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Short communication

Determination of 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol in papers treated with polyamidoamine–epichlorohydrin wet-strength resins by gas chromatography–mass spectrometry using selective ion monitoring

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Abstract

Polyamidoamine-epichlorohydrin wet-strength resins for paper contain small amounts of 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol formed by side reactions from epichlorohydrin used in the production process. Normally some residues of these substances are transferred to the wet-strength treated paper. An analytical method has therefore been developed for the simultaneous determination of 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol in paper in the 0.05–2 mg/kg range. The compounds are simultaneously extracted and silylated with a solution of *N,O*-bis-(trimethylsilyl)trifluoroacetamide in acetonitrile and finally determined by capillary gas chromatography–mass spectrometry in the selective ion monitoring mode against an internal standard. The detection limits are 0.04 mg/kg for both 1,3-dichloro-2-propanol and 3-chloro-1,2-propanediol. © 1997 Elsevier Science B.V.

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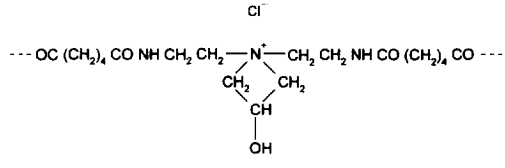
1. Introduction

There are a number of resins used by the paper industry for imparting wet-strength to paper, e.g. polyamidoamine–epichlorohydrin (PAAE) (other acronyms for this resin are PAE and PPE), urea–formaldehyde and melamine–formaldehyde resins. By far the most widely used today is PAAE resin. It is applied under neutral or alkaline conditions. This polymer is usually manufactured from adipic acid and diethylenetriamine to give a polyamidoamine oligomer, which is subsequently converted in a water solution with epichlorohydrin to a polymer of mainly the following structure:



The resin chemistry has been reviewed by several authors [1–4].

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During the conversion of polyamidoamine with epichlorohydrin two by-products are formed. 1,3-Dichloro-2-propanol (DCP) is formed in the reaction of epichlorohydrin (ECH) with chloride ions and 3-chloro-1,2-propanediol (CPD) is formed by hydrolysis of ECH in water. Since it was found that DCP may cause cancer in rats [5] the contents of these by-products, as well as ECH, in the polymer formulations have been substantially reduced and in current products are below the 0.1% level. All formulations which contain more than 0.1% of DCP have to be labelled as toxic and carcinogenic according to EU Directive 91/155/EEC [6]. In addition epichlorohydrin is considered carcinogenic [7].

So far there are no published methods for the determination of DCP and CPD at low concentrations in paper. One reason for this may be that DCP under alkaline and neutral conditions on the paper machine reacts to form ECH [8]; the conditions of the extraction and of the analytical method can therefore affect the amount of DCP actually measured.

Several papers describe the determination of low amounts of the compounds of interest in different matrices. DCP and CPD have been determined in PAAE resins by GC with electron-capture detection (ECD) after extraction into ethyl acetate [9]. An acetonitrile extract from a PAAE resin has been analyzed by GC for CPD after derivatization with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) [10]. Water solutions have been analyzed for CPD by GC–ECD after *n*-butylboronic acid derivatization and extraction into hexane to follow the potential migration from a packaging material [11]. DCP and CPD have been determined in seasonings, and foodstuffs containing seasonings, after water extraction and adsorption to an Extrelut column. DCP and CPD are then extracted with ethyl acetate and, after evaporation of the solvent, determined by GC–MS in the selective ion monitoring (SIM) mode [12]. Protein hydrolysates have been analyzed, also using an Extrelut column, either directly on the ethyl acetate eluate, using GC with electrolytic conductivity detection [13], or after derivatizing the organic eluate with heptafluorobutyrylimidazole and GC–ECD [14]. CPD has also been determined in the same matrix with GC after derivatization with phenylboronic acid and extraction into hexane [15].

