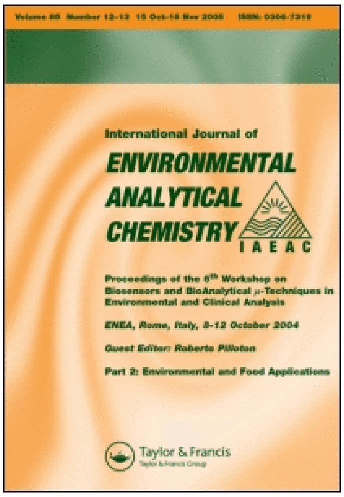

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SPECTROPHOTOMETRIC DETERMINATION OF ANILINE IN POLLUTED SURFACE WATER AND WASTEWATER – IMPROVED REAGENTS IN TEST KIT FORMAT

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A practical test kit based on diazotization reaction of aromatic amines followed by coupling with 2-methyl-8-hydroxyquinoline has been developed to determine trace aniline in wastewater and surface water samples. The test kit consists of four tablets, which are added to the sample in sequence. The maximum absorption wavelength of the orange dye formed is 482 nm. Molar absorptivity and detection limit were found to be $2.5 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ and $0.020\,\mathrm{mg\,L^{-1}}$, respectively. Linearity was excellent in the concentration range 0.10–$3.5\,\mathrm{mg\,L^{-1}}$ aniline in water. The test kit has been used to analyze aniline in polluted river water and wastewater samples from a pharmaceutical factory. The recoveries of addition of aniline in real water samples were between 95–106% ($n = 5$) and relative standard deviation was less than 5% for standard sample at a concentration of $2.0\,\mathrm{mg\,L^{-1}}$ aniline. It's a very sensitive and easy-to-operate method for *in situ* analysis of aniline in water.

Keywords: Aniline; Spectrophotometry; Test kit

INTRODUCTION

Aniline is listed as an environmental priority pollutant in many countries due to its high toxicity and possible carcinogenity[1]. Serving as the major

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raw material in the production of herbicides, dye, plastics, and pharmaceuticals, it may be present in large quantity in the wastewater from the related factories[2]. In addition, many natural processes, such as the degradation of nitroaromatic compounds or herbicides by microbials, may also form aniline or its analogues in the environment[3,4]. Therefore, not only the wastewater needs to be controlled before discharging but also the natural water near the possible pollution sources should be monitored regularly.

Many techniques are available now for aniline analysis, such as spectrophotometric methods[5–9], adsorptive stripping voltammetry[10], gas chromatography (GC) and high performance liquid chromatography (HPLC) [11]. Among them, the chromatographic methods are very sensitive and can tolerate high amount of coexisting compounds. For such measurement, samples are usually collected and sent back to the lab for analysis. However, there are some particular situations. For example, some aniline-related factories often need immediate results of the aniline concentration in wastewater to decide whether it is allowed to discharge or not. Many local environmental protection departments who are responsible for monitoring the quality of surface water do not have instrumentation such as GC or HPLC. In such cases, an analytical method in test kit format which only requires a portable spectrometer or even simply a color comparison card shall be quite practical. The research described in this paper has been designed for this purpose.

The most commonly used spectrophotometric method is based on the reaction of aniline with nitrite and N-(1-naphthyl)ethylenediamine dihydrochloride in acidic media[5–6]. But the slow coupling reaction (about 30 min) and short storage time of the reagent solution of N-(1-naphthyl)ethylenediamine dihydrochloride (≤ 2 weeks even at 4°C) hindered its *in situ* application. Some new spectrophotometric methods which are simple and fast have been developed in recent years[7–8]. However, they may suffer from serious interference of other active aromatic compounds when applied to heavily polluted water samples. The inhibitory kinetic spectrophotometric method[9] is sensitive but involves heating and cooling and other time-consuming operating steps.

