the effects of storage time, temperature, and sodium sulfite on AOX levels in the C-stage effluent from mill C. All AOX results were obtained using the column method. The initial 4–8% drop in AOX results for all samples over the first 1–2 days may be due to the degradation of particularly unstable AOX or the loss of volatile species such as chloroform during sampling of the effluent for AOX analyses. As indicated, sulfite had little effect on AOX stability suggesting that the addition of sulfite to remove residual chlorine and chlorine dioxide is unnecessary. At 4°C, the AOX concentration remained approximately constant over the study period. Samples stored at 25°C for 3 to 4 weeks exhibited a larger decrease in AOX than for samples stored for the same period at 4°C.

We observed similar trends for samples from mills D and E. These results indicate that C-stage effluent AOX is stable for up to 6 weeks provided samples are stored in the dark at 4°C and AOX is neither generated nor degraded in samples containing residual bleaching reagents. In our study, we monitored the stability of AOX in laboratory generated C:D-stage (30:70, 50:50) and D-stage (100) bleaching effluents by determining AOX concentrations using the column method hourly after sample production and for several days after that. Samples were stored in the dark at 4°C between daily analyses. As Table VII indicates, AOX concentrations were essentially constant in all effluents up to 3 weeks after sample generation. In the table, all AOX results were obtained using the column method. It therefore appears that substitution has a negligible impact on the stability of AOX present in the effluent.

Stability of AOX in mill E-stage samples. The results of the study of the effect of pH on AOX levels in E-stage effluents of mills C, D, and E indicated that AOX is about equally stable for periods of up to 9 weeks in samples stored at pH 2 and ambient pH and at 4°C or 25°C. A significant quantity of precipitate (probably largely chlorolignin) formed in samples adjusted to pH 2, however. These results indicate that pH adjustment of E-stage effluents is unnecessary and should be avoided to prevent precipitation of chlorolignin. In addition, AOX stability was not enhanced for samples stored at 4°C. Samples destined for AOX analysis may therefore be shipped or stored in the dark at ambient pH and 25°C without experiencing significant AOX losses for up to 9 weeks.

Stability of AOX in BKME samples. Figures 6 and 7 show the effects of pH, storage time, and temperature on AOX levels in BKME samples from mills C, D, and E, stored at 25°C and 4°C, respectively. A much larger drop in AOX occurs in all BKME effluents stored at 25°C and ambient pH than in samples stored at pH 2. For example, AOX decreased by approximately 50% in mill C effluent after three weeks storage at 25°C compared to a 13% decrease for the sample stored at pH 2. The most stable samples were those stored at 4°C and pH 2. It is interesting that all BKME samples exhibited similar AOX stability, although only mill E had a secondary treatment system.

The experimental evidence obtained thus far suggests that simply adjusting the pH of the effluent to approximately 2 with nitric or sulfuric acid and storing the sample at 4°C can very effectively stabilize the AOX in BKME samples. As is evident in Fig. 7, samples stored in this manner were stable for up to 9 weeks. The enhanced stability of AOX in BKME samples stored at pH 2 is likely due to the inhibition of bacterial growth or the inactivation of bacterial enzymes by the high acidity.

CONCLUSIONS

The discrepancy between shaker and column AOX results particularly for C-stage effluents that are rich in AOX below 1000 is due to poor adsorption by the shaker method of low molecular weight organohalogens present in kraft or sulfite samples. The column method appears better suited for samples containing high levels of these compounds as evidenced by the recovery of model organohalogens. The generally good

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agreement between column and shaker methods for E-stage and final mill effluents is due to the lower percentage of AOX below 1000 present in these samples. Much of the discrepancy in interlaboratory AOX data particularly for C-stage effluents may be partly due to factors identified in this work. Reducing the volume of water or increasing the quantity of GAC used during adsorption by the shaker method can considerably improve the agreement between both AOX methods. We recommend performing analyses at several dilutions on samples analyzed for the first time to determine the effect of sample loading on the AOX result.

To minimize AOX degradation, all samples must be refrigerated immediately after collection. No other precautions are necessary for C-stage and E-stage effluents, which were stable for up to 9 weeks. BKME samples should be acidified to pH 2, however, and preferably analyzed within 3 weeks of collection. TJ

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