This paper reports a method to quantitatively determine DCP and CPD in paper, which overcomes the DCP–ECH equilibrium problem. The paper sample is extracted with acetonitrile and simultaneously derivatized with BSTFA, thereby blocking DCP and CPD from further equilibrium reactions. The liquid phase is analyzed by GC–MS in the SIM mode using 1-fluoronaphthalene as internal standard. The robustness against moisture and common filler materials used in papers has been examined.

2. Experimental

2.1. Chemicals

1,3-Dichloro-2-propanol (>98%) and 3-chloro-1,2-propanediol (>98%) were obtained from Merck (Darmstadt, Germany). The internal standard, 1-fluoronaphthalene (99%), was supplied by Fluorochem (Old Glossop, UK). *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) was purchased from Pierce, Cat. No 38828 (Rockford, IL, USA). Acetonitrile (Far UV) was obtained from Fisons Scientific Equipment (Loughborough, UK).

2.2. Solutions

Separate standard stock solutions of DCP and CPD were prepared in acetonitrile, each containing 1 mg/ml. Separate DCP and CPD working standard solutions at 10, 1.0 and 0.1 μg/ml were prepared by dilution with acetonitrile. The 1-fluoronaphthalene internal standard solution was prepared at a concentration of 200 μg/ml in acetonitrile. The stock solutions as well as the internal standard solution were prepared every second month and the working standard solutions were prepared fresh for each batch of samples to be analyzed.

2.3. Extraction and derivatization procedure

The paper samples were stored wrapped in aluminium foil and plastic bags in a freezer (−15 to −25°C) between sampling and analysis.

Acetonitrile (2.5 ml) and 50 μl of internal standard solution (containing 10 μg of 1-fluoronaphthalene in acetonitrile) were added to a 20-ml

headspace glass vial (Supelco, Bellafonte, PA, USA, Cat. No. 2-7199), and also 1.0 g of the silylating agent, BSTFA. The paper sample was cut into 1×10 mm strips, weighed (0.50±0.01 g) and immediately put into the vial containing the solution. The vial was capped with a PTFE-faced butyl septum (Supelco, Cat. No. 2-7201) and an aluminium seal and vortex mixed for 10 s (Super-Mixer, Lab-Line Instruments, Melrose Park, IL, USA).

After 20 h at 40°C in a thermostated oven the vial was taken out, vortex mixed for 10 s and decapped. About 150 μl of solution was transferred to a 250-μl glass insert tube (Hewlett-Packard, Avondale, PA, USA, Part No. 5181-3377) positioned inside a 2-ml autoinjector glass vial (Hewlett-Packard, Part No. 5181-3375). After capping with a crimp vial closure (Hewlett-Packard, Part No. 5181-1210) the sample was ready for GC–MS analysis.

2.4. Calibration

Fifty and 100 μl of the 0.1 μg/ml working standard solutions of DCP and CPD, 25 and 100 μl of the 1.0 μg/ml solutions and 25 and 100 μl of the 10 μg/ml solutions were added after the internal standard addition both to a paper without PAAE resin and to the paper for analysis, giving added concentrations of 0.010, 0.020, 0.050, 0.20, 0.50 and 2.00 mg/kg, calculated on the paper samples.

2.5. Gas chromatography

A Hewlett-Packard HP 7673 autoinjector was attached to a Hewlett-Packard HP 5890 gas chromatograph equipped with a split/splitless injector and a 25 m×0.32 mm I.D. CP Sil 5 CB (100% methyl silicone) fused-silica capillary column with a phase thickness of 1.2 μm from Chrompack (Middelburg, The Netherlands).

The solution (1 μl) was injected into the splitless injection port with a purge delay of 0.3 min and at a temperature of 250°C. Helium (>99.996% AGA Gas, Sundbyberg, Sweden) was used as the carrier gas at a pressure of 0.030 MPa. The oven was initially set to 80°C for 2 min and then ramped at 10°C/min to a final temperature of 250°C.

The retention time for the DCP trimethylsilyl (TMS) derivative was 7.15 min, for 1-fluoronaphthalene 9.15 min and for the CPD TMS derivative 9.40 min.