Based on the existing methods, we established in this paper a new and more sensitive spectrophotometric method for rapid determination of aniline in wastewater and surface water and then further developed it into a test kit. In the proposed method, aniline was first diazotized with nitrous acid and then coupled with 2-methyl-8-hydroxyquinoline in alkaline medium. A stable orange azo-dye was quickly produced, which exhibited a maximum absorption at 482 nm. The molar absorptivity was found to be $2.5 \times 10^4\,L\,mol^{-1}\,cm^{-1}$ and Beer's law was obeyed from 0.10 to $3.5\,mg\,L^{-1}$ of aniline in water. All the reagents were prepared in the form of solid powder and incorporated into four tablets. The test kit has been applied to the analysis of aniline in surface and wastewater samples satisfactorily.

EXPERIMENTAL

Instrumentation

A Model 722 Spectrophotometer, manufactured by Shanghai Third Analytical Instruments Factory, was used to measure the absorbance. The absorption spectra were recorded on Cary 1E UV–Vis Spectrometer, Varian.

Reagents and materials

Aniline and sodium nitrite were purchased from Beijing Chemical Ltd. (Beijing, China). The 2-methyl-8-hydroxyquinoline was obtained from Merck-Schuchardt, Germany. A stock standard solution of aniline ($2000\,mg\,L^{-1}$) was prepared in $0.025\,mol\,L^{-1}$ sulfuric acid. A working standard aniline solution of $10\,mg\,L^{-1}$ was freshly prepared before use with deionized water.

Preparation of the test kit

The test kit is made up of four tablets. The formulation of each tablet is listed in Table I. First, 20.0 g of each group of mixed powder was prepared by weighing all the constituents accurately according to their percentages given in Table I and grinding them together to get a uniform mixture.

TABLE I Formulation of the four tablets in the test kit

Tablet 1 (100 mg)	*Tablet 2* (100 mg)	*Tablet 3* (100 mg)	*Tablet 4* (200 mg)
Potassium bisulfate (25%)	Sodium nitrite (1.0%)	Ammonium sulfamate (10%)	Sodium hydroxide (100%)
Potassium sodium tartrate (15%)	EDTA (15%)	2-methyl-8-hydroxyquinoline (15%)	
Sodium chloride (60%)	Sodium chloride (84%)	Sodium chloride (75%)	

Then a tablet-pressing machine in the lab was used to press the mixture powder into tablets with each tablet containing 100 ± 5 mg of the mixture powder. For tablet 4, 200 ± 5 mg of solid NaOH was packed up directly.

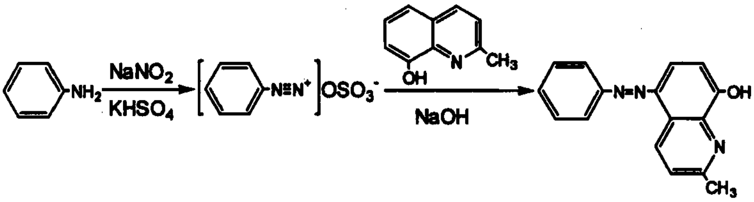
Operating procedure

A known amount of water sample or the working standard aniline solution was transferred to a 10 mL volumetric tube and brought up to the mark line with deionized water. To it Tablet 1 and 2 were added and dissolved in the solution. After 5 min, Tablet 3 was added and the solution was shaken rigorously intermittently for about 3 min to remove the small air bubbles completely. Then Tablet 4 was added and dissolved in the solution. A bright orange color developed immediately and reached the maximum within 5 min. The absorbance was measured at $\lambda = 482$ nm with the spectrophotometer (10 mm cell) against the reagent blank which was prepared in the same manner as the sample.

RESULTS AND DISCUSSION

Reaction mechanism

The reaction mechanism of the proposed method may be expressed as following[12].



The main coupling position is suggested to be at para-position of the hydroxy group in 2-methyl-8-hydroxyquinoline considering the steric effect. The coupling at the ortho-position is also possible.

