

**Evaluation of Methods to Determine AOX  
Concentrations in Solid and Liquid Samples**

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Abstract

Conditions have been optimised for the evaluation of AOX levels in effluent and solid samples with high efficiencies of detection in the range 5-25 µg chloride ion (r >0.997). These methods were then applied to a typical paper mill in the United Kingdom, where the levels of AOX determined in effluent outflows to river were found to be below 13 ppm (g/adt).

Keywords

AOX, organohalogen, organic chloride, effluent, paper products, sludge

Introduction

Given the prevailing situation of increasing consumer and governmental concern over adsorbable organohalogen (AOX) levels produced via industrial processes<sup>1-5</sup>, we were interested in examining this topic from the specific standpoint of the United Kingdom Paper industry.

Although in terms of the industry as a whole, pulping represents a relatively small sector in the United Kingdom, with AOX from this source arising principally from imported virgin bleached pulps, it was considered important to monitor AOX levels in paper mills across the country in order to determine where principal organohalogen loads might be arising, and to relate observed levels found in effluents to existing legislation in countries such as Germany.

The work presented here centres on the development of methods for the measurement of AOX in solid and liquid samples, and their application to a typical mill location in the United Kingdom.

Method Development

Methodology was developed by adapting existing DIN and SCAN methods for AOX analysis to the United Kingdom paper industry. Work was carried out employing a Mitsubishi MCI TOX-10 Organic Halogen Analyser.

- a. Efficiency of Chloride Ion Detection: aliquots of NaCl solution of known molarity were injected into the Coulometric cell directly, such that 2 µl solution contained 1 µg chloride. The results (Table 1) illustrated that chloride was being accurately determined in the range examined (1-25 µg Cl<sup>-1</sup>):-

**Table 1: Efficiency of Chloride Detection Via Injection into Coulometric Cell**

Volume injected ( $\mu$ l)	50	40	20	10	2
$\mu$ g Chloride detected (mean)	25.03	20.40	10.42	5.06	1.24
standard deviation	( $\pm 0.18$ )	( $\pm 0.24$ )	( $\pm 0.05$ )	( $\pm 0.12$ )	( $\pm 0.08$ )

Correlation (r) = 0.9997

2  $\mu$ l = 1  $\mu$ g Cl<sup>-1</sup>

- b. Optimisation of AOX Analysis Procedure: aliquots of a solution containing known quantities of a model compound p-chlorophenol (prepared such that 1 ml = 1  $\mu$ g Cl) in deionised water were diluted to a total volume of 100 ml; 5 ml standard nitrate solution was added (17.0 g NaNO<sub>3</sub>/1.4 ml conc. HNO<sub>3</sub> in 1 L deionized water), and the mixture acidified to pH 2 (HNO<sub>3</sub>). Each sample was shaken over 50 mg activated carbon for varying periods ranging from  $\frac{1}{2}$  hr to 2 $\frac{1}{2}$  hrs. Results indicated that optimum conditions for analysis were obtained with a shaking time of at least 1 h and where a minimum 5  $\mu$ g organic chlorine was present. Figures in Table 2 represents  $\mu$ g organic halogen detected, in each case being expressed as a mean of three separate determinations, with standard deviations and percentage of theoretical chlorine detected.

