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Determination of Cotton-Bound Glyoxal via an Internal Cannizzaro Reaction by Means of High-Performance Liquid Chromatography

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Glyoxal, a non-formaldehyde cross-linking agent, was applied in combination with aluminum sulfate hexadecahydrate to impart durable-press properties to cellulosic materials. The cotton fabric was impregnated with a pad bath formulation containing 6% (w/w) glyoxal and 4.5% (w/w) aluminum sulfate hexadecahydrate. The curing process was conducted at 140 °C for 3 min, thus affecting a cross-linkage between the cellulose chains. For the first time, a chromatographic method is presented that enables both qualitative and quantitative analysis of the portion of glyoxal that has reacted with the cellulosic material. For this purpose, the glyoxal-treated fabric was treated with an NaOH solution ($c = 4$ mol L^{-1}) at 100 °C for 20 min. As a result, glyoxal was extracted from the cellulosic sample and converted into glycolate via an internal Cannizzaro reaction. Subsequently, the glycolate was analyzed chromatographically using the strong cation-exchange column Aminex HPX-87H as the stationary phase and sulfuric acid as the mobile phase. The detection limit was 1.87 mg L^{-1} (UV detection). The recovery was 85%. Dry crease wrinkle recovery measurements gave evidence that the cross-linkage was removed completely. The application of the analytical technique developed in the present study demonstrated that the amount of glyoxal that had reacted with the cellulose was 15.7 ± 0.72 mg/g of fabric. In addition, glycolate thus formed was well separated from non-formaldehyde durable-press finishing agents based on polycarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid or citric acid.

Cotton fabric must be chemically modified in order to impart durable-press properties (shrinkage resistance, crease recovery). For this purpose, dimethylol-dihydroxyethyleneurea, bis(1,3-dihydroxymethyl)-3,4-dihydroxyimidazolidin-2-one (DMDHEU) is the most widely used formaldehyde-based chemical (Figure 1a). However, cotton fabrics having been treated with a pad bath containing DMDHEU as cross-linking agent tend to release formaldehyde during the curing process, storage, and consumer use.[1] Due to the fact that formaldehyde is regarded to have carcinogen potential, intensive investigations have been undertaken to find substitutions for the formaldehyde-based reagents. As a consequence, several cross-linking systems that do not contain formaldehyde have been developed. Since the late 1980s, extensive efforts have been made to use polycarboxylic acids (PCAs) such as 1,2,3,4-butanetetracarboxylic acid (Figure 1c) as a non-formaldehyde durable-press agent to replace *N*-methylol-type chemicals.[2−5] PCAs react in combination with an appropriate catalyst such as sodium hypophosphite monohydrate, thus forming ester linkages.[6] Also various investigations were undertaken in order to evaluate the effectiveness of glyoxal (ethanedial) (Figure 1b) as a durable-press agent.[7−9]

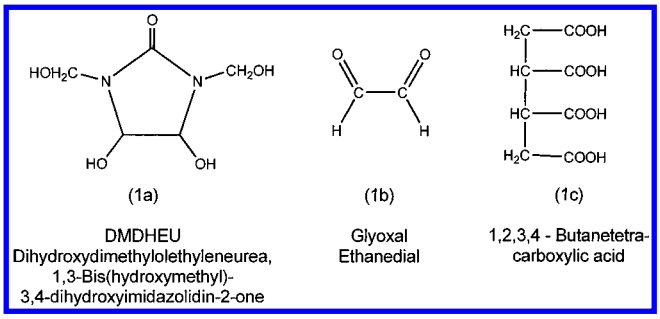

Figure 1. Cross-linking agents for cellulosic material. DMDHEU tends to release formaldehyde. Glyoxal and 1,2,3,4-butanetetracarboxylic acid are non-formaldehyde durable-press agents.

