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CHROMATOGRAPHIC METHOD FOR DETERMINATION OF OXALIC ACID IN BLEACHING FILTRATES FROM THE PULP AND PAPER INDUSTRY[*]

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Abstract Analysis and control of oxalic acid in bleaching filtrates has recently gained considerable attention in the pulp and paper industry due to problems with the formation of calcium oxalate scaling Chromatographic methods, such as HPLC and ion chromatography(IC), are generally valuable as standard methods for determination of oxalic acid. In this study, a HPLC system equipped with an Aminex HPX-87H column was applied to determine oxalic acid in authentic bleaching filtrates. An established IC method based on separation with an anion-exchange column was used as reference method. The results showed that bleaching filtrates contain compounds interfering with the HPLC method. A strategy, dilution of the samples followed by treatment with activated carbon, was needed to obtain similar oxalic acid concentrations as provided by the reference method The correlation($R = 0.994$) between the HPLC method and the IC method is described by the equation $y = 1.2947x$. The method improves the possibility for control of critical oxalic acid concentration in closed-loop bleaching streams

Key words: oxalic acid; bleaching filtrates; activated carbon; pulp and paper industry

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：近年来草酸钙 (草酸垢)的形成在制浆造纸工业中造成诸多问题,因此如何分析及控制漂白废液中的草酸浓度就显得尤为重要　高效液相色谱和离子交换色谱等色谱法 一般可以作为测定草酸的标准方法　本研究以 一个基于阴离子交换柱的离子交换色谱法作为对照方法,利用 一套配备了 Aminex HPX- 87H 液相色谱柱的高效液相色谱系统测定漂白废液中的草酸浓度　结果显示,漂白废液中含有 一些干扰高效液相色谱法测定的化合物　通过采用稀释样品后再经活性炭吸附的处理方法,可以得到较为满意的结果　分析发现高效液相色谱法与离子交换色谱 (对照法)之间的相关性较好,相关系数为 0.994　该方法的建立将有利于监控制浆造纸企业中闭路循环漂液中形成草酸钙时的临界草酸浓度

：草酸; 漂白废液; 活性炭; 制浆造纸工业

Nowadays bleaching with oxygen-containing reagents and the use of counter-current washing with closure of the water streams in the pulp mill, together with external wastewater treatment, have made bleaching of pulp

more environmentally friendly than previously. However, oxygen bleaching and the use of strong oxidizing agents like hydrogen peroxide and ozone result in extensive oxidation of the dissolved lignocellulosic material and formation of various acids like oxalic, formic and acetic acid[1]. Since process water is recirculated in order to decrease fresh water consumption, the concentration of oxalic acid from bleaching, pulping and also from native wood will increase. The accumulation of oxalic acid causes a considerably urgent problem, namely the precipitation of calcium oxalate, also known as scaling which is a major obstacle to system closure. Selective elimination of oxalic acid by using oxalate-degrading enzymes like oxalate oxidase and oxalate decarboxylase is a potential approach to prevent scaling[2-3]. Therefore, the ability to perform rapid assays and control of the concentration of oxalic acid in bleaching filtrates is of particular importance for the pulp and paper industry.

Previously, a method using ion chromatography(IC) to separate and detect organic acids including oxalic acid in bleaching filtrates was reported [4-5]. However, this is a very specialized analytical system and also relatively expensive. A simple and convenient method for detection of oxalic acid in bleaching filtrates has not been constructed yet. Here, we investigated an alternative approach, namely ordinary HPLC utilizing a Bio-Rad Aminex HPX–87H ion-exclusion resin column. This study is the first in which HPLC is used for determination of oxalic acid in bleaching filtrates from the pulp and paper industry.

In the study, the influences of column temperature and acid strength of eluant on the retention and separation of oxalic acid of bleaching filtrates on the Aminex ion-exclusion column HPX–87H were investigated. The effect of pretreatment with activated carbon(AC) prior to separation and identification of oxalic acid by HPLC was examined in detail. The accuracy of the method in authentic bleaching filtrate was compared with a reference method consisting of an ion chromatography system equipped with a conductimetric detector and an IonPac AS4A–SC anion–exchange column.

