An Improved Method for Determination of Pentosans in Pulps using Dual-Wavelength Spectroscopy

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The aim of this study was to determine the pentosan content in pulps by a dual-wavelength spectrophotometric method. The method was based on the boiling reaction between pentosan and 12% hydrochloric acid, in which pentosan was subsequently converted to furfural. The concentration of furfural in the distillate was determined by the absorbance at 280 nm and 290 nm. Several different simultaneous equations were solved to obtain the concentrations of furfural in the distillate. The results showed that the method had an excellent accuracy (RSD ≤ 0.61%) and reproducibility (RSD = 3.25%). The spectral interference of the 5-hydroxymethyl-2-furaldehyde in the distillate was eliminated by the dual-wavelength measurement technique. Compared with the TAPPI method (colorimetric method), this method is simple, user-friendly, and practical and has high detection sensitivity.

Keywords: Pentosans; Dual-wavelength spectroscopy; Furfural; HMF

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INTRODUCTION

Biomass, which is primarily composed of cellulose, hemicellulose, and lignin, is a renewable resource that can be converted to value-added chemicals and fuels (Yang *et al*. 2007; Zhang *et al*. 2014). Pentosan, a mixture of polysaccharides containing xylose, arabinose, and other sugars, is often the primary hemicellulose (Launer and Wilson 1939). In various raw materials such as softwood, hardwood, and grasses, the pentosan contents are 7% to 10%, 19% to 24%, and 18% to 25%, respectively. Different kinds of pulps, *e.g.*, dissolving pulps and normal pulps, contain various amounts of pentosan (Ma *et al*. 2011). Because pentosan has a considerable influence on the properties of papers, a method that accurately determines the pentosan content in pulps is important to control and optimize the process of pulp and paper (Ververis *et al*. 2007).

Several different analytical methods such as gas chromatography (Folkes 2006), Duffau distillation method, colorimetric method (Dubois *et al*. 1956), and ion chromatography (Dan and Bunker 1989) have been widely used to determine pentosan content in pulps. The colorimetric method (Pham *et al*. 2011) is used in the TAPPI standard (T223 cm-01 2001) to determine the pentosan content in pulps. This method is based on the amount of furfural that is converted from pentosan in a reaction containing 12% hydrochloric acid (HCl) conditions (Fig. 1) (Li *et al*. 2013). The furfural reacts with color reagent (orcinol-ferric chloride) within 1 h at 25 °C. The products of this chromogenic reaction have a characteristic absorbance at 630 nm. However, orcinol-ferric chloride is easily oxidized by oxygen during the process. Other drawbacks include safety problems and the bad odour of the color reaction reagent. Because the chromogenic reaction is relatively time-consuming, complicated, and unsafe, it needs improvement to meet the needs of the pulp and paper industry.

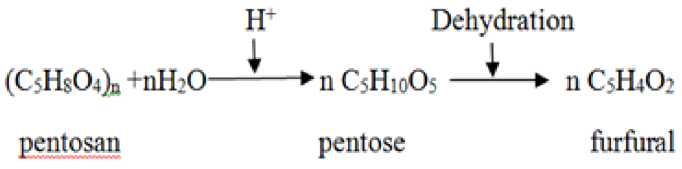


Fig. 1. The formation of furfural from pentosan

In this work, an improved and well-designed method (dual-wavelength UV spectrophotometry) to determine the furfural content in the distillate is reported. At a high temperature and under acidic conditions, furfural and 5-hydroxymethyl-2-furaldehyde (HMF) were easily converted from pentoses and hexoses, respectively. Martinez *et al*. (2000) found that furfural and HMF had different specific absorption peaks at 278 nm and 284 nm, respectively. When only one of them was dissolved in the distillate, furfural and HMF could be accurately determined by the UV spectrophotometric method. However, both HMF and furfural were formed from hexoses and pentoses, which are present in carbohydrates. Consequently, HMF could interfere with the precise measurement of furfural during the process. Therefore, a dual-wavelength UV spectrophotometric method that allowed accurate determination of furfural while simultaneously alleviating the interference of HMF by measuring the absorbance of the difference spectrum at 280 nm and 290 nm was developed. Because acid soluble lignin, which also has a characteristic absorption at 280 nm, was not present in the distillate, it did not affect the precise determination of furfural and HMF.