2.6. Mass spectrometry

The mass spectrometric detection was performed with a Hewlett-Packard mass selective detector HP 5972, operating in the SIM mode. The peak areas were calculated by using the Hewlett-Packard Chem-Station software (G1034C).

The mass selective detector was used with electron impact (EI) ionization tuned with 'Maximum Sensitivity Autotune'. The electron multiplier was operated at a nominal value of 2388 V. The interface temperature was 280°C, yielding a source temperature of 180°C. A solvent delay of 6.00 min was used.

The full scan mass spectra of the TMS derivatives of DCP and CPD and of 1-fluoronaphthalene are shown in Fig. 1.

The characteristic ions used for the quantitation by SIM were m/z 185 (187) for the DCP TMS derivative, m/z 239 (116) for the CPD TMS derivative and m/z 146 for 1-fluoronaphthalene. The fragments m/z 187 and m/z 116 were only used for control purposes. The dwell time per ion was 20 ms.

The GC–MS-SIM mass fragments for the DCP TMS derivative (m/z 185), the CPD TMS derivative (m/z 239) and 1-fluoronaphthalene (m/z 146) for a PAAE-treated paper, containing 0.42 mg/kg of DCP and 0.63 mg/kg of CPD, are shown in Fig. 2.

2.7. Calculations

Calibration curves were made by plotting the peak-area ratios DCP/I.S. and CPD/I.S. against the standard additions of DCP and CPD to the paper, expressed in mg/kg. When external calibration curves made from a DCP- and CPD-free paper are used, the sample concentrations are directly obtained from the calibration curves. If calibrations are performed with standard additions to the paper for analysis, the calibration curves are read where the curves intersect the abscissa.

The results are also corrected for the moisture content, determined on a separate paper sample using, e.g. Tappi method T412.

