Determination of organic chloride impurities in polyaminoamide-epichlorohydrin resins by gas chromatography

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ABSTRACT *A routine simultaneous analysis of the organic chloride compounds epichlorohydrin, 3-chloro-1,2-propanediol, and 1,3-dichloro-2-propanol from an aqueous solution of a newly developed low total organic chloride (TOCl) polyaminoamide-epichlorohydrin (PAE) wet-strength resin uses an ethyl acetate extraction followed by gas chromatography and electron capture detection. Detection limits at micrograms-per-gram levels, repeatability of the method, linear accuracy and precision of response, and experimental details are reported.*

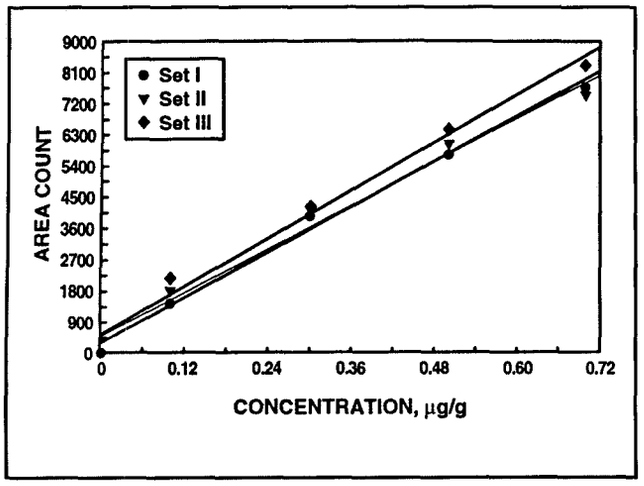
KEYWORDS
Amino groups
Chlorine compounds
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There is an increasing awareness on the part of the paper industry and its suppliers to continue improving the environmental soundness of additives to the papermaking process. To accompany these improvements, demands for routine analytical techniques to measure ever decreasing amounts of a given substance have grown.

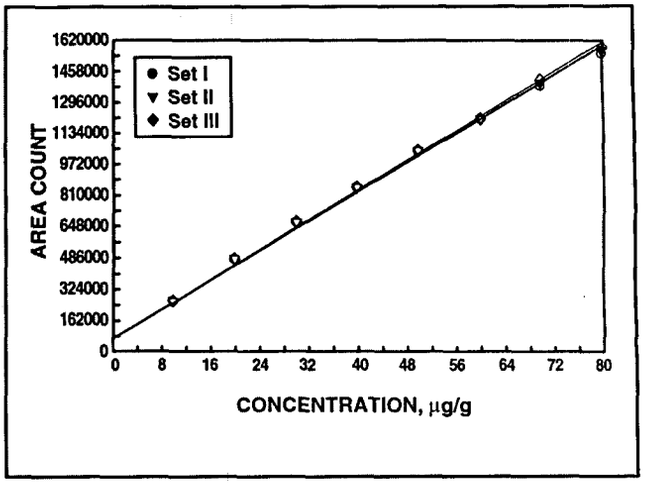
Specifically, for organic chloride containing compounds, total organic chloride (TOCl) can be measured by a variety of methods (*1-3*), as can adsorbable organic halogen (AOX) (*4, 5*). Measurement of epichlorohydrin as an individual compound has been reported previously using head space analysis followed by flame ionization detection (*6, 7*), methylene chloride extraction followed by selective ion monitoring (*8*), and most recently by hexane extraction from an aqueous solution in the presence of 3-chloro-1,2-propanediol followed by gas chromatography using electron capture detection of epichlorohydrin and the *n*-butylboronic acid derivative of 3-chloro-1,2-propanediol (*9*). As methods for routine aqueous analysis, the above three procedures have limitations in analytical sensitivity or long equilibration times for the first two, and derivatization requirements for the hydrolysis product of epichlorohydrin in the third. In addition, chromatographic methods for the measurement of 3-chloro-1,2-propanediol have been reported using both the *n*-butylboronic acid (*10*) and the phenyl boronate derivatives (*11*).