1 Experimental

1. 1 Chemicals and oxalic acid standard solution

Unless otherwise stated, all chemicals used were obtained from Sigma-Aldrich(St Louis, MO, USA). This includes AC(acid washed with hydrochloric acid, Cat No. C 4386). A sample diluent buffer for AC treatment was made with succinic acid (50 mmol/L) and adjusted to pH value 6. 5 with NaOH. Oxalic acid standard solutions were made by dissolving oxalic acid in distilled water to achieve the required concentrations from 0. 2 to 2. 0mmol/L.

1. 2 Bleaching filtrate preparation

A set of bleaching filtrates from pulp and paper mills was collected from OP, Z, Obc, O, Q and P–stages. Just before analysis with HPLC or AC treatment, the pH value of the bleaching filtrates was adjusted to 4 – 6 using 20% H_2SO_4 or 10 mol/L NaOH.

1. 3 Pretreatment of bleaching filtrates with activated carbon

The pH–adjusted bleaching filtrate was diluted with an equal volume of sample diluent (50 mmol/L, pH value 6. 5). The pH value of the diluted bleaching filtrate was checked by using a pH–meter to make sure that the pH value should be 6. 5. If not, the pH value was adjusted with H_2SO_4 or NaOH. Thereafter, the diluted bleaching filtrate was mixed with 150 or 200 g/L AC in 15–mL centrifuge tubes for 5 min by using a rotating mixer. Then, the mixture was filtered with Whatman filter paper(1F quality filter papers, Munktell Filter AB, Grycksbo, Sweden) under vacuum, or alternatively, was centrifuged for 5 min at 2 500 r/min in Oxalate standard solutions were prepared and treated in the same way as the bleaching filtrates. The pH value was checked and adjusted as for the bleaching filtrates. The filtrates or supernatants were analyzed with HPLC method.

1. 4 Analysis of oxalic acid by HPLC

Oxalic acid was separated by an HPLC system (Shimadzu, Kyoto, Japan) equipped with an Aminex HPX–87H column (resin in hydrogen form of sulfonated divinylbenzene–styrene copolymer, mean particle diameter 9 μm, 300 mm × 7. 8 mm i d; Bio–Rad, Hercules, CA) at 35 or 60 ℃ with 2, 5 or 12 5 mmol/L H_2SO_4 as mobile phase at a flow rate of 0. 6 mL/min. The system was equipped with a Cation–H Refill Cartridge (Bio–Rad) prior to the HPX–87H column. Oxalic acid was detected by using a UV detector (SPD–6A, Shimadzu) at 210 nm. All chromatographic data were recorded and analyzed by using a Gilson Unipoint System Software (Middleton, WI, USA). For all analyses, 20 μL of sample was injected. Oxalic acid was identified by the retention times compared to those of external standards. The concentration of oxalic acid was calculated by comparing the obtained peak area to a calibration curve. The pH value of bleaching filtrates was adjusted to around 4–6 by using 20% sulfuric acid or 10 mol/L NaOH. Thereafter, the bleaching filtrates were filtered through 0. 2 μm membrane filters (Advantec MFS, Pleasanton, CA, USA). All analyses were carried out in duplicates and mean values are presented. If the value of oxalic acid exceeded the standard ranges, the sample was diluted appropriately with water.

1. 5 Determination of oxalic acid by IC

The chromatographic equipment consisted of a Dionex 2020i–series ion chromatography system equipped with a conductimetric detector (ED–40). An IonPac AS4A–SC anion–exchange column (250 mm × 4 mm i d) and an AG4A guard column were used. A membrane suppressor (ASRS–I) was used to convert the eluant and the separated anions to their respective acid forms and to lower the conductivity of the eluant relative to that of the ions of interest. All instrumentation including the columns and the suppressor, was supplied by Dionex (Sunnyvale, CA, USA). The mobile phase consisted of 1. 7 mmol/L $NaHCO_3$ and 1. 8 mmol/L Na_2CO_3 and was applied at a flow rate of 2. 0 mL/min. For all analyses, 20 μL of sample was injected. Ions were identified by their retention times compared to those of external standards. Quantification of oxalic acid was accomplished by comparing the obtained peak area to a calibration curve. The EZchrom software system, version 2. 31 (Scientific Software Inc., Pleasanton, CA, USA) was used for the quantification procedure. A detailed description of the methods used for determination of oxalic acid and calcium oxalate was presented and discussed previously[5].