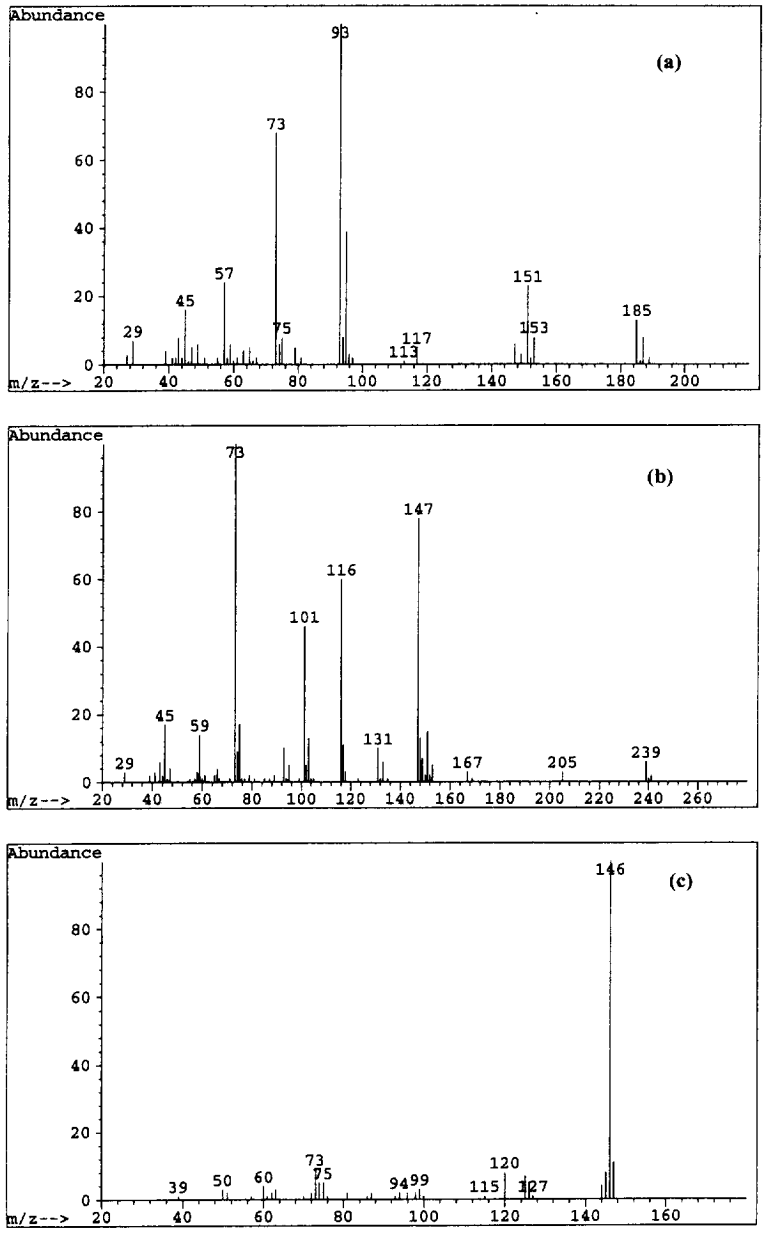

Fig. 1. Mass spectra of (a) 1,3-dichloro-2-propanol trimethylsilyl derivative, (b) 3-chloro-1,2-propanediol trimethylsilyl derivative and (c) 1-fluoronaphthalene.

3. Results and discussion

3.1. The equilibrium between 1,3-dichloro-2-propanol and epichlorohydrin

1,3-Dichloro-2-propanol is easily converted to epichlorohydrin in alkaline conditions. Some mills apply PAAE resin at a wet end pH of 8–9 or even higher, resulting in a high pH in the paper. In calcium carbonate-filled grades inherent alkalinity is high and permanent. Any analytical method has to be worked out so that the DCP–ECH equilibrium in the

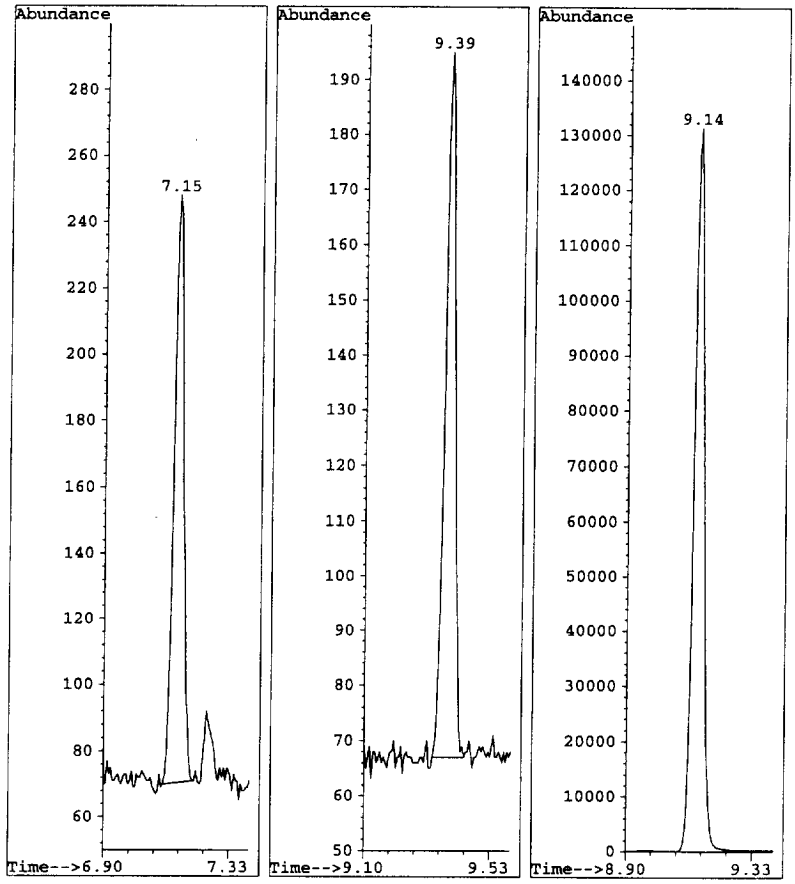

Fig. 2. GC-selective ion monitoring (SIM) mass fragments obtained from (a) 1,3-dichloro-2-propanol trimethylsilyl derivative, *m/z* 185, (b) 3-chloro-1,2-propanediol trimethylsilyl derivative, *m/z* 239 and (c) 1-fluoronaphthalene, *m/z* 146.

paper will not be altered during extraction and that no DCP or CPD will react to other compounds within the parameters used.