Spectral characteristics

The absorption spectra of the azo-dye against the reagent blank and the reagent blank against deionized water were shown in Fig. 1. It can be seen that the orange dye has a maximum absorption at the wavelength of

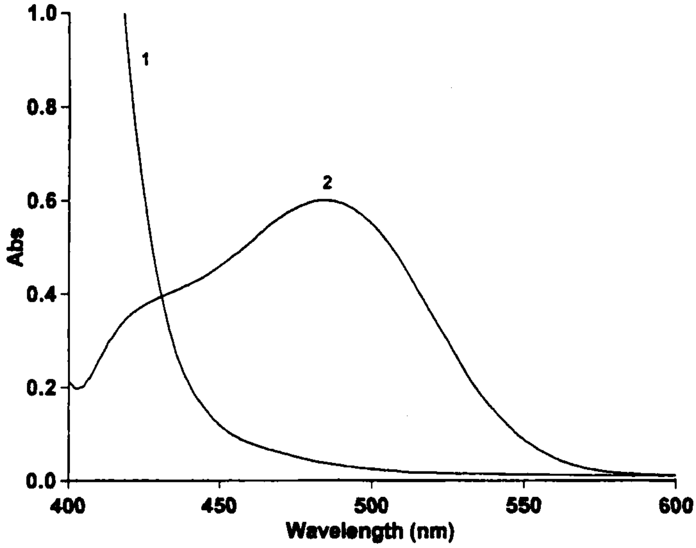


FIGURE 1 Absorption spectra. 1: Absorption spectrum of the reagent blank against deionized water; 2: Absorption spectrum of the azo-dye (aniline concentration 2.0 mg L^{-1}) against the reagent blank.

482 nm, whereas the reagent blank has little absorption at this wavelength range.

Linearity, sensitivity and reproducibility

For the proposed procedure, Beer's Law is obeyed over the range of 0.10–3.5 mg L^{-1} aniline in water. Solutions of higher concentrations should be diluted in proportion before being measured, otherwise the absorbance may exceed 1.0. The linear regression equation is determined to be $A = 0.2704\,C_{\mathrm{aniline}}(\mathrm{mg\,L^{-1}}) + 0.0005$ and R^2 is 0.9998. Detection limit and molar absorptivity were found to be 0.020 mg L^{-1} and 2.5×10^4 L mol^{-1} cm^{-1}, respectively. Reproducibility of the proposed procedure was also checked and the RSD was less than 5% for the standard sample at a concentration of 2.0 mg L^{-1} ($n = 10$). The azo-dye formed was stable for at least two hours at room temperature.

Optimization of the reagents and their composition in the kit

Reagents 2-methyl-8-hydroxyquinoline and *o*-methoxyphenol were both tested as the coupling reagents. It was found that *o*-methoxyphenol could form a yellow dye at the same experimental conditions. However, the molar absorptivity of this yellow dye at its λ_{max} (450 nm) was lower than that of the 2-methyl-8-hydroxyquinoline at 482 nm. Moreover, 2-methyl-8-hydroxyquinoline occurs as solid powder at room temperature, whereas *o*-methoxyphenol is liquid, which is not suitable for the test kit. Therefore, 2-methyl-8-hydroxyquinoline was chosen as the coupling reagent. The optimum amount of 2-methyl-8-hydroxyquinoline was found to be 15 mg for 0–36 µg aniline in 10 mL water sample. The amount of other reagents was also optimized under the experimental conditions.

Ammonium sulfamate was included in Tablet III to remove the excess $NaNO_2$ in the solution after the diazotization reaction, otherwise the remaining $NaNO_2$ may affect the later coupling reaction. 2-methyl-8-hydroxyquinoline could be added together with ammonium sulfamate in Tablet 3 because ammonium sulfamate dissolves much more easily than 2-methyl-8-hydroxyquinoline in water and the coupling reaction won't take place until the solution is adjusted to alkali by adding NaOH. The optimum pH for the coupling reaction was found to be 11–12.

NaCl was used as the diluting agent in the reagent tablets. The absorbance of the azo-dye in the presence of different concentrations of NaCl was measured. It was found that NaCl had no significant influence on the absorbance measurement even at the concentration as high as 25 mg mL^{-1}.