2 Results and discussions

2. 1 Analysis of oxalic acid using the HPLC system

The results obtained by Dionex ion exchange chromatography equipped with an IonPac AS4A–SC anion–exchange column were used as references for oxalic acid determination in bleaching filtrates. Three different concentrations of sulfuric acid (2, 5 and 12 5 mmol/L) were used as mobile phase at a flow rate of 0. 6 mL/min at 35 ℃ for HPLC analysis. Mean values of retention times of oxalic acid were 7. 03, 7. 33 and

Table 1   Oxalic acid analysis by HPLC and ion chromatography without AC treatment

| samples	original pH value	HPLC data[2]			IC[3]
		2 (Rt= 7. 03)	5 (Rt= 7. 33)	12 5 (Rt= 8 02)	
0 2[1]	—	0. 22	0. 20	0. 21	—
OP	12 37	21. 29	22. 26	9. 01	2 40
Z	2 08	4. 91	4. 49	2. 01	0 90
Obc	10 82	12. 18	10. 06	5. 83	5 84
O_1	10 22	13. 89	6. 14	1. 09	1 46
O_2	12 38	8. 16	8. 20	7. 33	1 91
Q	5 64	5. 15	4. 09	0. 13	0 17
P_1	9 69	4. 74	4. 16	0. 68	0 20
P_2	9 53	2. 75	2. 29	0. 58	0 28

1) 0 2–2 0 mmol/L aqueous oxalate solutions were used as standards and here the data from the 0. 2 mmol/L standard are shown;

2) Mean value of the retention time of a series of oxalic acid standards, HPLC conditions 35 ℃, 0 6 mL/min, 2 5 and 12 5 are the concn. of H_2SO_4 in eluant (mmol·L^{-1});

3) Ion chromatography was used as the reference method

8 02 min, respectively, when 2, 5 and 12 5 mmol/L sulfuric acid was used (Table 1). The retention time of oxalic acid increased by 14% as the acid concentration increased from 2 to 12 5 mmol/L. These concentrations

of sulfuric acid did not affect the shape of oxalic acid peak and slightly changed the peak areas. The relative standard deviation in the change of peak area was 5. 8% with 1. 0 mmol/L aqueous solution of oxalic acid.

With these three different acid concentrations (2, 5 and 12. 5 mmol/L), the values of oxalic acid in several bleaching filtrates, obtained from OP, Z, Obc, O, Q and P-stages, largely diverged from the data obtained by IC. These data show that the concentration obtained for oxalic acid decreased with increasing concentration of sulfuric acid in the mobile phase. The determinations made with 12. 5 mmol/L H_2SO_4 as mobile phase started to draw near to the actual concentration of oxalic acid detected by IC. The chromatograms demonstrate that oxalic acid was not separated on the Aminex HPX– 87H column with 2 mmol/L sulfuric acid whereas the resolution was slightly improved with increasing acid concentration and more peaks appeared with 12. 5 mmol/L H_2SO_4 as the mobile phase (Fig. 1). Analytical conditions: 0. 6 mL/min, 35 ℃.
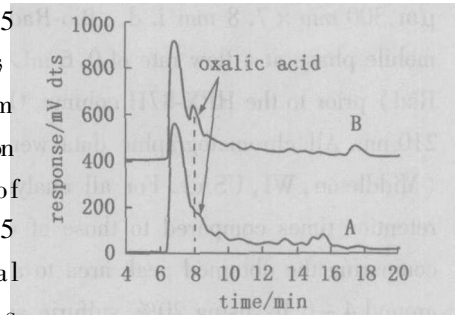
A. 2 mmol/L H_2SO_4; B. 12. 5 mmol/L H_2SO_4

Fig 1   Chromatogram of Obc bleaching filtrate from oxygen bleaching stage in HPLC analysis

In an attempt to resolve the problems with the compounds that eluted closely together, the separation temperature was raised from 35 to 60 ℃, but no further improvement was achieved and in contrast, the mean value for the retention time of oxalic acid decreased slightly to 7. 89 min with 12. 5 mmol/L sulfuric acid as the mobile phase at 60 ℃ and 0. 6 mL/min (data not shown). An increase in separation temperature did not change the peak shape and slightly influenced peak areas. The relative standard deviation in the change of peak area was 5. 5% with 1. 0 mmol/L aqueous solution of oxalic acid.

