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**A NEW SPECTROPHOTOMETRIC METHOD FOR THE
DETERMINATION OF ANILINE IN ENVIRONMENTAL WATER
SAMPLES**

Keywords: Aniline, Spectrophotometric, Water sample, Routine analysis, 8-hydroxyquinoline, N-chlorosuccinimide

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ABSTRACT

A new spectrophotometric method has been established to determine trace aniline in water samples. A mixture solution of N-chlorosuccinimide and 8-hydroxyquinoline in N,N-dimethylformamide (DMF) was used to react with the aniline in water at room temperature (20°C). When the solution was adjusted to pH 10-11 by adding 3 mol/L NaOH, a clear and blue-colored dye formed immediately with the maximum absorption wavelength at 615 nm. Molar absorptivity

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and detection limit were found to be $1.0 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and $30 \text{ } \mu\text{g/L}$, respectively. Linearity was excellent in the concentration range of 0.2 to 15 mg/L aniline in water sample. The proposed method has been used to analyze aniline in surface and sewage water samples with the recoveries 96-103% and relative standard deviation less than 3%. It's a promising method to be applied for routine analysis of aniline in water.

INTRODUCTION

Aniline has for a long time been regarded as a kind of highly toxic and carcinogenic substance. It can not only be inhaled and digested by human body, but also be absorbed into the blood through the skin, causing a variety of healthy problems such as vomiting, liver damage and even cyanosis. Natural water can be heavily polluted by the aniline-bearing wastewater from medicine and dye industry if not treated properly and sufficiently. So it's very important to control the aniline concentration in wastewater before it's discharged into the environment. Meanwhile, the surface water also needs to be monitored regularly because aniline is relatively stable in water and accumulation may occur in certain conditions. For these purposes, it's quite necessary to establish a practical and reliable method for routine analysis of aniline in water samples.

So far, several types of methods have been employed to analyze aniline in water, such as titration¹, spectrophotometric method²⁻³, adsorptive stripping voltammetry⁴, gas chromatography and high performance liquid chromatography⁵. The electrochemical method is sensitive but involves the use of mercury, which is also a hazardous substance to the environment. Methods based on GC and HPLC are quite expensive for routine use and the sensitivity is somehow limited. The most commonly used spectrophotometric method is based on the reaction of aniline with nitrite and N-(1-naphthyl)ethylenediamine

dihydrochloride in acidic media. This method, however, includes very complicated procedures and suffers from serious interference⁶.

In this paper, we reported a simple spectrophotometric method for quick determination of aniline in surface and sewage water. 8-Hydroxyquinoline and N-chlorosuccinimide were premixed and dissolved in DMF, which was used as chromogenic reagent. The color reaction is very fast at room temperature (20 °C). The determination limit is found to be 30 µg/L. The Beer's law is obeyed from 0.2 to 15 mg/L of aniline in water. The method has been successfully applied to the determination of aniline in surface and water samples.

EXPERIMENTAL

Apparatus

Spectrophotometer (Model 722, manufactured by Shanghai Third Analytical Instruments Factory) and UV-Visible Spectrophotometer (CARY IE, Varian) were used to measure the absorbance and record the absorption spectra.

Reagents

Aniline and 8-hydroxyquinoline were purchased from Beijing Chemical Ltd. (Beijing, China). The N-chlorosuccinimide was obtained from Wuhan Shengshi Fine Chemical Ltd. (Wuhan, China). A stock standard solution of aniline (2000 mg/L) was prepared in distilled water. A working standard aniline solution of 20 mg/L was freshly prepared before use. Chromogenic reagent solution was freshly prepared by dissolving 0.75 g 8-hydroxyquinoline and 0.5 g N-chlorosuccinimide in 25 mL DMF before use.

Operating Procedure

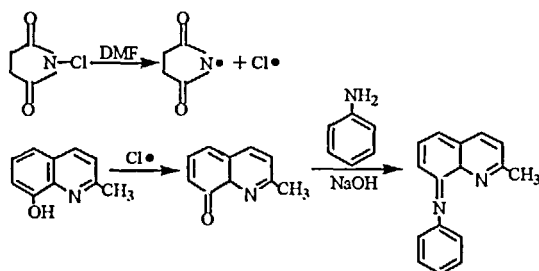
To a 10 mL volumetric tube containing the standard aniline solution or the real water sample, 0.3 mL of the chromogenic reagent was added. The reaction

mixture was changed to a yellow-orange turbid solution within 3 minutes. To the turbid solution 0.5 mL of 3 mol/L NaOH was added. A clear blue-colored solution appeared immediately. The absorbance was measured at $\lambda=615$ nm with the Spectrophotometer (10 mm cell) against the reagent blank which was prepared in the same manner as the samples.

