

Primary-Secondary Wavelength Spectrophotometric Determination of Trace Amounts of Lignin and Tannin in Water

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The conventional reaction of lignin and tannin with phosphowolframate in the presence of sodium carbonate to form blue complex has been applied for the determination of trace amounts of lignin and tannin in water and wastewater by the updated method named primary-secondary wavelengths spectrophotometry (PSWS). The results show that the analytical precision and accuracy were increased and gave higher determining sensitivity than in ordinary spectrophotometry. The relative standard deviations were less than 3.1% and the recovery rate of lignin and tannin were between 91.3 and 101%.

INTRODUCTION

Lignin and tannin usually exist in water polluted by paper, leather, chemical and other industries. At present lignin and tannin are usually determined by colorimetry^{1,2}. The reaction of lignin and tannin with phosphowolframate in sodium carbonate solution can give high sensitivity and selectivity, and accurate results; so it remains to be applied widely for the analysis of trace amounts of lignin and tannin in environmental water. Here the above reaction was first to be used for improvement of determination of trace amounts of lignin and tannin by the updated method named primary-secondary wavelength spectrophotometry (PSWS). Because PSWS can give higher precision and sensitivity than conventional spectrophotometry and give a stable calibration model, the results were all satisfactory. The recovery rate of lignin and tannin was between 91.3% and 101%, the relative standard deviations (RSDs) less than 3.1% and the detection limit only 0.05 mg/L, which was half of the conventional value.

Principle

From absorption spectra (Figure 1), moved curve 2 (color solution) 1 unit absorbance up to curve 3 and it crossed curve 1 (absorption spectra of suspension liquid, absorption equation: $A = k\lambda^{-y}$). Both B and C are crosspoints and they meet the above equation, and the following relationship was further obtained:

$$\left(\frac{A_p + 1}{A_s + 1}\right) = \left(\frac{\lambda_p}{\lambda_s}\right)^{-y}$$

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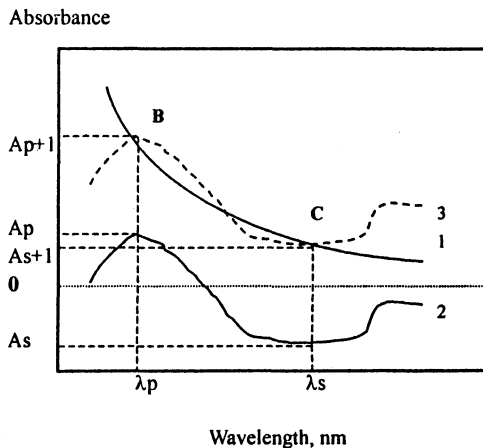


Fig. 1. Adsorption spectra sketch: 1, suspension liquid against water; 2, colour solution against reagent blank; 3, same as 2 but up 1 unit absorbance.

where λ_p named as primary wavelength was often selected at peak absorption of color solution and λ_s named as secondary wavelength at valley absorption or half-peak absorption. They are shown in Figure 1. If both λ_p and λ_s are selected, $y = k' \lg [(a_p + 1)/(A_s + 1)]$ (k' is a constant) and the following formula is established³.

$$\lg \left(\frac{A_p + 1}{A_s + 1} \right) = \alpha X^\beta$$

where both α and β are constants and the main variable X indicates the color-developed substance concentration (mg/L or μg). Because of the buffer function of $(A_p + 1)/(A_s + 1)$ the above equation is considered to stabilize the effect of variable work environment on both α and β and to improve the precision and accuracy of trace analysis. In fact, this method named as primary-secondary spectrophotometry (PSWS) is also one of the dual-wavelength methods but different from the others^{4,5}.

EXPERIMENTAL

Visible spectra were recorded with a Model 721 spectrophotometer (Shanghai, China), in a 30 mm glass cell. Standard tannin solution, 1.000 mg/mL is prepared by dissolving 1.000 g of tannic acid (A.R., Shanghai Chemical) in 100 mL of ion exchange water and diluted to 1000 mL. Standard tannin use solution, 50.0 mg/L: was prepared from the above standard lignin and tannin solutions.

Ligand reagent: Weighed 100 g of sodium wolframate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, AR, Shanghai Chemical), 20 g of phosphomolybdic acid ($20\text{MoO}_3 \cdot 2\text{H}_3\text{PO}_4 \cdot 48\text{H}_2\text{O}$, Shanghai Chemical) and dissolved both in 75 mL of ion exchange water. Then added 50 mL of 85% phosphoric acid (Beijing Organic Chemical). Heated it and refluxed for 2 h. Finally diluted to 1000 mL after cooling.

Saturated sodium carbonate solution was prepared by dissolving 200 g of anhydrous sodium carbonate (AR, Beijing Chemical) in 500 mL of water and diluted to 1000 mL.

Recommended Procedures: A known volume (less than 40 mL) of a water sample containing less than 150 μg of lignin and tannin was taken in a 50 mL volumetric flask. Added 2 mL of ligand reagent. After 5 min, added 10 mL of saturated sodium carbonate solution and diluted to 50 mL with ion exchange water and mixed well. After 20 min, measured the absorbance at 420 and 700 nm, respectively against a reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra: Fig. 2 gives the absorption spectra of the coloured solution of lignin and tannin with phosphowolframate. This solution's absorption reached maximal at 700 nm. According to the above principle the primary wavelength should be selected at 700 nm. The secondary wavelength was arranged at 420 nm here, that is $\lambda_p = 700 \text{ nm}$ and $\lambda_s = 420 \text{ nm}$.