This paper describes a procedure for a routine analysis of ranges examined in micrograms-per-gram (μg/g) levels of the organic chloride compounds epichlorohydrin (0.1-0.7 μg/g), 3-chloro-1,2-propanediol (10-80 μg/g), and 1,3-dichloro-2-propanol (10-80 μg/g), by the simultaneous extraction of all three components from low TOCl containing aqueous polyaminoamide-epichlorohydrin (PAE) wet-strength resin solutions and subsequent measurement using gas chromatography and electron capture detection. The procedure requires no derivatization of the epichlorohydrin hydrolysis products and allows for the quantitation of all three components at the μg/g levels usually found in such resins. The method has been applied to the detection of μg/g levels of epich-

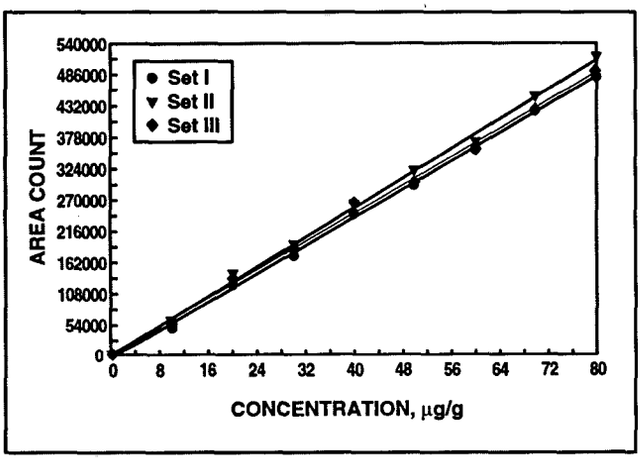
1. Calibration plots of epichlorohydrin



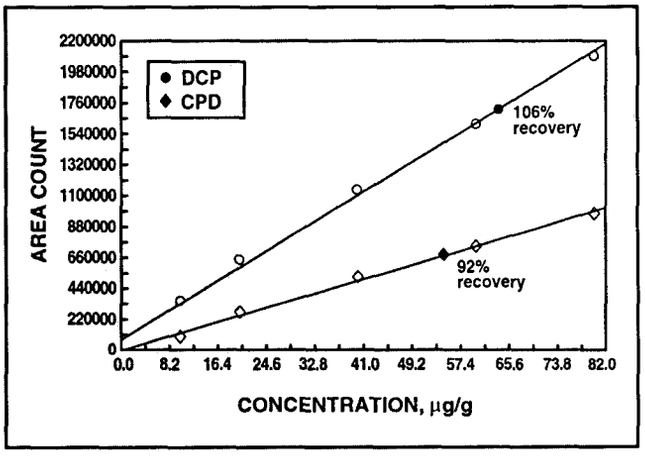
2. Calibration plots of 1,3-dichloro-2-propanol



3. Calibration plots of 3-chloro-1,2-propanediol



6. 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol spike recovery



lorohydrin, 1,3-dichloro-2-propanol, and 3-chloro-1,2-propanediol in paper mill white waters (*12*), although more documentation may be required to validate this method for that use.

Methods

Chemicals

"Baker Resi-Analyzed" ethyl acetate was obtained from VWR Scientific Products. 3-chloro-1,2-propanediol (99% purity) and epichlorohydrin (99% purity) were obtained from Aldrich. 1,3-dichloro-2-propanol (99% purity) was received from Kodak. Anhydrous sodium sulfate was obtained from Fisher Scientific. All chemicals were used as received.

Preparation of standards

Stock solutions, at concentrations equal to 1000 µg/g of epichlorohydrin, 1,3-dichloro-2-propanol, and 3-chloro-1,2-propanediol were prepared separately by diluting 60 mg of each material with ethyl acetate to a total weight of 60 g. A series of dilutions were made with the stock solutions to prepare final stock solutions of 1 µg/g of epichlorohydrin, 100 µg/g of 1,3-dichloro-2-propanol, and 100 µg/g of 3-chloro-1,2-propanediol. The epichlorohydrin working standards of 0.1–0.7 µg/g were prepared by dilution of the final stock solution with ethyl acetate. The 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol working standards of 10–80 µg/g were prepared by dilution of the final stock solutions with ethyl acetate.

