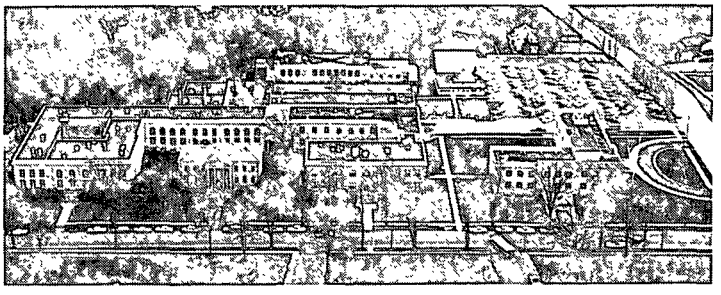

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DETERMINATION OF TOTAL ORGANIC CHLORINE IN PULP

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ABSTRACT

A method has been developed for the determination of total organic chlorine (TOCl) in pulp samples. After the pulp is formed into a column in the stem of a funnel, KNO_3 solution is passed through the column to remove chloride. The pulp is then pyrolyzed, and chloride produced by combustion of organic chlorine compounds is determined by coulometric titration. Repeatability of the procedure is about 8%, and the detection limit is 5-10 ppm. Pulps from which chloride had been removed yielded comparable results by this method and by neutron activation analysis.

Introduction

The finding of trace amounts of chlorinated dioxins and furans in products, effluents, and sludges from pulp bleaching has raised the general level of concern over chlorinated compounds produced in bleaching processes. Determinations of individual chlorinated compounds are time consuming and expensive, and only a portion of these species generated in bleaching have been identified (1). Consequently, methods for measuring the sum of the chlorine-containing compounds in bleaching effluents have been developed and are in wide use. The need exists for a comparable technique to measure total organic chlorine in pulps and other solid samples. This investigation has been devoted to development of such a method.

Total organic chlorine in bleach liquors and effluents may be determined by manual or instrumental methods. The manual method employs sorption on XAD resin, Schöniger flash combustion of the organics eluted from the resin, and potentiometric titration of the resultant chloride (2). This technique is commonly referred to as the TOX or TOCl procedure. Analysis of a single sample may require a day or longer.

Specialized instruments for organic chlorine measurements[a] are based on adsorption of the organics on activated carbon, combustion of the carbon in a tube furnace, and automated microcoulometric titration of the chloride (3). In the pulp and paper industry this determination is often termed adsorbable organic halogen (AOX) to avoid confusion with the manual TOX/TOCl method. Depending on a laboratory's quality assurance program, sample throughput on an AOX analyzer may amount to 3-4 samples in duplicate per day.

[a]Instruments are available from Dohrmann (Rosemount Analytical Division), Mitsubishi (Cosa Instrument Corp.), and Euroglas.

Total organic chlorine in solid samples may be determined by a two step manual procedure. Pulp mill sludge was combusted in an oxygen bomb; chloride measured in the bomb washings represented total chlorine in the sludge (4). Chloride was determined in an aqueous wash of the original sample and subtracted from the total chlorine to yield a value for organic chlorine. The chloride may be measured by titration, ion-selective electrode, or ion chromatography.

Organic chlorine in a pulp may be determined by neutron activation analysis as the total chlorine remaining after chloride is removed by aqueous extraction. Use of this technique requires access to a nuclear reactor.

A European method termed "AOX in pulp" is designed to estimate the sum of the chlorine compounds extracted from pulp during papermaking (5). Pulp is soaked, disintegrated, diluted to 0.12%, and filtered; AOX is measured in the filtrate. Results from this method would be expected to represent only the water-soluble organic chlorine in the pulp.

The goal of current research has been to develop and validate an instrumental method for total organic chlorine in pulp. Features of the new method include formation of a column of the pulp sample in the stem of a glass funnel, elution of chloride with KNO_3 solution, extrusion of the washed pulp into a platinum or quartz boat, and combustion of the pulp and titration of the chloride in an AOX analyzer. Included in this report are details of the procedure, comparison of results with other methods, and data on commercial pulps and pulps from various bleaching stages.

Results and Discussion

Results from the AOX analyzer method for TOCl in pulp were compared with those from neutron activation analysis (NAA). Prior to analysis the pulps were washed chloride-free with KNO_3 solution and then air dried. Data are shown in Table 1. Values obtained by the two methods were in general agreement. Agreement between these independent methods is especially favorable when compared with the approximate 40% reproducibility for AOX analyses of bleach effluents by the same method in different laboratories (6). Neutron activation values in Table 1 are single analyses; AOX data are means of three or more determinations.

Table 1 here

Routine determinations of TOCl in pulp are performed in duplicate. The precision of the method is indicated by the standard deviation computed from differences between duplicate values. Relative standard deviation was about 4%. This value increased to over 20% for measurements made near the detection limit of the method, about 5-10 ppm. Repeatability (not at the detection limit), where a test result is the mean of duplicate determinations, was about 8%.