Different analytical methods were tested in respect to the qualitative and quantitative determination of the non-formaldehyde finishing agents that have reacted with the cellulosic material. FT-IR measurements proved a useful tool for quantification of PCAs linked to the cellulose.[10−13] However, FT-IR did not offer the possibility for qualitative evaluation. The FT-IR technique enabled the identification of the cyclic five-membered anhydride intermediate.[14] The application of thermoanalytical methods required a large

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amount of data to identify and quantify the cross-linking agents.[15−20] In addition, the NMR technique was used to determine the decomposition products, when citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) was applied as the cross-linking agent. However, only the formation of *cis*-/*trans*-aconitic acid ((1*Z*/1*E*)-1-propene-1,2,3-tricarboxylic acid) could be confirmed.[21] The introduction of the isocratic HPLC method using Aminex HPX-87H as the stationary phase and dilute sulfuric acid as the mobile phase rendered possible both qualitative and quantitative determination of the PCAs having reacted with the cellulosic material. Prior to the chromatographic analysis, the PCA-treated cotton fabric was subjected to a saponification procedure.[21−26]

To date, no analytical method exists that enables the qualitative and quantitative determination of the portion of glyoxal that has reacted with the cellulose. Therefore, the present study is focused on the quantitative measurement of glyoxal bound to cellulosic material by means of isocratic HPLC. This method is of high interest because glyoxal is a promising substitute for the formaldehyde-releasing *N*-methylol compounds, which are applied in a large commercial scale.

EXPERIMENTAL SECTION

Chemicals. Glyoxal (>98%; 40% w/w) and aluminum sulfate hexadecahydrate $Al_2(SO_4)_3 \cdot 16H_2O$ (>98%) were purchased form Merck GmbH, Germany.

Fabric/Fabric Treatment. Desized, scoured, bleached 100% cotton fabric weighing 122 g m^{-2} was used throughout the investigations. The preweighed fabric was impregnated in a finish bath containing glyoxal and aluminum sulfate hexadecahydrate as the curing catalyst. The corresponding weight fractions are specified in the text. No softener was applied. Subsequently, the sample (20 cm × 30 cm) was passed through a two-roll laboratory padder (HVL 500 Mathis AG, Niederhasli, Switzerland; air pressure 1 bar, fabric speed 3 m/min). This treatment was repeated to give a wet pickup of 95−100% based on the original weight of fabric. After drying (3 min, 105 °C), the fabric was cured for 3 min at 140 °C in a laboratory dryer (LTE, W. Mathis AG, Switzerland), washed under occasional stirring (1 g L^{-1} Na_2CO_3, 10 min, 50 °C, 1000 mL), and finally dried again (3 min, 80 °C).

Chromatographic Measurement. HPLC was performed using an autosampler (model Marathon, Spark BV, Emmen, Netherlands), an Altex model 100 pump, and an 7010 Rheodyne (Cotati, CA) model 7010 sample injection valve with a 20-μL loop. Separations were carried out using the strong cationic exchange 300 mm × 7.8 mm column Aminex HPX-87H (Bio-Rad Labs., Richmond, CA). The column was thermostated in a Shimadzu CTO-2A (Kyoto, Japan) oven compartment. The detector was the UV detector Gynkothek SP-4 (Germering, Germany). Data acquisition was carried out with the chromatography software Borwin (JMBS Developpements, Le Fontanil, France). Chromatographic conditions were as follows: mobile phase, H_2SO_4 ($c_{1/2}$ = 0.01 mol L^{-1}); flow rate, 0.7 mL min^{-1}; column oven temperature, 80 °C; UV detector wavelength, 210 nm.

DCRA Measurements. The measurements of the dry crease recovery angle (DCRA) were performed according DIN 53 890 with a device from Karl Schröder (Weinheim, Germany).