EXPERIMENTAL

Chemicals and Materials

All analytical grade chemicals, including furfural, HMF, were obtained from commercial sources (Guangzhou Chemical Reagent Factory, Gangdong, China). Eucalyptus pulps, bamboo pulps, and bagasse pulps were obtained from Guangdong Dingfeng Paper Co. Ltd. (China). Standard solutions of furfural and HMF were prepared and ranged from 20 to 100 μM.

Apparatus

The experiment was carried out in a furfural distillation apparatus, including a boiling flask, condenser pipe, separatory funnel, and volumetric flask. Spectroscopic measurements were recorded on a spectrophotometer (Agilent 8453, Santa Clara, USA) equipped with a 10 mm quartz cuvette.

Methods

Sample preparation

Distillation experiments were carried out in a boiling flask with 0.5 g of eucalyptus pulps, 100 mL of 12% HCl, 10 g sodium hydroxide, and several glass beads. During the process, 30 mL of distilled liquid was transferred to volumetric flasks every 10 min, and 30 mL 12% HCl was added to the boiling flask from separatory funnel. The experiment was terminated by aniline acetate, which was used to determine if furfural was completely distilled.

Spectral measurement and effect factors

The absorbance of the distillate in the visible region (280 nm and 290 nm) was measured with the UV spectrophotometer, using 12% HCl as the reference solution. Other factors such as hydrochloric acid concentrations and time were taken into consideration in this experiment. The reference experiment also carried out, according to the TAPPI T223cm-01 (2001) standard.

RESULTS AND DISCUSSION

UV Spectra of Furfural, HMF, and Samples

The mechanism used in the experiment was based on the boiling reaction of pentosan and 12% HCl, in which pentosan was converted to furfural. Figure 2 reveals that furfural, HMF, and distillate sample had the characteristic absorbance peaks at 278 nm, 284 nm, and 280 nm, respectively. Because HMF interfered with the accuracy of furfural measurements at 280 nm, it was not acceptable to determine furfural in the solution. Therefore, a dual-wavelength UV spectrophotometric method designed was necessary to determine the furfural in distillate.

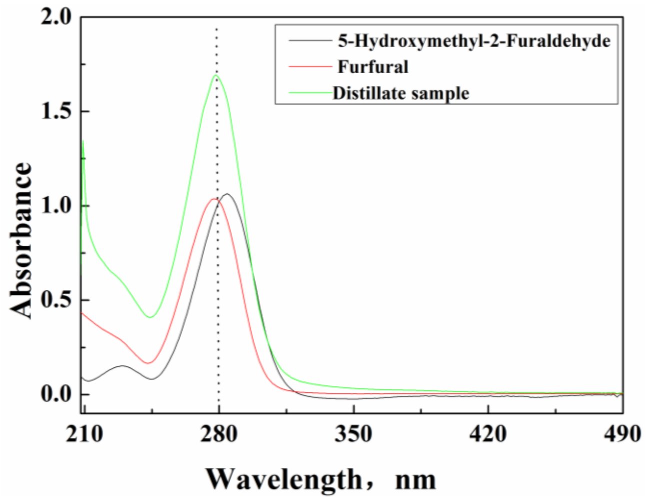


Fig. 2. UV spectra of distillate sample, furfural, and HMF in 280 nm

Determination of Furfural by Dual-Wavelength Spectroscopy

The UV spectra of furfural and HMF at various standard concentrations are shown in Fig. 3. In addition, Fig. 4 shows the relationships between absorptions and concentrations of HMF and furfural at 280 nm. In both figures, excellent linear relationships existed for furfural and HMF, which was expected by the Lambert-Beer Law. Therefore, isoabsorptive point wavelength (280 nm) and determined wavelength (290 nm) were selected to deduce the concentrations of furfural. The HMF and furfural absorption equations were based on the Lambert-Beer Law (Eqs. 2 and 3),

$$A_{280} = \xi_{280}^{1}C_1 + \xi_{280}^{2}C_2 \quad (2)$$

$$A_{290} = \xi_{290}^{1}C_1 + \xi_{290}^{2}C_2 \quad (3)$$

where A_{280} and A_{290} were the absorbance values at 280 nm and 290 nm, and ξ_{280}^{1}, ξ_{290}^{1} ξ_{280}^{2}， ξ_{290}^{2} were the molar absorption coefficient of furfural and HMF at 280 nm and 290 nm, respectively. C_1 and C_2 were the molar concentrations of furfural and HMF.