## 2. 2 Study on various pretreatments for bleaching filtrate using HPLC to detect oxalic acid

Since bleaching filtrates contained some compounds interfering with the HPLC method, several different kinds of pretreatment were evaluated. The sample chosen for this study was the O–stage bleaching filtrate containing 1. 91 mmol/L oxalic acid(determined by IC). Table 2 indicates that HPLC gave erroneous values when no pretreatment was made or when only dilution was used.

Table 2   Comparison on various pre–treatment prior to oxalate assays with HPLC[1]

| filtrates	pretreatment	HPLC data[2]	
		5	12. 5
O_2 f-1	None	8. 66±0. 65	7. 33
O_2 f-2	Dilution 2 times	9. 40±0. 34	6. 69
O_2 f-3	150 g/L AC	2. 09±0. 01	2. 11
O_2 f-4	200 g/L AC	2. 40±0. 09	2. 20
O_2 f-5	200 g/L AC, dilution 2 times	2. 10±0. 37	2. 25
O_2 f-6	Dilution 2 times first, 150 g/L AC	2. 72±0. 17	2. 27
O_2 f-7	Dilution 2 times first, 200 g/L AC	2. 40±0. 01	2. 27
O_2 f-8	Dilution 2 times first, 10 mmol/L EDTA, 200 g/L AC	2. 42±0. 02	2. 41
O_2 f-9	200 g/L AC, dilution 2 times, 5 mmol/L EDTA	2. 44±0. 11	2. 36

1) The concentration of oxalate is 1. 91 mmol/L, which was obtained by IC. Conditions: 0. 6 mL/min, 35 ℃; 2) 5 and 12. 5 are the concn. of H_2SO_4(mmol L^{-1})

However, if AC treatment was applied prior to HPLC, values around 2. 28 mmol/L, close to 1. 91 mmol/L, were obtained in the samples from O_2 f-3 to O_2 f-9 with 12. 5 mmol/L H_2SO_4 as mobile phase at 35 ℃ and 0. 6 mL/min. The decolorization was observed obviously after AC treatment. The chromatogram shows that the front peak was reduced significantly, and the separation of oxalic acid was satisfactory after treatment with AC(Fig. 2). However, when 2 mmol/L H_2SO_4 was used as the eluant, the separation of oxalic acid was still poor even after treatment with AC(Fig. 3) and incorrect values were obtained (data not shown).
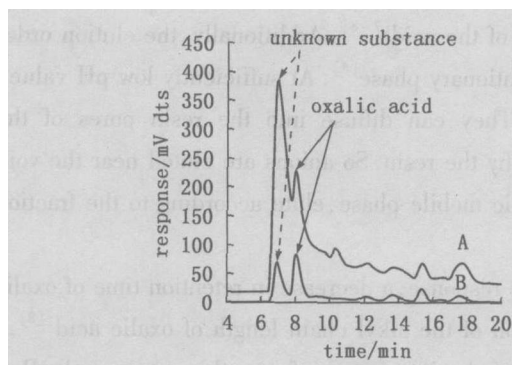
A. before treatment； B after treated w ith 200 g/L AC

F ig 2   Chromatograms of O_2 f bleaching filtrate from oxygen bleaching stage conditions 0. 6 mL/m in, 35 ℃, 12. 5 mmol/L H_2SO_4
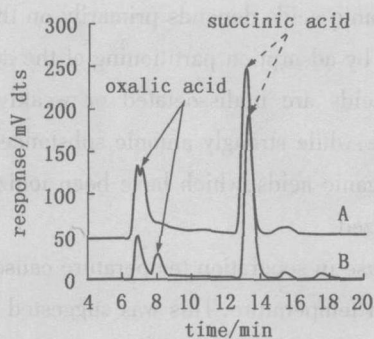
A. 2 mmol/L H_2SO_4;   B 12. 5 mmol/L H_2SO_4