Tolerance limit of coexisting compounds

Since the coupling reaction proceeds in alkaline medium, under which some metal ions may form hydroxide precipitate and thus interferes with the absorbance measurement, ethylenediamine-tetraacetic acid disodium salt (EDTA) and potassium sodium tartrate are included in the reagent tablets as masking agents. The tolerance limits of some commonly coexisting metal ions (mg L^{-1}) were found to be Ca^{2+} (150), Mg^{2+} (80), Cu^{2+} (3.7), Al^{3+} (3.8), Fe^{3+} (3.0), Ni^{2+} (5.0), Zn^{2+} (23), Mn^{2+} (9.0), Cd^{2+} (84), Cr^{3+} (4.0), Pb^{2+} (56) and Hg^{2+} (2.5), respectively.

The tolerance limits of possible interfering aromatic compounds were found to be phenol (700 mg L^{-1}), p-nitrophenol (40 mg L^{-1}) and catechol (1.0 mg L^{-1}), respectively. All the above tolerance limits were determined using 2.0 mg L^{-1} aniline as reference and based on causing an error of less than 5%. It can be seen from the results that these species won't cause significant interference in the determination of aniline at the normal concentration in waste and surface water.

Application and recovery tests

The test kit was applied to analyze the wastewater samples from a pharmaceutical factory (Beijing Third Pharmaceutical Factory) and a polluted river (The Qinghe River in Beijing). Recoveries were also tested by spiking the real water samples with known amount of the standard solution of aniline. The results were shown in Table II.

Comparison with existing methods

It was found in our experiment that the well-known spectrophotometric method[5–6] where N-(1-naphthyl)ethylenediamine dihydrochloride was used as the coupling reagent was not easy to control in the following aspects. First, in our experience, heating and filtration are always needed to make the reagent solution of N-(1-napthyl)ethylenediamine dihydrochloride. And the solution easily turns turbid during storage, which is disadvantageous for test kit development. Another drawback of the method was the tardiness of the coupling reaction. The absorbance of the formed purple-red dye was unstable for more than half an hour before it could achieve the maximum.

Another type of spectrophotometric method[7–8] uses N-chlorosuccinimide as the oxidizing agent. In our further study, it was found that this oxidant was less selective than the diazotization reaction for the detection of aromatic amines though it was simple and fast, i.e. other reductive aromatic compounds might be oxidized as well and interfere with the later coupling reaction. Furthermore, the sensitivity of the proposed method is 2–3 times higher than the above-mentioned two methods[7–8], and this new method eliminated the usage of toxic organic solvents, e.g. N,N-dimethylformamide, which is a suspected carcinogen.

TABLE II Determination of aniline in wastewater and polluted river and recovery test results

Sample Source	*Sample amount* (mL)	*Aniline*		*Recovery* (%) ($n = 5$)	*Actual concentration*[a] ($\mathrm{mg\,L^{-1}}$)
		Added ($\mathrm{mg\,L^{-1}}$)	*Found* ($\mathrm{mg\,L^{-1}}$)		
Wastewater from Beijing Third Pharmaceutical Factory	5.0	0	0.19 ± 0.02	–	0.38 ± 0.04
	5.0	2.0	2.2 ± 0.1	95–106	–
Beijing Qinghe River	5.0	0	0.09 ± 0.02		0.18 ± 0.04
	5.0	2.0	2.1 ± 0.1	99–103	

[a] Samples diluted 1 + 1 with deionized water prior to reagent additions.

Other primary arylamines and derivatives of aniline may give similar reactions as aniline. If the λ_{max} of the dye formed by them is significantly different from aniline itself, they can also be measured separately. Otherwise, they will be measured together with aniline and the detected concentration represents the total level of aniline and related compounds. This may be a common limitation of the spectrophotometric methods compared to chromatographic methods.

Overall, the presented method is very simple and practical. Though it's less selective than GC or HPLC, it can obtain rapid and sensitive results without depending on complicated instrumentation. Furthermore, the test kit is easy to store and carry, which is particularly suitable for *in situ* measurement of aniline in industrial wastewater and surface water.

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