In initial experiments which added a pH 9 buffer to an extraction solution with a DCP- and ECH-containing paper, a detectable decrease in the DCP content and an increase in the ECH content was found by GC analysis on the underivatized substances. Thus a derivatization method with BSTFA was developed. Experiments with headspace GC–MS on epichlorohydrin-spiked papers, without derivatization, have also shown that the recovery for ECH is far over 100% when also spiking with DCP.

There are different approaches to overcome this DCP–ECH equilibrium problem. The one chosen here is to derivatize DCP and CPD directly at the extraction step, thereby blocking both substances from further reactions. BSTFA is known to be a fast reacting derivatizing agent which gives compounds of low polarity which are stable to heat. As the paper matrix contains many hydroxyl groups and also some moisture a sufficient excess of silylating reagent is necessary.

For CPD, which is much more polar, there are no equilibrium problems. With the method described, CPD can conveniently be co-analyzed with DCP.

3.2. BSTFA demand

The cellulose matrix and the moisture in a paper sample need theoretically a large amount of BSTFA for silylating all hydroxyl groups. This would also

need a large volume of solvent, together resulting in high detection limits. As not all hydroxyl groups in the cellulose fibre should be accessible for derivatization for migration reasons, a study was performed to find the minimum BSTFA amount needed for a total derivatization of DCP and CPD, enabling the lowest possible detection limits.

The paper used for this determination, Paper 0, was produced on a laboratory paper machine with a pulp consisting of 30% pine sulfate, 35% birch sulfite, 35% beech sulfite and 10% calcium carbonate added to fibre. No wet-strength resin was added. There was no detectable DCP or CPD in the paper. The paper used for the optimization of the extraction parameters, Paper A, was produced on the same machine using a wet-strength resin of 24.3% polymer content and with 2.2% of DCP and 0.41% of CPD, which was added to pulp (0.6% resin) consisting of the same furnish as above. The paper contained 0.42 mg/kg of DCP and 0.63 mg/kg of CPD. The reason for the different DCP/CPD ratios in resin and paper is partly conversion of DCP to ECH and then removal of DCP and ECH by azeotropic steam distillation in the drying section of the paper machine.

Varying amounts of BSTFA, ranging from 0.5 to 3.0 g, were added to 0.5 g of the paper without wet-strength resin, Paper 0. It was found that 1.0 g of BSTFA was sufficient for a total derivatization of spiked DCP and CPD. It was also found that 1.0 g of BSTFA was enough for a total silylation of spiked DCP and CPD with up to 5% of extra water added to the paper, which had an original moisture content of 5.9%.

Three types of common paper fillers were tested, calcium carbonate, kaolinate and titanium dioxide, originally intended as pH monitors for checking the DCP–ECH equilibrium. It was found that some of them influenced the demand for the silylating agent. Producers of silanes for hydrophobizing purposes classify the filler reactivities towards silanes in order of decreasing effect: kaolinate (good), titanium dioxide (good) and calcium carbonate (slight). Barium sulfate is said to have no reactivity.