RESULTS AND DISCUSSION

Reaction Mechanism

Amlathe et.al.³ reported a similar method using guaiacol as the coupling reagent. It was thought that in the color reaction, aniline was oxidized by N-chlorosuccinimide and subsequently coupled with guaiacol. Based on this, our initial operating procedure was designed in such a way that the N-chlorosuccinimide and 8-hydroxyquinoline were prepared separately and added to the aniline sample in sequence. During the experiment, however, we found that it was very difficult for the reaction to take place at room temperature (20 °C). On a water bath of 35-40 °C, the reaction still took at least 15 minutes to be completed. But when the N-chlorosuccinimide and 8-hydroxyquinoline were premixed in DMF before adding to the samples, the color reaction took place immediately and is complete in about 3 minutes at room temperature. It's quite possible that an active mid-product has been formed in the mixture reagent, which makes the reaction much easier. Therefore, we suggest a different probable reaction mechanism shown as following for the presented procedure.



In DMF, N-chlorosuccinimide underwent homolysis and produced oxidative chlorine radicals⁷, which oxidized 8-hydroxyquinaldine to its corresponding carbonyl compound. When the chromogenic reagent was added to the aniline sample, condensation occurred between the carbonyl group and the amino group and thus produced an imine compound (Schiff Base) in alkaline medium.

Spectral Characteristics

The absorption spectra of the reagent blank and the chromogenic reaction product of aniline (5 mg/L) with distilled water as reference are shown in Figure 1. It can be seen that the blue dye formed in the color reaction of aniline has a maximum absorption at the wavelength of 615 nm, whereas the reagent blank has little absorption at this wavelength range. Fig. 1 also shows the absorption spectrum of the reagent blank in the presence of phenol (1000 mg/L), a major interference in the previously reported spectrophotometric method⁶. Obviously, it has no significant interference in the determination of aniline with the proposed method.

Optimization of the Chromogenic Reaction

Besides 8-hydroxyquinaldine, some other structurally similar compounds, such as 8-hydroxyquinoline and 5,7-dibromo-8-hydroxyquinoline, were also tested for the chromogenic reaction. It was found that 8-hydroxyquinoline also formed the blue dye but the absorbance was lower than that of the 8-hydroxyquinaldine at the same concentration, resulting in a lower sensitivity. 5,7-Dibromo-8-hydroxyquinoline was discarded because it formed large quantity of white precipitates instead of the blue dye. The amount of N-chlorosuccinimide, 8-hydroxyquinaldine and NaOH were all optimized under the experimental conditions. Test results showed that for a total volume of 10 mL with the aniline concentration lower than 15 mg/L, 0.3 mL of the chromogenic reagent is enough. Adding more will only increase the blank

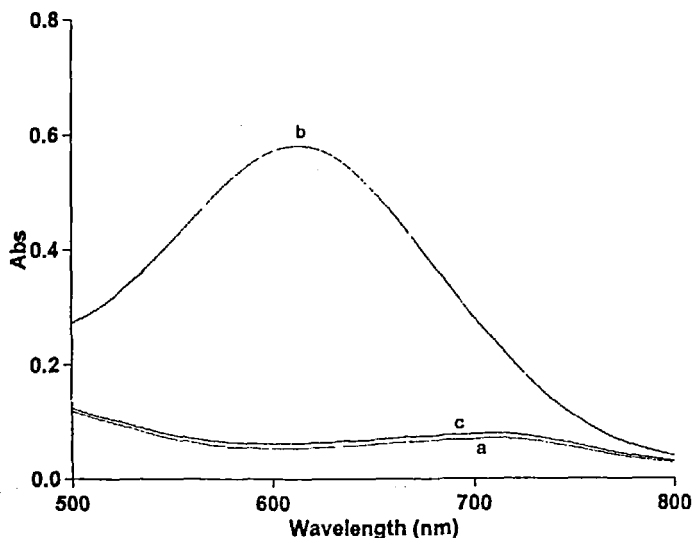


Fig. 1 The absorption spectra of the reagent blank (curve a), the reaction product of aniline (5 mg/L) with the chromogenic reagent (curve b), and the reagent blank in the presence of phenol (1000 mg/L) (curve c). Curves a, b and c were all recorded against distilled water.

absorbance without improving the sensitivity. The optimal amount of 3 mol/L NaOH to get the maximum absorption is found to be 0.5 mL.

