

Primary-Secondary Wavelengths Spectrophotometry to Improve the Direct Determination of Trace Amounts of Volatile Phenol in Wastewater

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In alkaline solution and in the presence of potassium ferricyanide the reaction between volatile phenol and 4-aminoantipyrine was applied for the improvement of volatile phenol's determination in wastewater by primary-secondary wavelengths spectrophotometry (PSWS). Results showed that the analytical precision and accuracy were increased and a higher determination sensitivity was given than that obtained by ordinary spectrophotometry.

INTRODUCTION

Phenol compounds often exist in wastewater polluted by, for example oil-refining, coking, coal gas washing, paper, chemical and other industries. They consist of a series of derivants and are classified as volatile and non-volatile ones. Phenols belong to the highly poisonous compounds. The volatile phenols can often be separated from wastewater by distillation and then determined by spectrophotometry^{1, 2}. The reaction of phenol with 4-amino-antipyrine at pH 9.8 and in the presence of potassium ferricyanide was very sensitive and highly selective. In this paper the updated method, primary-secondary wavelength spectrophotometry^{3, 4}, was applied for the determination of trace amounts of volatile phenol in wastewater, which was more accurate and precise than ordinary spectrophotometry. In addition, the new method gave a stable calibration graph which is hardly affected by the operation conditions. The volatile phenol's recovery rate was between 98.5% and 112%, the relative standard deviations (RSDs) less than 4.7% and the detection limit only 0.02 mg/L.

Principle

From Ref. 3 the main equation of PSWS is expressed as follows:

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

where λ_p is the primary wavelength often selected at peak absorption of colour solution and λ_s the secondary wavelength often selected at valley absorption or half-peak absorption. Both α and β are constant and the main variable X indicates the colour-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 others⁵⁻⁷.

EXPERIMENTAL

Visible spectra were recorded with a Model 721 spectrophotometer (made in Shanghai, China) in a 2-cm glass cell.

Standard volatile phenol solution was prepared by dissolving 1.0 g of phenol (AR, Shanghai Organic Chemicals) in 1000 mL of distilled water. Its standardization was carried out with 0.025 mol/L sodium thiosulfate in the presence of potassium bromate-potassium bromide mixed solution, potassium iodide and starch indicator.

Standard volatile phenol use solution, 10.0 mg/L, was prepared with the above standard volatile phenol solution.

Methylene orange (Shanghai Reagent) solution, 0.05%

Phosphoric acid (AR, Huainan Chemicals, China) solution, 8%

Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, AR, Shanghai China) solution, 10%

Potassium ferricyanide (AR, Shanghai Chemicals), 8%

Buffer solution, pH 9.8 was prepared by dissolving 20 g of ammonium chloride (AR, Shanghai Chemical) in 100 mL of concentrated ammonia water (AR, Shanghai Chemicals) and adjusting pH to 9.8.

Chromogenic agent, 4% 4-aminoantipyrine, was prepared by dissolving 2 g of 4-aminoantipyrine (Shanghai Reagents) in 100 mL of distilled water and storing in a dark flask

Recommended Procedures: The distillation of wastewater sample should be carried out. At first 250 mL of a sample is taken in a 500 mL flask and add 2 drops of 0.05% methylene orange. Adjust the sample to orange with 8% phosphoric acid solution. Then add 5 mL of copper sulfate solution and distill it. Stop the distillation while the accepted solution reaches about 220 mL. Dilute this solution to 250 mL with distilled water. 50 mL of the above solution containing less than 125 μg volatile phenol is taken in a 50 mL colorimetric tube. Add 0.5 mL of pH 9.8 buffer solution, 1 mL of chromogenic agent and 1 mL of 8% potassium ferricyanide. Mix well. After 10 min, measure the absorbances at wavelengths 510 and 565 nm, respectively, against a reagent blank.

RESULTS AND DISCUSSION

Absorption Spectra: Fig. 1 shows the absorption spectra of the reaction

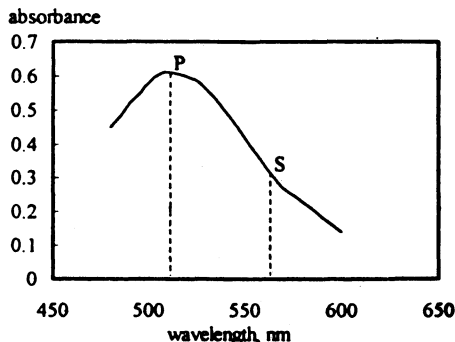


Fig. 1. Absorption spectra of the reaction solution between volatile phenol and 4-aminoantipyrine at pH 9.8 and in the presence of potassium ferricyanide against reagent blank: P point, 510 nm and S point, 565 nm

solution between volatile phenol and 4-aminoantipyrine. This solution's absorption reached maximum at 510 nm. The primary wavelength should be selected at peak absorption 510 nm. The secondary wavelength was arranged at 565 nm which was near to the half-peak absorption.