Hydrolysis. One to two grams of the glyoxal-cured fabric was cut into small pieces, accurately weighed, and placed in the reaction vessel. NaOH (40 mL; c = 4 mol L^{-1}) were added. The reaction mixture was treated at 100 °C for 20 min. After hydrolysis, the extraction solution and the wash liquors were transferred to a 50-mL volumetric flask and allowed to cool. Finally, the volumetric flask was adjusted to the mark with NaOH (c = 4 mol L^{-1}). Prior to the chromatographic analysis, the solution was filtered through a PTFE disposable filter unit.

Concentration of Glyoxal. A 1-g aliquot of a 40% (w/w) glyoxal solution was accurately weighed and mixed with 2 mL of a 30% (w/w) sodium peroxide solution in 50 mL of deionized water. The reaction mixture was stirred overnight. The formic acid that has been produced was analyzed potentiometrically using NaOH (c = 1 mol L^{-1}). A 1000-mg sample of 40% (w/w) glyoxal contained 402.5 ± 3.91 mg of glyoxal (n = 6).[27]

RESULTS AND DISCUSSION

When glyoxal is applied as a non-formaldehyde cross-linking agent, acetal or hemiacetal linkages are formed between glyoxal and the hydroxyl groups of the cellulose during the curing process, usually performed at 140 °C for 3 min, thus imparting durable-press properties to the cotton material (Figure 2). At present time, however, no analytical method is available for quantification of the portion of glyoxal that has reacted with the cellulosic material. To conduct the chromatographic determination, glyoxal must be released from the cotton fabric. The cleavage of the acetal or hemiacetal linkages was achieved using a strong alkaline solution, and at the same time, glyoxal was converted into the sodium salt of glycolic acid (hydroxyacetic acid) via an internal Cannizzaro reaction, as can be seen in Figure 3.[28] Subsequently, the glycolate thus formed was measured chromatographically. Various chromatographic approaches were already adopted for the determination of short-chain carboxylic acids, such as glycolic acid, in different matrixes. The techniques were focused on gas chromatography after derivatization and on HPLC.[29−32] However, no chromatographic method has yet been reported for the assay of glyoxal linked to cellulosic material.

Calibration. To quantify sodium glycolate by means of HPLC, five standard solutions were prepared in concentration ranges of

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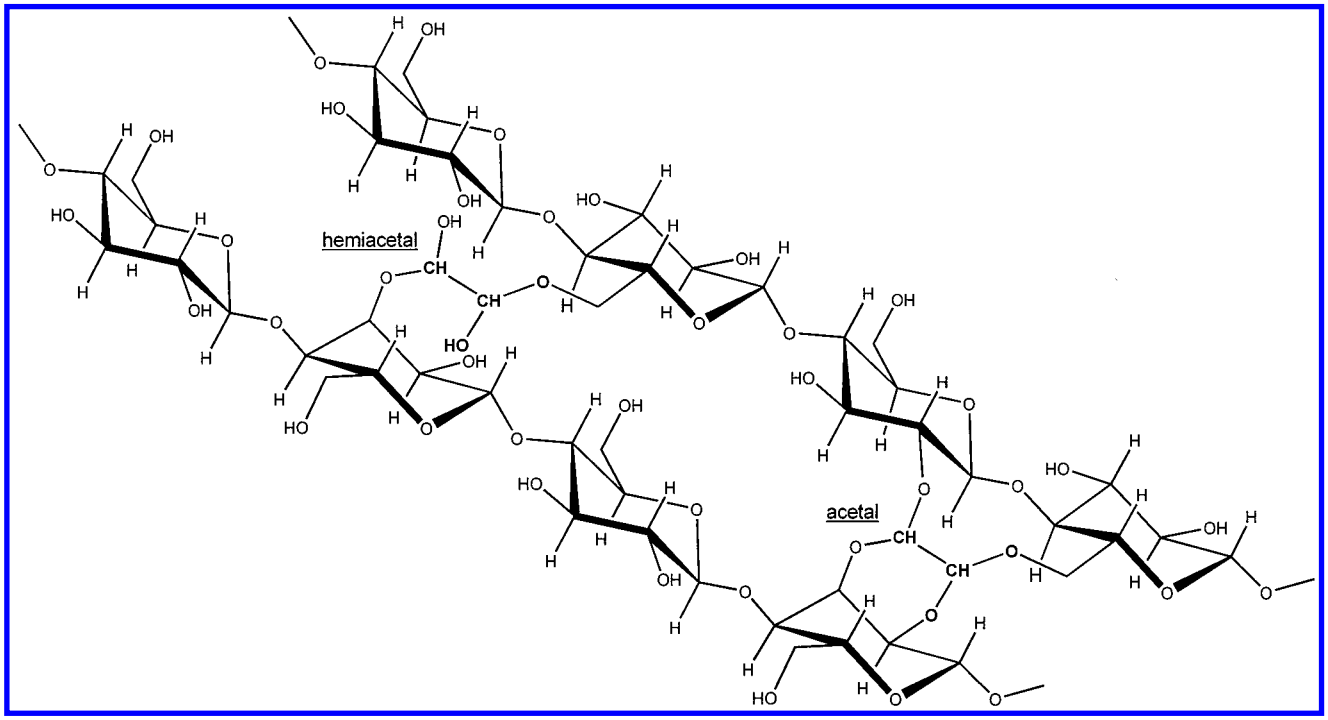