Filler (0.05 g; four different) mixed in with 0.45 g of Paper 0 or Paper A and spiked with DCP and CPD corresponding to 2.00 mg/g were analyzed using varying amounts of BSTFA. The results in Table 1 are not unambiguous. Probably there are competing processes going on: the BSTFA–DCP/CPD reaction, the BSTFA–filler reaction and possibly a DCP/CPD adsorption onto the fillers. Calcium carbonate, despite being very alkaline, does not seem to reduce the DCP and CPD recoveries and to be a problem, while 68–98% recoveries were found for kaolinate and titanium dioxide in Paper A, when

Table 1
Extraction recovery for 1,3-dichloro-2-propanol (DCP) and 3-chloro-1,2-propanediol (CPD) as a function of filler and BSTFA (silylating agent) additions

Sample	Filler addition (g)	BSTFA amount (g)	Recovery (%)	
			DCP	CPD
Paper 0	10% calcium carbonate	1.00	102	98
		1.50	99	96
	10% kaolinate	1.00	85	85
		1.50	81	75
		2.00	82	72
	10% titanium dioxide	1.00	99	68
		1.50	101	86
	10% barium sulfate	1.00	97	97
Paper A	10% calcium carbonate	1.00	100	102
		1.50	99	96
	10% kaolinate	0.50	13	12
		1.00	92	78
		1.50	97	89
	10% titanium dioxide	1.00	98	89
		1.50	100	91

1.0 g of BSTFA was used. An increased amount of BSTFA will not necessarily improve the recoveries. As expected barium sulfate showed no significant effect.

Spiking of filled or unfilled paper with ECH, corresponding to 2.00 mg/kg, does not result in any detectable amounts of DCP or CPD. No transformation of DCP to CPD or vice versa could be detected.

3.3. Effect of alkaline pH

Two commercial buffer solutions (500 μl each; Titrisol, Merck) of pH 7 and 9 were added to Paper 0. After drying for 2 h at 105°C and remoisturing in the ambient air, the paper pH values were measured to 7.3 and 8.7, respectively, by a pH-meter (8135SC Ross, Orion Research, Boston, MA, USA) using Tappi method T509. Analysis of DCP- and CPD-spiked paper for the pH 7 paper gave DCP and CPD recoveries of 98 and 101%, respectively, and for the pH 9 paper 98 and 104%, respectively. Evidently no equilibrium problem was experienced at neutral or alkaline pH.

3.4. Optimization of extraction time

The extraction efficiencies for DCP and CPD were tested as a function of time for Paper A. Sample solutions were taken out after 1, 3, 6, 20 and 44 h at 40°C. A sample was also vortex mixed for 60 s at room temperature and the liquid phase was immediately sampled for GC–MS analysis to see how much DCP and CPD were directly accessible.

The extraction efficiency curves in Fig. 3 show that DCP reaches a maximum level after 6 h. The extraction result for CPD after 20 h is 94% of the result after 44 h. The fact that only 6% of total DCP and 9% of total CPD are found after 1 min of vortex mixing indicates that the major amounts are distributed within the PAAE bulk polymer or within the cellulose fibre structure, not easily accessible to the extractant. An extraction time of 20 h was chosen for practical reasons. The derivatization reactions were checked and found to be complete at the times used for the extractions.

3.5. Linearity, precision

Calibration graphs were obtained by plotting the ratio of the peak areas of the calibration standard and the internal standard, against the concentration in the paper. Six concentration levels, 0.010, 0.020, 0.050, 0.20, 0.50 and 2.00 mg/kg, of DCP and CPD were used and triplicate additions were made at each concentration level to both Paper 0 and Paper A (Table 2).