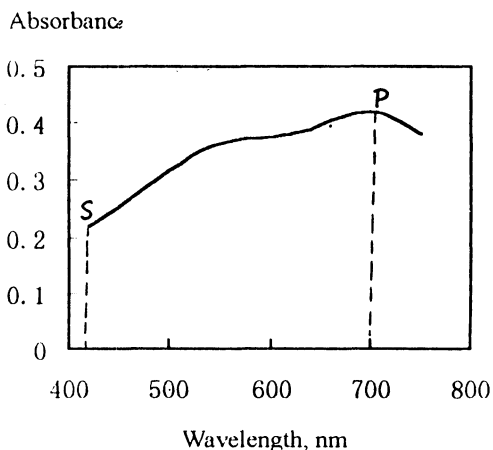


Fig. 2. Absorption spectrum of lignin and tannin coloured solution with phosphowolframate against reagent blank: P point 700 nm and S point 420 nm

Effect of Ligand Reagent Addition: Figure 3 shows the effect of the addition of ligand reagent solution on factor y calculated. We found while the addition of ligand reagent solution was more than 1.5 mL, y remained almost constant and reached maximal. In this work, 2 mL of ligand reagent solution was selected.

Calibration Graph: A series of standard tannin solutions were prepared and the absorbance of each was measured and plotted. Curve of $\lg y$ with $\lg x$ is shown in Fig. 4. We found that the curve linearity was better. The cut distance $\log \alpha$ was calculated to be -2.30 and the oblique rate β to be 0.831 from the straight line in Fig. 4. The relation of y with x was therefore obtained by the following expression: $y = 0.005x^{0.831}$.

Effect of Foreign Ions: None of the following ions will affect the direct determination of 20 μg of lignin and tannin (< 10% error): 20 mg of Cl^- , SO_4^{2-} ,

PO_4^{3-} , CO_3^{2-} , NO_3^- , Ca(II) , Mg(II) , Ti(IV) , Br^- , SiO_3^{2-} ; 20 mg of Al(III) , I^- , F^- , NH_4^+ , Fe(II) , Zn(II) , Cu(II) , Co(II) , Ni(II) ; 1 mg of Cr(III) , Sn(II) , Cd(II) .

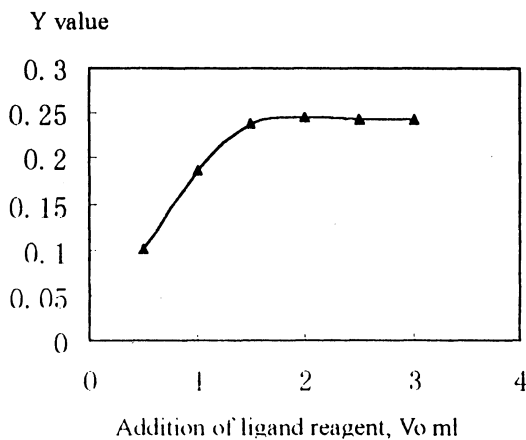


Fig. 3. Effect of ligand reagent addition on factor y

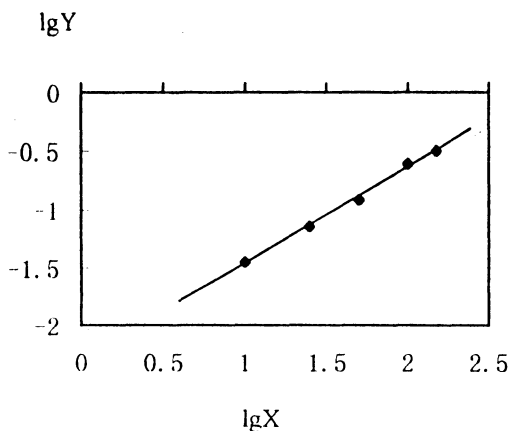


Fig. 4. Standard curve for the determination of lignin and tannin

Precision and Detection Limit: Six replicate determinations of standard tannin solutions containing 0.100 and 2.50 mg/L were carried out, respectively, the relative standard deviations (RSDs) being 3.4% and 1.5%. However, the RSDs with the single wavelength method were 6.1% and 3.3%. The precision for PSWS was therefore better than that for the ordinary spectrophotometric method.

We used $L_{\min} = kS_b/S$ to calculate the detection limit of lignin and tannin by PSWS, where $k = 3$, S_b is standard deviation and S is sensitivity. Replicate determination of twenty reagent blanks gave S_b of y value computed from $(A_p + 1)/(A_s + 1)$ was equal to 0.004. The analytical sensitivity S was equal to the above α value, 0.005. Therefore the detection limit of lignin and tannin was $L_{\min} = 0.05$ mg/L.

Sample Analysed: As a test of the method lignin and tannin were determined in, for example, wastewater and surface water. The results were listed in Table-1. We found that the results by the recommended method agreed with the conventional method. The RSDs were less than 3.1% and the recovery rate of lignin and tannin between 91.3 and 101%.

TABLE-1
DETERMINATION OF LIGNIN AND TANNIN IN WATER SAMPLES

Sample title	By conventional method	By PSWS				
		Added	Found		Recovery, %	
Wastewater	4.34	0	4.52	4.33	4.47	101
			4.32	4.50	4.39	
		5.00	9.47	9.39	9.55	
Sewage	0.15	0	0.151	0.144		91.3
			0.153	0.148		
			0.151	0.141		
River water	2.38	0.10	0.239	0.241	0.238	101
		0	2.41	2.29	2.33	
		2.00	4.39	4.40	4.32	
Lake water	1.68	0	1.75	1.69	1.71	91.3
		1.00	2.645	2.59	2.66	

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