Figure 2. Acetal or hemiacetal linkages formed by reaction of glyoxal with the hydroxyl groups of the cellulose, thus imparting crease-resistance properties to the cotton fabric.

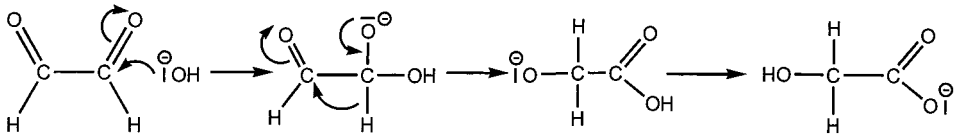

Figure 3. Glyoxal disproportionation, in alkaline medium, by an internal Cannizzaro reaction to glycolate.

10−100 and 100−1000 mg L^{-1} glycolic acid, respectively, using NaOH ($c = 4$ mol L^{-1}) as solvent. The regression analysis showed good linear correlation, $y = 577.6x - 72.1$, $r = 0.9996$. The detection limit was 1.87 mg L^{-1} (S/N = 3).

Correction of the Peak Area. To compare the results of the experiments, the peak area were normalized to 1 g of fabric weight and 100% wet pickup according to following equations:

$$PA_{nor} = [PA_{meas}] \times 100/WPU$$

$$\text{mg of glyoxal/g of fabric} = (PA_{nor} - b)/aV/1000/WOF_{ini} \times 0.7632$$

where PA_{nor} is the peak area normalized (μV·s), PA_{meas} is the peak area measured (μV·s), WPU is the wet pickup (%), b is the intercept of the calibration graph, a is the slope of the calibration graph, V is the volume of the volumetric flask (mL), WOF_{ini} is the initial weight of the fabric (g), and M_r(glyoxal)/M_r(glycolic acid) = 0.7632.

Reaction of Glyoxal with a Sodium Hydroxide Solution. To determine the optimum hydrolysis conditions, 250 mg of 40% (w/w) glyoxal was heated in 40 mL of NaOH ($c = 1$, 2 and 4 mol L^{-1}) at 100 °C for various periods (5, 10, 15, and 20 min). At the end of the reaction, the solution was chilled in ice, transferred to a 50-mL volumetric flask, and immediately analyzed chromatographically. The same runs were performed in the presence of 2 g of cellulosic raw material in an attempt to evaluate the influence of the cotton fabric on the chromatographic determination of glycolate. The results that are summarized in Table 1 clearly make evident that glyoxal was completely converted into glycolate after a reaction period of 10 min when a NaOH solution ($c = 1$ mol L^{-1}) was applied as extraction media. In the absence of the raw material, ∼93% of the theoretical amount of glycolic acid was determined. When ∼2 g of the cotton sample was added to the reaction mixture, the value of the theoretical amount of glycolate decreased to 85%.