**Table 2: Efficiency of AOX Detection Related in Terms of Volume (Quantity) Organohalogen and Shaking Time**

Volume Time (hr) % Th. det*	1 ml	5 ml	10 ml	20 ml	25 ml
$\frac{1}{2}$ % Th. det	1.4( $\pm 0.4$ ) 140	4.6( $\pm 0.2$ ) 92	9.5( $\pm 0.3$ ) 95	17.6( $\pm 1.1$ ) 88	22.9( $\pm 0.3$ ) 92
1 % Th. det	1.1( $\pm 0.5$ ) 110	4.9( $\pm 0.2$ ) 98	9.6( $\pm 0.2$ ) 96	19.3( $\pm 0.8$ ) 97	22.7( $\pm 0.8$ ) 91
1 $\frac{1}{2}$ % Th. det	1.0( $\pm 0.3$ ) 100	4.5( $\pm 0.2$ ) 90	8.3( $\pm 0.2$ ) 83	18.5( $\pm 0.3$ ) 93	23.1( $\pm 0.4$ ) 92
2 % Th. det	1.4( $\pm 0.4$ ) 140	5.1( $\pm 0.7$ ) 102	9.2( $\pm 0.4$ ) 92	18.5( $\pm 0.6$ ) 93	22.7( $\pm 0.6$ ) 91
2 $\frac{1}{2}$ % Th. det	1.1( $\pm 0.2$ ) 110	5.1( $\pm 0.3$ ) 102	9.1( $\pm 0.4$ ) 91	18.5( $\pm 0.5$ ) 93	22.8( $\pm 0.9$ ) 91
Mean % Th. det	120	97	91	93	91

\* % Th. det = % Theoretical Detection

Overall mean % detection = 98.

Correlation Coefficient, r = 0.9976

1 ml = 1  $\mu$ g chlorine

- c. Optimisation of AOX Extraction Medium: samples of bleached softwood kraft pulp (2.4 g OD equivalent) were suspended for four hours at room temperature prior to blending for five minutes, in the following media: (i) deionized water; (ii) deionized water adjusted to pH 10; (iii) standard nitrate solution adjusted to pH 10. After blending, solutions were made up to 1000 mL with further medium addition.

200 mL aliquots were shaken for 30 mins, and filtered onto 50 mg activated carbon through nylon mesh. AOX was then determined on the filtrate as described above (b). Two further extractions of the pulp collected by filtration showed AOX levels to have dropped to minimal levels. The experiment was performed in triplicate for each medium, the mean total organohalogen extracted appearing in Table 3:-

Table 3: AOX Levels Determined on Bleached Softwood Kraft Pulp Using Media (i) - (iv)

Medium	(i)	(ii)	(iii)	(iv)
AOX( $\mu\text{g/g}$ )	5.8	7.4	3.3	5.0
SD	( $\pm 0.5$ )	( $\pm 1.0$ )	( $\pm 0.3$ )	( $\pm 0.8$ )

The results suggest that greater efficiency of extraction is observed where deionized water is used rather than standard nitrate solution, and where pH is adjusted to 10.

#### Application To United Kingdom Mill Situation

The above methods were applied to a number of United Kingdom paper mills and the results relating to a representative mill producing newsprint and corrugated case materials are presented below. The effluent treatment system for this mill comprises of essentially two independent but partially interconnected systems operating in parallel. Mill effluent was sampled at a number of points to determine the loss of AOX by effluent treatment (Table 4). Samples of sludge were also taken along with paper product samples, for analysis by the solid AOX extraction procedure.

Results of AOX analysis on the effluent samples appear in Table 4, quoted as g/adt.

Table 4: AOX Levels Determined in Effluent Samples

Effluent Sample	AOX (g/adt)	Comments
I	29.8 ( $\pm 0.8$ )	raw
II	1.6 ( $\pm 0.2$ )	post 1 <sup>o</sup>
III a)	11.6 ( $\pm 0.9$ )	outflow to river
III b)	12.0 ( $\pm 0.4$ )	outflow to river
IV	1.1 ( $\pm 0.2$ )	outflow to river
T	5.4 ( $\pm 0.6$ )	plant overall outflow

Results of AOX analyses on sludge and paper samples appear in Table 5, with figures quoted as ppm.

Table 5: AOX Levels Extracted from Solid Samples

Solid Sample	AOX ( $\mu\text{g/g}$ )
RF Liner	20 ( $\pm 4$ )
RF Fluting	29 ( $\pm 6$ )
Sludge	28 ( $\pm 3$ )

### Conclusion

AOX levels discharged from the mill under investigation are shown to be very low, as might be expected from a waste fibre operation, meeting AOX limits at present prevailing in Germany for waste paper-based products of 12 g/tonne. Our results also indicate that the loss of AOX from the effluent by primary and secondary treatment was as much as 60% and 30%, respectively.

Levels of AOX extracted from the sludge and paper product samples compare with averages for hard- and softwood pulps of 26-40 g AOX/tonne<sup>6</sup>.

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