Pulp sample weights taken for TOCl determination range between 10 and 50 mg, depending on expected chlorine content. An optimum amount of chlorine measured in a determination is 10 µg. Successful measurements have been made on pulps which were torn apart, ground in a Wiley mill, or fluffed in an Abbe mill; grinding makes it easier to secure a small, representative sample. The rapid burning of dry pulps carries combustion products throughout the pyrolysis tube; as a result, the tube must be cleaned after each sample. This problem is

avoided if the pulp is contained in a 1.5 x 10-mm quartz capillary tube during pyrolysis or if it is combusted while moist with the KNO_3 solution used to elute chloride.

Chloride removal is achieved by passing 6 mL of KNO_3 solution through the column of pulp at a rate of about 3 mL/min. No organic chlorine has been detected in the column effluent. Doubling the amount of KNO_3 solution did not affect the TOCl content of the pulp; this demonstrated that all chloride had been washed from the sample.

Spike recovery studies were performed by adding to pulp known amounts of pentachlorophenol dissolved in methanol. After the methanol evaporated, the pulp samples were combusted. Results indicated that the recovery of the organic chlorine in the pentachlorophenol was quantitative. However, when the spiked pulp was eluted with acidified KNO_3 before combustion, the recovery dropped to 40%. This result suggests that the organic chlorine-containing compounds present in bleached pulps are more tightly bound than pentachlorophenol.

The usefulness of the instrumental method for measuring TOCl in pulps is shown by the data in Table 2. Included in the table are TOCl values for pulps from several experimental laboratory bleaching stages and AOX data on the corresponding bleach liquors. The intent of these data is to illustrate the versatility of the analytical method rather than demonstrate the levels of TOCl and AOX produced by different bleaching sequences.

Table 2 here

Results obtained in this investigation indicate that the procedure which has been developed is a valid, efficient, and sensitive method for measuring total organic chlorine in pulp.

Experimental

A sample of pulp (10-50 mg) was weighed and then formed into a column between ceramic wool plugs in the 4.5-mm diameter stem of a glass funnel. The ceramic wool is the type used to support the activated carbon column for AOX analysis of water and effluents (7). The funnel was inserted in a filter flask, 6 mL of KNO_3 solution (5 g NO_3^-/L) was added, and gentle vacuum was used to draw the KNO_3 solution through the sample. (Excessive vacuum will draw the column of sample out of the funnel stem.) A rod was used to extrude the sample from the funnel into a 3 x 0.5-cm platinum boat, which was then placed in a Mitsubishi TOX-10 AOX analyzer. Sample pyrolysis and coulometric titration of chloride were performed according to the instrument manufacturer's operating instructions. Pyrolysis was conducted at 950° in an oxygen atmosphere. Time required for a single determination was about 30 min.

Titration cell maintenance and analyzer performance checks were conducted daily. Two AOX determinations were performed on trichlorophenol solutions of known concentration each morning, and a third known was run at the end of each day. Measured amounts were between 95 and 105% of expected values.

Neutron activation analyses were performed by General Activation Analysis, Inc., San Diego, CA.

Acknowledgment

Experimental pulps and bleaching liquors were prepared by T. W. Paulson.

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Table 1. Comparison of total organic chlorine in pulps using AOX analyzer and neutron activation analysis.

Pulp	AOX, ppm	NAA, ppm
Brownstock	11	< 50
O stage[a]	5	< 60
C/D stage[a]	1940	2600
E/O stage[a]	506	478
Commercial softwood	576	664
Commercial hardwood	446	443

[a]Pulp from experimental laboratory bleaching.

Table 2. TOCl in pulps and AOX in bleaching liquors.

Bleaching Process	TOCl in Pulp, µg/g	AOX in Liquor mg/L	AOX in Liquor µg/g pulp
C[a]	10,000	160	5,200
C-E	940	85	2,700
C[a]	11,000	150	4,800
C-E	1,100	130	4,200
Brownstock	< 10	NA	NA
C-E[b]	1,000	120	3,300
C-E-D	590	32	880
C-E-D-E-D	280	3.7	100
O	< 10	NA	NA
O-D-E/OP-D[c]	120	0.83	7.5
O-D-E/OP-D-E-D	80	NA	NA

NA = not analyzed.

[a]Kappa no. before bleaching, 31.8. Chlorination: % Cl_2 = 0.25 x kappa no., no ClO_2 substitution, no carryover of black liquor.

[b]Kappa no. before bleaching, 30.6. Chlorination: % CL_2 = 0.22 x kappa no., 10% substitution of Cl_2 by ClO_2, 1% carryover of black liquor.

[c]Kappa no. before bleaching, 20.4. Chlorination: % Cl_2 = 0.16 x kappa no., 100% substitution of Cl_2 by ClO_2.