Alkaline Hydrolysis of Glyoxal-Treated Cotton Fabric. Cotton samples were impregnated with a pad bath solution containing 6% (w/w) glyoxal and 4.5% (w/w) $Al_2(SO_4)_3 \cdot 16H_2O$, dried for 5 min at 105 °C, cured for 3 min at 140 °C, finally washed, and dried again as described in the Experimental Section. Accurately weighed glyoxal-treated cotton fabrics (∼2 g) were hydrolyzed in 40 mL of an NaOH solution of different concentrations (1, 2, and, 4 mol/L) for 5, 10, 15, and 20 min. The data shown in Table 2 prove that the portion of glycolate in the reaction mixture reached a constant level after 15 min. Figure 4 A shows the chromatogram that was obtained when 2 g of the raw material was treated with 40 mL of NaOH ($c = 4$ mol L^{-1}). Figure 4B demonstrates the chromatogram of a standard solution (glycolic acid 501.4 mg L^{-1}, NaOH, $c = 4$ mol L^{-1}). Peak 1 is assigned to glycolic acid. Figure 4C shows the chromatogram that was

Table 1. Recovery of Glycolate in the Absence and Presence of an Untreated Cotton Sample[a]

hydrolysis time (min)	recovery of glycolic acid (%)					
	in absence of cotton sample NaOH			in presence of cotton sample NaOH		
	c = 1 mol/L	c = 2 mol/L	c = 4 mol/L	c = 1 mol/L	c = 2 mol/L	c = 4 mol/L
5	90.5	92.7	94.8	77.2	82.2	84.5
10	96.5	93.3	90.0	91.1	83.7	87.2
15	93.3	91.3	91.3	88.9	84.7	84.5
20	91.7	94.4	92.5	91.3	88.6	85.6

[a] A total of 46.3 mg of glyoxal was treated in 40 mL of NaOH (c = 1, 2, 4 mol L^{-1}) for various periods at 100 °C. The glycolate, formed via n internal Cannizzaro reaction, was analyzed chromatographically. Conditions: $c(^1/_2H_2SO_4)$ = 0.01 and L^{-1}; BioRad Aminex HPX-87H, flow rate, 0.7 mL min^{-1}; column oven temperature, 80 °C; UV detector wavelength, 210 nm.

Table 2. Amount of Glyoxal Extracted from a Treated Cotton Fabric by Applying Various NaOH Concentrations and Extraction Periods[a]

hydrolysis time (min)	mg of glyoxal/g of fabric NaOH		
	c = 1 mol/L	c = 2 mol/L	c = 4 mol/L
5	14.2	13.4	12.6
10	16.0	15.8	15.1
15	16.8	16.3	16.7
20	17.8	16.7	17.1

[a] The glyoxal-treated cotton fabric (2 g) was hydrolyzed in 40 mL of NaOH (c = 1, 2, 4 mol L^{-1}) for various periods (5, 10, 15, 20 min) at 100 °C. The glycolate was analyzed chromatographically. Conditions: $c(^1/_2H_2SO_4)$ = 0.01 mol L^{-1}; BioRad Aminex HPX-87H, flow rate, 0.7 mL min^{-1}; column oven temperature, 80 °C; UV detector wavelength, 210 nm.

obtained, when 2 g of glyoxal-treated fabric was hydrolyzed and subsequently subjected to a chromatographic analysis. It can be seen that the additional peaks in Figure 4C must come from compounds produced by the influence of alkali on the raw material.