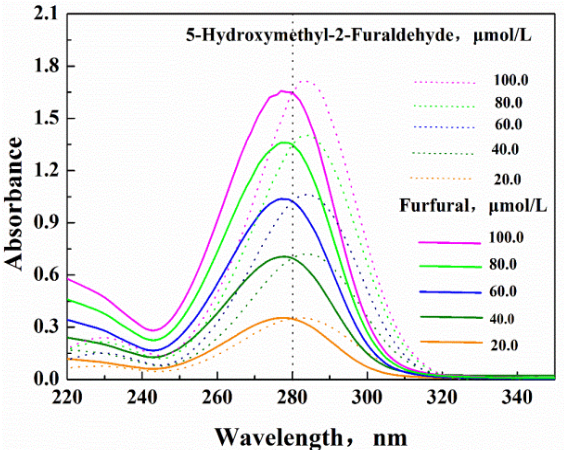


Fig. 3. The ultraviolet spectra of furfural and HMF

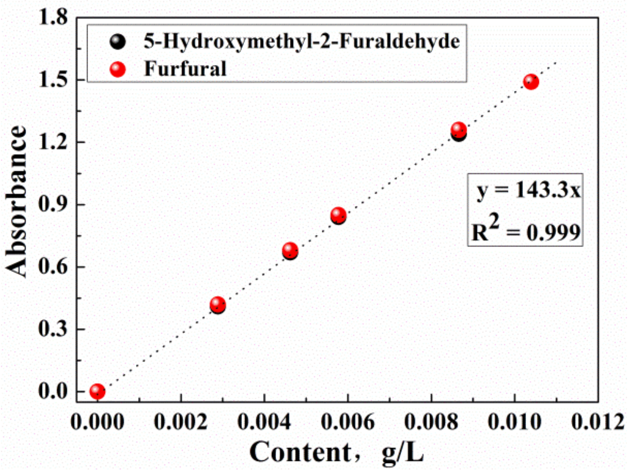


Fig. 4. Standard calibration curve

Because 280 nm was the isoabsorptive point wavelength of furfural and HMF, their molar absorption coefficients were equal (Eq. 4). Additionally, the ratios of A_{280} to A_{290} (furfural and HMF) were constant (Eqs. 5 and 6). The concentrations of furfural were calculated from simultaneous equations (Eq. 7),

$$\xi_{280}^{1} = \xi_{280}^{2} = \xi \quad (4)$$

$$\frac{A_{280}^{1}}{A_{290}^{1}} = \alpha \quad (5)$$

$$\frac{A_{280}^{2}}{A_{290}^{2}} = \beta \quad (6)$$

$$C_1 = \frac{\alpha(A_{280} - \beta A_{290})}{\xi(\alpha - \beta)} \quad (7)$$

where A_{280}^{1}, A_{290}^{1}, A_{280}^{2}, and A_{290}^{2} were the absorbance values of furfural and HMF at 280 nm and 290 nm, respectively.