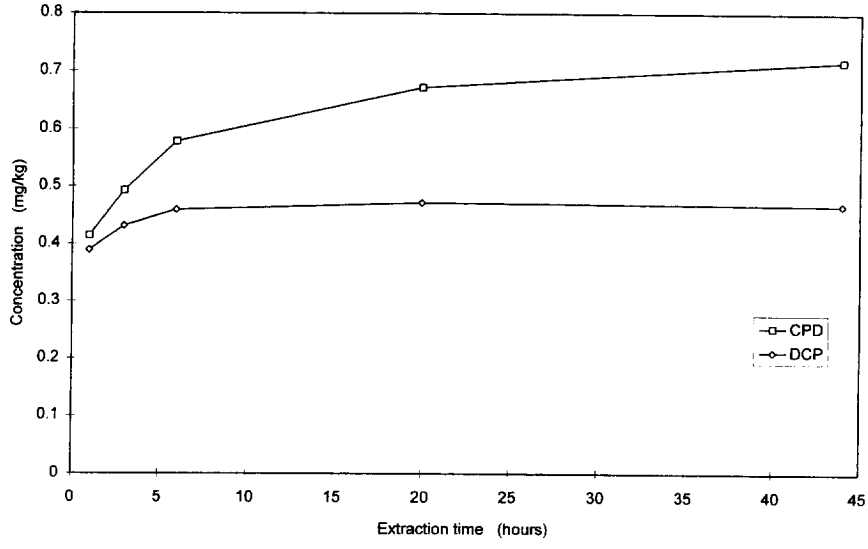

Fig. 3. Extraction efficiency for 1,3-dichloro-2-propanol (DCP) and 3-chloro-1,2-propanediol (CPD) as a function of extraction time.

Table 2
Calibration data for the determination of 1,3-dichloro-2-propanol (DCP) and 3-chloro-1,2-propanediol (CPD): triplicate additions

Substance	Range (mg/kg)	No. of addition levels	No. of data points	Slope (% R.S.D.)	Intercept (% R.S.D.)	r
Addition to Paper 0						
DCP	0–2.00	6	21	3.159×10^{-3} (0.31)	7.084×10^{-6}	0.9999
DCP	0–0.20	4	15	3.093×10^{-3} (1.80)	7.074×10^{-6}	0.9978
CPD	0–2.00	6	21	1.579×10^{-3} (0.49)	4.571×10^{-6}	0.9998
CPD	0–0.20	4	15	1.554×10^{-3} (3.32)	8.196×10^{-6}	0.9923
Addition to Paper A						
DCP	0–2.00	6	21	3.166×10^{-3} (0.58)	1.344×10^{-3} (1.07)	0.9997
CPD	0–2.00	6	21	1.555×10^{-3} (0.93)	9.826×10^{-4} (1.16)	0.9992

The original content of DCP Paper A was measured to 0.42 mg/kg and CPD to 0.63 mg/kg. The repeatabilities, calculated from the Paper A (without addition) triplicates were 3.8% for DCP and 3.2% for CPD as the relative standard deviations.

The precision given as relative standard deviations from triplicates at different addition levels to Paper 0 is shown in Table 3.

3.6. Recovery

The recoveries for DCP and CPD added at a concentration of 2.00 mg/kg to Paper A were determined to be 99 and 97%, respectively, compared to the calibration curves from Paper 0. For the 0.20 mg/kg addition level the recoveries were 91 and 106%, respectively. This means that a calibration can be performed either by a calibration curve based on a PAAE resin-free paper or with standard additions to the paper for analysis.

3.7. Limits of detection

The limits of detection, calculated as the concentrations that gave signals 3 times the standard deviations of the blanks, were found to be 0.04 mg/kg for DCP and 0.04 mg/kg for CPD.

Table 3
Relative standard deviations for 1,3-dichloro-2-propanol (DCP) and 3-chloro-1,2-propanediol (CPD) additions to Paper 0

Addition level (mg/kg)	R.S.D. (%)	
	DCP	CPD
0.01	55	58
0.02	24	48
0.05	3.1	9.9
0.20	3.9	7.2
0.50	3.5	4.9
2.00	0.9	1.5

4. Conclusions

Analysis of DCP and CPD in PAAE wet-strength resin-treated papers can now be performed with good recoveries, precisions and sensitivies by a simultaneous extraction with acetonitrile and derivatization with BSTFA and a GC–MS-SIM determination using an internal standard. Alkaline pH in the paper does not affect the DCP or CPD recoveries. The method is applicable to paper samples with normal moisture levels (<10%) and also with calcium carbonate fillers. Kaolinate and titanium dioxide fillers give rise to somewhat lower DCP and CPD recoveries: about 80–100%.

Substantial amounts of food-grade papers are wet-strengthed with PAAE resins and this analytical method has already been extensively used to monitor the production of such papers.

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