Total Removal of Glyoxal. To use this chromatographic technique for the quantification of the portion of glyoxal bound to the cotton fabric, it was necessary to provide evidence that a complete removal of glyoxal occurred. Because no analytical method is available to detect the portion of glyoxal that has reacted with the cellulose, the evaluation of the DCRA before and after the hydrolysis procedure was applied to prove the complete removal of glyoxal. In this procedure, 20 test specimens (10 warp, 10 fill, 20 × 50 mm) were creased and compressed under controlled conditions of time (30 min) and load (1 kg) and then suspended for a controlled recovery period (30 min), after which the recovery angles were measured and the average values of warp and fill were added. The DCRA values were as follows: untreated fabric 188° (warp, 103.6 ± 4.86; fill, 84.4 ± 7.19) glyoxal-treated fabric 299° (warp, 155.2 ± 1.54; fill, 144.4 ± 2.22), and corresponding hydrolyzed specimen 190° (warp, 104.8 ± 7.34; fill, 85.2 ± 3.84)°. These results indicated that the cross-linkage was removed, thus confirming that the acetal or hemiacetal linkages to the cellulosic material were completely cleaved, and as a consequence, glyoxal was converted into glycolate.

Application of the Method. Four cotton samples were impregnated with finishing solutions containing 2, 4, 6, and 8% (w/w) glyoxal and 1.5, 3.0, 4.5, and 6.0% (w/w) aluminum sulfate hexadecahydrate as curing catalyst. The fabrics were finished,

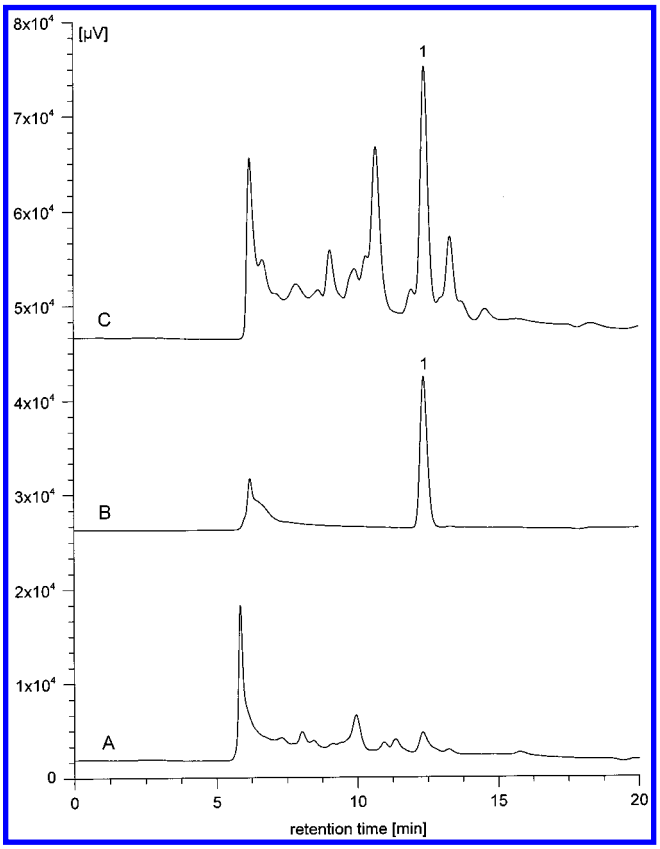

Figure 4. Chromatograms of the hydrolysis solutions (NaOH c = 4 mol L^{-1}, 100 °C, 20 min): (A) hydrolysis solution of 2 g of untreated cotton sample; (B) standard solution of 501.4 mg L^{-1} glycolic acid in NaOH c = 4 mol L^{-1}; (C) hydrolysis solution of 2 g of treated cotton sample. (1) Glycolic acid, $c(^1/_2H_2SO_4)$ = 0.01 mol L^{-1}; BioRad Aminex HPX-87H; flow rate, 0.7 mL min^{-1}; column oven temperature, 80 °C; UV detector wavelength, 210 nm.