α, β, and ξ were calculated (Table 1) from the absorbance values at 280 nm and 290 nm of furfural and HMF (Fig. 2). Furthermore, the concentration of furfural was calculated from the above α and β and simultaneous Eq. 7 and expressed in mole/L as shown in Eq. 8.

$$C_{furfural}(mmol/L) = 0.1943 \times (A_{280} - 1.0672A_{290}) \qquad (8)$$

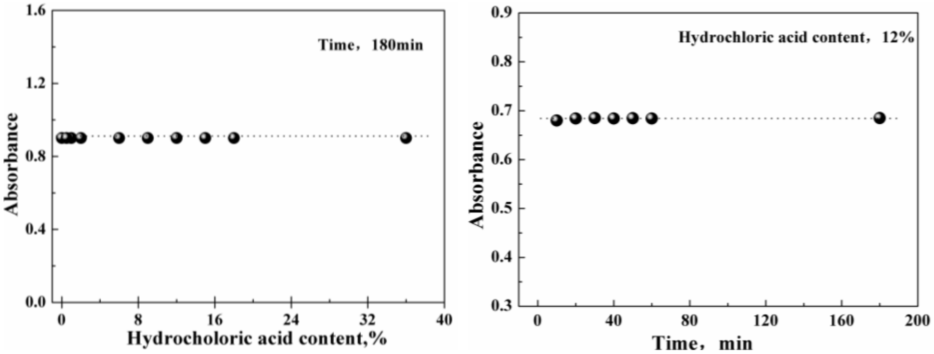
Ultimately, the content of pentosan in pulps was estimated by using the absorbance at 280 nm and 290 nm. It was expressed in percentage (Eq. 9),

$$\text{Pentosan（\%）} = \frac{[0.01865 \times (A_{280} - 1.0672A_{290}) \times V \times 1.38]}{\text{m}} \times 100\% \qquad (9)$$

where V was the volume of the distilled liquid (L), m was the oven dry weight of the samples (g), and 1.38 was the conversion coefficient of furfural to pentose.

Table 1. Absorbance Ratios in Various Concentrations at 280 nm and 290 nm

Concentration (μmol/L)	α	β
100	1.5251	1.0880
80	1.5521	1.0735
60	1.5583	1.0578
40	1.5420	1.0576
20	1.5605	1.0589
Average	1.5470	1.0670
RSD (%)	1.0620	0.7910



(a) (b)

Fig. 5. Effect of hydrochloric acid content and time on the absorbance of furfural

Effect of Factors Treatment on Absorbance Values

Effect of hydrochloric acid concentrations

The effect of HCl concentrations on the absorbance values of furfural is shown in Fig. 5(a). The furfural content in the solution was constant with increasing HCl concentration, which indicated that the HCl concentration had no effect on ultraviolet absorption of furfural.

Effect of time

As shown in Fig. 5(b), the absorbance of furfural in the distilled liquor also maintained a constant value as time rose from 10 min to 180 min. Thus, furfural was stable in 12% HCl liquor.

Method Calibration, Precision, and Comparison

Repeatability testing was used to evaluate this method (Table 2). The relative standard deviation (RSD) of this experiment was 3.25%, which indicated that the method had a high level of repeatability.

Table 2. Repeatability Testing

Sample	Pentosan content (%)
1	17.02
2	17.04
3	16.98
4	16.95
5	17.02
Average	17.00
RSD (%)	3.25

The spectroscopic method was also evaluated by comparing the test results with the results from the TAPPI T223cm-01 (2001) standard method, which was applied to eucalyptus pulps, bamboo pulps, and bagasse pulps (Table 3). There was ample agreement between the different methods. The RSD exhibited less than 0.61%, which justified application of the present method for analyzing pentosan in different pulps. In addition, this method could save experiment time, which just took 5 ± 1min to determine the furfural in the distillate. However, it took about 2 h for TAPPI method to determinate the furfural content in the distillate.

Table 3. Comparison of the Methods

Pulp	Pentosan Content (%)		RSD (%)
	This method	TAPPI method	
Unbleached eucalyptus	16.27	16.37	0.61
Bleached eucalyptus	20.51	20.40	0.54
Unbleached bamboo	18.04	18.05	0.05
Unbleached bagasse	31.38	31.36	0.06

CONCLUSIONS

1. A dual-wavelength UV spectroscopy method for the determination of pentosan content in pulps was developed with minimal interference from 5-hydroxymethyl-2-furaldehyde.
2. Compared with the TAPPI method, the improved method had some advantages such as the simplicity of sample detection and that no color reagent was required.
3. This method is also suitable for determining the pentosan content of different pulps in laboratory or industrial applications.

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