Effect of Chromogenic Reagent: Fig. 2. showed the effect of the addition of chromogenic agent, 4-aminoantipyrine solution, on factor Y. While the addition

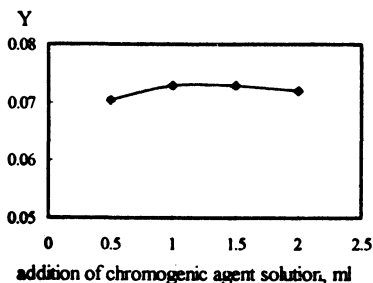


Fig. 2. Effect of 4-aminoantipyrine solution on factor Y

of chromogenic agent solution was more than 0.5 mL, Y reached maximum and remained almost constant. In this study, 1.0 mL of the chromogenic agent was used.

Calibration Graph: A series of standard volatile phenol solutions were prepared and the absorbance of each was measured and plotted. The measurement results are shown in Fig. 3. Curve 2 is more linear than curve 1. The relationship

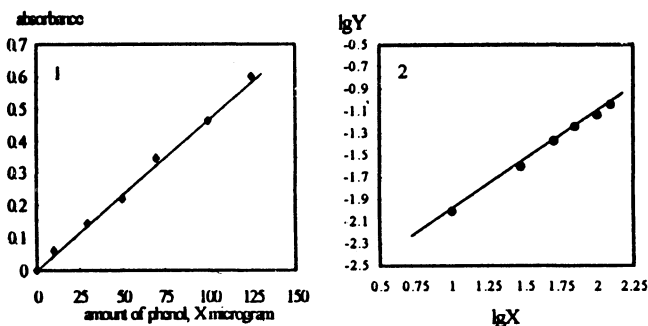


Fig. 3. Standard curves for the determination of volatile phenol: 1. A(X), 2. L gY(l g X)

of Y with X was therefore obtained as follows: $Y = 0.00138X^{0.873}$.

Effect of Foreign Ions: According to the distillation procedure, none of the following ions affected the direct determination of 1.00 mg/L volatile phenol (< 10% error): 1000 mg/L Cl^- , Mg^{2+} , Ca^{2+} , Al(III), SO_4^{2-} , NO_3^- , NH_4^+ ; 100 mg/L Fe(II), Mn^{2+} , Cu(II), Ni(II), Zn(II); 10 mg/L of d(II), 10 mg/L of Hg(II), Sn(II), Cr(VI), SO_3^{2-} , S^{2-} .

Precision and Detection Limit: Six replicate determinations of 10.0 and 100 g standard volatile phenol were carried out, the relative standard deviations

(RSDs) being 1.9% and 0.95%, respectively. However, the RSDs with the single wavelength method were 3.5% and 1.9%. 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 PSWS, where $k = 3$, S_b is standard deviation and S is sensitivity. Replicate determination of twenty reagent blanks gave S_b of $\lg(A_p + 1)/(A_s + 1)$ value computed was equal to 0.0005. The analytical sensitivity (S) was equal to the above α value, 0.00138. Therefore the detection limit (L_{\min}) of volatile phenol was 1 μg (0.02 mg/L).

Samples Analyzed: As a test of the method volatile phenol was determined in sewage and wastewater. The results have been listed in Table-1. We found that the averages by the recommended method were similar to the conventional method². The RSDs were than 4.7% and the recovery rate of volatile phenol between 98.5 and 112%.

TABLE-1
DETERMINATION RESULTS OF VOLATILE PHENOL IN WASTEWATER SAMPLES

Sample	With Ref. 2 mg/L	Added mg/L	Found mg/L	Aver. Recovery, %
Sewage	0.064	0	0.062 0.063 0.061 0.065 0.059 0.057	112
		0.050	0.113 0.121	
		0	0.314 0.324 0.319 0.331 0.324 0.328	
Wastewater 1#	0.331	0.200	0.528 0.543	106
		0	1.19 1.14 2.21 2.09	98.5
Wastewater 2#	1.08	1.00		

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