and the amount of glyoxal on the fabric was measured as described in the Experimental Section. Each cotton sample was analyzed three times, whereby each hydrolysis liquor was subjected to a triplicate injection. As can be seen in Table 3, the amount of glyoxal linked to the cellulose increases as the weight fraction in the formulation increases. The DCRA value reaches only a low level when 2% (w/w) glyoxal is incorporated into the pad bath formulation. The addition of 4% (w/w) glyoxal results in a significant improvement of the DCRA. A slight enhancement of the DCRA is obtained when the weight fraction of glyoxal is increased to 6 (w/w) and 8% (w/w). A noteworthy aspect of the data in Table 3 is that the application of 6 (w/w) and 8% (w/w)

Table 3. Amount of Glyoxal That Has Reacted with Cellulosic Material

glyoxal in formulation (%, w/w)	$Al_2(SO_4)_3 \cdot 16H_2O$ in formulation (%, w/w)	glyoxal on fabric ($n = 3$) (mg/g)[a]	DCRA[b] (w + f)[c] (deg)
2	1.5	2.3 + 0.06	233
4	3.0	5.9 + 0.51	285
6	4.5	15.7 + 0.72	294
8	6.0	31.2 + 0.67	292
raw material			201

[a] Grams of fabric. [b] Dry crease recovery angle indicates the extent of cross-linking. [c] Warp and fill.

glyoxal results in an increase of the portion of glyoxal on the fabric, whereas the DCRA values are reaching nearly the same level.

Standard Additions Method. To confirm the data obtained, the standard additions method was applied. For this purpose, a cotton fabric was treated as described in the Experimental Section, incorporating 6.0% (w/w) glyoxal and 4.5% (w/w) $Al_2(SO_4)_3 \cdot 16H_2O$ into the pad bath formulation. The finished cellulosic fabric was cut to small pieces and accurately weighed portions (1 g) were placed in five different reaction vessels. Prior to the alkaline treatment, 0, 1, 2, 3, and 4 mL of a stock 40% (w/w) glyoxal solution (20.4 mg of glyoxal mL^{-1}) was added and hydrolyzed in 40 mL NaOH ($c = 4$ mol L^{-1}). This procedure was carried out three times for each addition. Each extraction solution was injected three times and the average data obtained (peak area corrected, mg of glyoxal added) were subjected to a linear regression analysis ($y = 13877.5x + 221801.3$, $r^2 = 0.9974$). The amount of glyoxal that was bound to 1 g of fabric corresponds to the ratio b/a, where b is the intercept and a is the slope of the regression line.[33] Therefore, the standard additions method provides the value of 16.0 mg/g of fabric being consistent with those (15.7 mg/g) obtained by the calibration curve method (Table 3).

Glyoxal and Polycarboxylic Acids. As mentioned above, PCAs such as 1,2,3,4-butanetetracarboxylic acid or citric acid have been introduced successfully as non-formaldehyde durable-press finishing agents. Therefore, it was also of high interest to evaluate whether the analytical method described enables the mutual separation of the PCAs and glycolate. Since the cross-linking reaction is achieved in terms of ester linkages, the identification and quantification of the portion of the PCA that has reacted with the cellulose were readily accomplished using the same procedure as described in the present study. However, when citric acid was used as the cross-linking agent, the unsaturated carboxylic acids *cis*-/*trans*-aconitic acid, citraconic acid ((2*Z*)-2-methyl-2-butenedioic acid), itaconic acid (methylenebutanedioic acid), and mesaconic acid ((2*E*)−2-methyl-2-butenedioic acid) were formed during the curing process (180 °C, 90 s) due to decarboxylation and dehydration reactions of citric acid.[25] Figure 5 shows the chromatogram of a mixture consisting of 1,2,3,4-butanetetracarboxylic acid (503.8 mg L^{-1}), citric acid (552.0 mg L^{-1}), *cis*-/*trans*-aconitic acid (24.8 mg L^{-1}), citraconic acid (48.2 mg L^{-1}), itaconic acid (21.0 mg L^{-1}), mesaconic acid (20.8 mg L^{-1}), and glycolic acid (1605 mg L^{-1}). The chromatogram demonstrates that glycolic acid (peak 6) is well separated from the PCAs. The peak of glycolic acid solely overlaps with the peak of itaconic acid (peak 7). However, since itaconic acid is a decomposition product of citric acid, it is only present in the analysis mixture when citric acid was applied as durable-press agent. Therefore, an identification of glycolate under the chromatographic conditions chosen is readily obtainable.