F ig 3   Chromatograms of O bc bleaching filtrate from oxygen bleaching stage after treated w ith 150 g/L AC

2 3   Pretreatment by dilution followed by AC treatment in bleaching filtrates

F ive b leaching filtrates obtained from Obc, O, Q, P_1 and P_2-stages were employed to verify the strategy with dilution (w ith a sample diluent containing 10 mmol/L EDTA) follow ed by AC treatment (150 g /L). Table 3 indicates that after using the strategy, both results obtained with the HPLC analys is correlated with those obtained with IC very well, with the exception of the value obtained by HPLC analysis of the Q-stage filtrate. L inear regression analysis of the 5 results gave the equation $y = 1. 294. 7x$ and the correlation coefficient (R) was 0. 994

Table 3   M ore assays using the strategy dilution first followed by AC treatment (150 g/L) in HPLC analyses

bleaching filtrates	HPLC[1]	IC[2]
V 001 (O bc)	3. 96	3 02
V 002 (O f)	0. 41	0 58
V 003 (Q f)	0. 13	0. 028
V 005 (P_1 f)	0. 14	0. 12
V 008 (P_2 f)	0. 14	0. 16

1)HPLC conditions 12. 5 mmol/L H_2SO_4, 0. 6 mL /m in, 35 ℃;   2) IC method was used as a reference here A ll assays w ere performed in duplicates and mean value was presented

3   Conclusion

3 1   Analyses performed with the Am inex HPX-87H column show ed good precision and accuracy w ith aqueous solution of oxalic acid H ow ever, it d id not efficiently separate oxalic acid from other compounds in bleaching filtrates under the conditions investigated E rroneous results were obtained even under optimized conditions, where the concentration of sulfuric acid in the mobile phase was increased from 2 to 12. 5 mmol/L and the separation temperature was raised from 35 to 60 ℃. Nevertheless, the tendency to approach the correct value and higher resolution was improved when 2 mmol/L H_2SO_4 w as replaced with 12. 5 mmol/L

3 2   An increase in the concentration of acid in the mobile phase resulted in longer retention time of oxalic acid and consequently improved resolution of separation of organic acids. The most dramatic increase (14%) in retention time of oxalic acid was seen when the strength of sulfuric acid was increased from 2 to 12. 5 mmol/L The result is in accordance with a previous report with respect to the effect of sulfuric acid concentration [6]. A good separation could be obtained at a h igher acid concentration of the eluant since the elevated concentration of sulfuric acid in the eluant affects the d issociation of oxalic acid How ever obviously, this improvement was insufficient for separation of oxalic acid from other compounds in the b leaching filtrates These compounds(the first peak in the chromatograms) w ere always eluted near the void volume together with oxalic acid The first peak before oxalic ac id m ight be some other anions since there are several different anions present in bleaching filtrates, such as chloride and carbonate, or other matrix from lignocellu bse. W hen d ilute sulfuric ac id is used as the eluant, organic acids elute from the column in the order of increasing pK_a, since the

retention of organic acids depends primarily on the dissociation of the acid[7-8]. Additionally, the elution order is also affected by adsorption partitioning of the acid with the stationary phase[8]. At sufficiently low pH value, weak organic acids are undissociated or weakly dissociated. They can diffuse into the resin pores of the stationary phase, while strongly anionic substances are rejected by the resin. So anions are eluted near the void volume. The organic acids, which have been ionized in the acidic mobile phase, elute according to the fraction of the acid ionized.

3. 3 An increase in separation temperature caused the opposite response, a decrease in retention time of oxalic acid at elevated temperature. This was suggested to be a function of the alkyl chain length of oxalic acid[8].

3. 4 Pretreatment with AC afforded a way to get rid of most of the interference from other compounds. Pretreatment with 150 g/L AC was sufficient for the HPLC analysis. Nevertheless, with 2 mmol/L H_2SO_4 as the eluant, an incorrect value was still obtained even if AC treatment was used since the resolution was very poor. The mobile phase consisting of 12. 5 mmol/L sulfuric acid must therefore be combined with AC treatment.

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