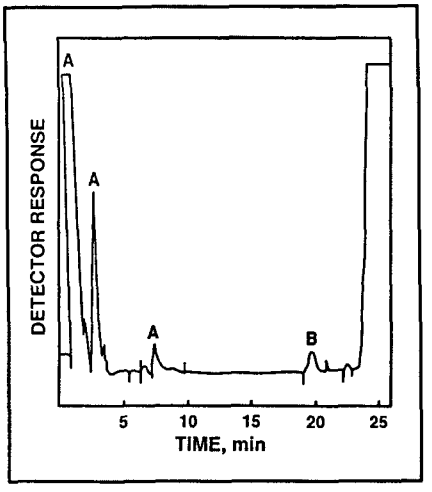
Preparation of spiked samples

A "clean" PAE resin was prepared by removing all organic chloride impurities. The "clean" PAE resin was separately spiked with known concentrations of epichlorohydrin, 1,3-dichloro-2-propanol, and 3-chloro-1,2-propanediol and each sample was mechanically mixed for 2 h.

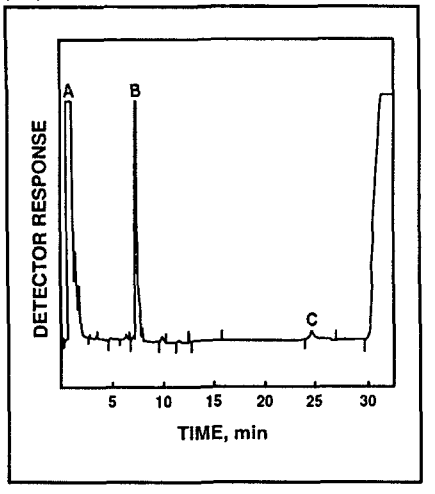
Gas chromatography

Determinations were made with a Hewlett-Packard 5890 Gas Chromatograph equipped with a NI63 Electron-Capture Detector and a 7671 Hewlett-Packard Autosampler. A split/splitless injection port was used in the splitless mode with a purge delay of 0.5 min. An auxiliary makeup of nitrogen was used. The column was 30 m × 0.54 mm × 2.5 µm AT-Wax from Attech (Catalog No. 16885). Helium was used as the carrier gas at a flow rate of about 25 cm/s. The injection

4. Sample chromatogram of *A* = solvent peak, *B* = epichlorohydrin (working standard at 0.7 μg/L)



5. Sample chromatogram of *A* = solvent peak, *B* = 1,3-dichloro-2-propanol, *C* = 3-chloro-1,2-propanediol



I. Precision data for detection of epichlorohydrin, 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol in μg/L ranges of interest

Standard, μg/g	*Peak area*			*Std. dev.*	*CV*
	Set 1	*Set 2*	*Set 3*		
		Epichlorohydrin			
0.1	1474	1809	2179	353	19.4
0.3	3978	4028	4217	126	3.4
0.5	5791	6030	6489	355	5.8
0.7	7728	7474	8332	441	5.6
		1,3-dichloro-2-propanol			
10	262163	261620	262496	442	0.2
20	481523	479400	486750	3783	0.8
30	679737	672093	679853	4447	0.7
40	857140	851503	855850	2953	0.3
50	1048966	1047700	1043833	2674	0.3
60	1217966	1215266	1225200	5137	0.4
70	1393800	1393333	1417066	13569	1.0
80	1564033	1578066	1590300	13144	0.8
		3-chloro-1-2-propanediol			
10	51798	58832	60875	4727	8.3
20	127737	137530	141993	7298	5.4
30	176490	186777	190543	7274	3.9
40	250110	265490	264193	8530	3.3
50	296340	303986	319863	1999	3.9
60	362733	363457	376543	7773	2.1
70	430987	428703	452187	12950	3.0
80	487086	493887	520090	17427	3.5

port temperature was 210°C and the detector temperature was 210°C. The injection volumes were 1 μL and peak measurements were determined by area on a 3392A Hewlett-Packard integrator. For the detection of epichlorohydrin, the oven was initially set at 50°C for 15 min and then ramped at 60°C/min to a final temperature of 200°C. For the detection of 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol, the oven was initially set at 175°C for 15 min and then ramped at 60°C/min to a final temperature of 200°C.