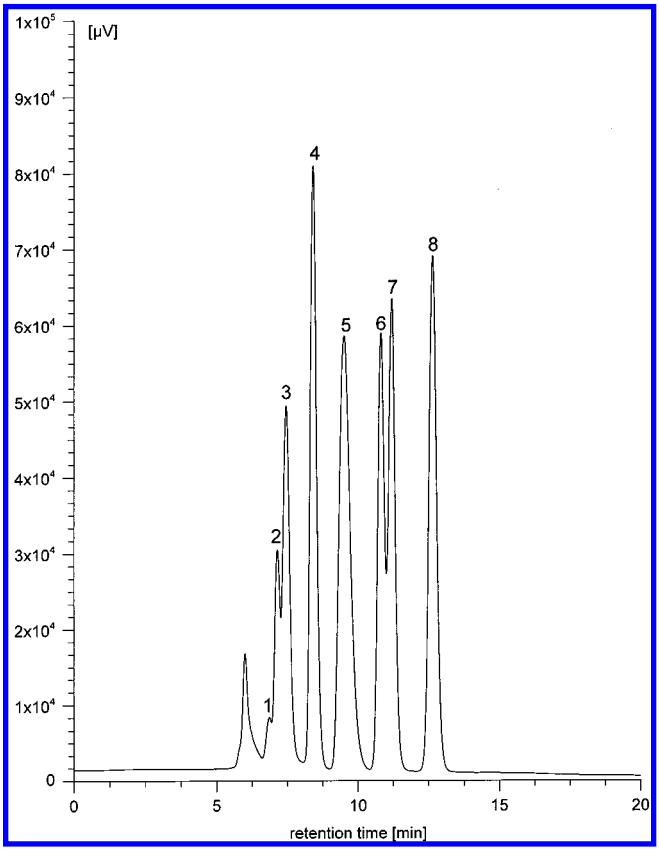

Figure 5. Chromatogram of a solution containing (1) *cis*-aconitic acid, (2) 1,2,3,4-butanetetracarboxylic acid (503.8 mg L^{-1}), (3) citric acid (552.0 mg L^{-1}), (4) aconitic acid (24.8 mg L^{-1}), (5) citraconic acid (48.2 mg L^{-1}), (6) itaconic acid (21.0 mg L^{-1}), (7) glycolic acid (1605 mg L^{-1}), and (8) mesaconic acid (20.8 mg L^{-1}), $c(^1/_2H_2SO_4) =$ 0.01 mol L^{-1}; BioRad Aminex HPX-87H, flow rate, 0.7 mL min^{-1}; column oven temperature, 80 °C; UV detector wavelength, 210 nm.

CONCLUSIONS

For the first time, an analytical method was developed capable of identifying and quantifying the portion of glyoxal that has reacted with cellulosic material. The alkaline treatment of glyoxal-finished cotton samples resulted in the formation of sodium glycolate via an internal Cannizzaro reaction. However, the method does not allow us to evaluate whether the cross-linkage is achieved by an acetal or hemiacetal linkage. In addition, the current method permits us to distinguish whether a PCA or glyoxal was applied as the cross-linking agent.

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