Detection limit and molar absorptivity were found to be 30 $\mu\text{g/L}$ and $1.0 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, respectively. The valid range for Beer's Law was 0.2–15 mg/L aniline in water. The linear regression equation is determined to be $A = 0.109C \text{ (mg/L)} - 0.0298$, with the coefficient 0.998. Reproducibility of the proposed procedure was also checked and the RSD was less than 3% for the standard sample at the concentration of 2 mg/L ($n=7$).

Interference and Tolerance Limit

Ca^{2+} , Mg^{2+} , Cu^{2+} and other metallic ions that may interfere with the measurement by forming hydroxide precipitates can be effectively masked by 0.02 mol/L ethylenediamine-tetraacetic acid disodium salt (EDTA). It was found that EDTA must be added after the oxidative coupling reaction; otherwise, an error greater than 5% may occur. The tolerance limits of some possible interfering metallic ions are found to be Ca^{2+} (600 mg/L), Mg^{2+} (200 mg/L), Ba^{2+} (700 mg/L), Cu^{2+} (2 mg/L), Al^{3+} (1 mg/L) and Ni^{2+} (2 mg/L), respectively. It shows that these ions won't interfere in the determination of aniline at the normal concentration in surface and sewage water.

It is remarkable that Fe^{3+} may interfere with the measurement in a different way. It seems to react with the chromogenic reagent and block the chromogenic reaction of aniline. Sulfosalicylic acid, sodium citrate and potassium sodium tartrate were tested as the masking reagent. It's found that sodium citrate at the concentration of 0.02 mol/L, which was added before the color reaction, could be used to mask Fe^{3+} (≤ 1.5 mg/L).

Aromatic compounds such as o-phenylenediamine and p-nitroaniline will also affect the analysis at high concentrations. But phenol does not interfere with the presented method even at the concentration of 1 g/L. The tolerance limits of o-phenylenediamine and p-nitroaniline are found to be 5 mg/L and 20 mg/L, respectively. All the above tolerance limits were determined using 2 mg/L aniline as reference and based on causing an error of less than 5%.

Recovery Results and Application

Synthetic samples were prepared by spiking the water samples with known amounts of aniline. Recovery tests were performed for both surface water (from the Nameless Lake of Peking University) and sewage water. For aniline concentration in the range from 1 up to 4 mg/L, the recoveries were 96-103% in five runs.

Comparison with Other Methods

The presented method is simpler and less time-consuming compared to the commonly used spectrophotometric method using N-(1-naphthyl)ethylenediamine dihydrochloride in acidic media. In the N-(1-naphthyl)ethylenediamine method, the aniline samples must be adjusted to pH 1.5-2.0 for the diazotization reaction of aniline with sodium nitrite; and the excess NaNO_2 needs to be removed before adding of N-(1-naphthyl)ethylenediamine. Moreover, it takes about 40 minutes for the diazotization and color reaction to be completed. In the present study, the oxidative-coupling reaction occurs within the normal pH range of natural water (i.e. pH 6-9). The whole process takes no longer than 10 minutes.

Compared to the guaiacol method³, this premixing modification not only simplified the operating steps but also accelerated the whole process. It also achieved a broader linear range.

Another remarkable advantage of the proposed method is the relatively less interference. Phenol, one of the most commonly interfering species in spectrophotometric method for aniline analysis, causes no interference with the presented method at the concentration of 1000 mg/L.

In comparison with GC and HPLC based chromatographic method, the present approach is more practical and economical.

In conclusion, the spectrophotometric method presented in this paper provides a very simple and practical procedure for trace aniline analysis. It's a promising technique to be applied for routine analysis of aniline in wastewater and natural water.

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