PAE resin extraction procedure

Approximately 1.5 g, accurately weighed to the nearest mg, of PAE resin was added to a Kimble 50 mL glass screw-top disposable centrifuge tube (Baxter No. C3795-50) and diluted to a total weight of 15 g with ethyl acetate. The contents of the centrifuge tube were shaken thoroughly by hand for 5 min, allowed to stand for 5 min and then re-shaken for 5 min. The tube was then centrifuged at 6000 rpm for 5 min or until the upper solvent layer was clear. About 10 mL of the solvent layer was transferred to a 20 mL scintillation vial. Approximately 1 g of anhydrous sodium sulfate was added to the vial to dry the solvent layer.

Results and discussion

Linear calibration plots of epichlorohydrin, 1,3-dichloro-2-propanol, and 3-chloro-1,2-propanediol standards, shown in **Figs. 1-3**, were generated from three sets of data, where each standard was separately prepared and analyzed in triplicate. Sample chromatograms are shown in **Figs. 4 and 5**. The limit of quantitation for epichlorohydrin was determined to be 0.1 μg/g; it was not determined for 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol. The precision data for each standard (**Table I**) are best described by the Coefficient of Variance, *CV*. Coefficient of Variance is defined as [standard deviation/mean] × 100. Low *CV* values (< 10) indicate the accuracy of the data, which is related to the reliability of the method. For the 1,3-dichloro-2-propanol standards, the *CV* data were between 0.2 and 1, and for the 3-chloro-1,2-propanediol standards the *CV* data were between 2.1 and 8.3. The *CV* data for epichlorohydrin standards were between 3.4 and 5.8 for the 0.3-0.7 μg/g range; however, at the 0.1 μg/g concentration, the *CV* value was 19.4. This was not unexpected because this concentration was the limit of quantitation for epichlorohydrin.

Precision data for spike recovery of epichlorohydrin, 1,3-dichloro-2-propanol, and 3-chloro-1,2-propanediol from a "clean" PAE resin are listed in **Table II** and illustrated in

Fig. 6. The spiked resin was extracted three times and each extract was analyzed three times. The low spike recovery of epichlorohydrin could have been caused by the acid-catalyzed S_N2 cleavage of the epoxide by free HCl in the PAE resin (*13*). Attempts were not made to confirm the generation of 1,3-dichloro-2-propanol in the epichlorohydrin-spiked PAE resin sample. The spike recovery of 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol, at 106% and 92%, respectively, and their calculated *CV* values were within the *CV* values from the standard calibration plots.

A commercial PAE resin was obtained and extracted six times. Each extract was analyzed one time and the precision data from the reproducibility of the extractions are in **Table III**. The *CV* data from the extraction study for 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol were found to be within the *CV* values of their respective standard calibration plots. *CV* data were not generated for epichlorohydrin, because the PAE resin was found to contain < 0.1 μg/g epichlorohydrin.

II. Precision data for spike recovery of epichlorohydrin, 1,3-dichloro-2-propanol, and 3-chloro-1,2-propanediol

	Prepared concentration, μg/g	*Determined concentration, (N=3), μg/g*	*Recovery, %*	*Std. dev.*	*CV*
Epichlorohydrin	6	0.7	12	0.0	0.0
1,3-dichloro-2-propanol	611	646	106	6.0	0.9
3-chloro-1,2-propanediol	589	542	92	37.0	6.8

III. Precision data for the reproducibility of PAE resin extraction

	Organic chloride components found in aqueous resin, μg/g		
Extraction	*Epichlorohydrin*	*1,3-dichloro-2-propanol*	*3-chloro-1,2-propanediol*
1	< 0.1	2380	690
2	< 0.1	2383	670
3	< 0.1	2378	630
4	< 0.1	2400	685
5	< 0.1	2362	627
6	< 0.1	2372	656
Mean	...	2379	660
Std. dev.	...	13	27
CV	...	0.5	4.1

Conclusion

Epichlorohydrin and its hydrolysis by-products, 3-chloro-1,2-propanediol and 1,3-dichloro-2-propanol, were detected in the micrograms-per-gram range using a gas chromatograph equipped with an electron capture detector. The precision of the spike recovery and standard curves over the ranges investigated coupled with the resin extraction repeatability data show the reliability of the method and the ability to quantitatively determine the concentration of all three components simultaneously in a resin matrix. These features make this a cost-effective rapid method for determination of trace amounts of organic chloride compounds in commercial PAE resins.□

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