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Kinetic-Spectrophotometric Determination of Trace Amounts of Formaldehyde Based on its Catalytic Effect on Oxidation of Neutral Red in Acidic Media

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A simple, sensitive and rapid kinetic-spectrophotometric method for the determination of trace amounts of formaldehyde is reported. The method is based on the catalytic effect of formaldehyde on the rate of oxidation of neutral red by bromate in acidic media at 33°C. The reaction is monitored spectrophotometrically by measuring the decrease in absorbance of neutral red at 524 nm using a variable time method. The method shows two linear calibration graphs in the concentration ranges of 25–600 ng mL^{-1} and 0.6–6.0 μg mL^{-1} of formaldehyde. The limit of detection is 23 ng mL^{-1} and the relative standard deviation for ten replicate measurements of 1 μg mL^{-1} of formaldehyde is 0.93%. The method was successfully applied to the determination of formaldehyde in melamine-formaldehyde resins.

Key Words: Kinetic-spectrophotometric, Formaldehyde, Bromate, Neutral red.

INTRODUCTION

The widespread use of formaldehyde and its adverse health effects have created great concern on the monitoring and control of exposure to this chemical, both in industry and in environment[1]. Formaldehyde is present in the environment and biological specimens as a result of human activities, the major source being the discharge of industrial wastes and oxidative water treatment such as ozonation and chlorination[2]. Formaldehyde is also present in many interior construction materials of the houses and can be emitted slowly into the environment.

The most frequently used methods for the determination of formaldehyde are high performance liquid chromatography (HPLC)[3–5] and spectrophotometry[6, 7]. Techniques such as near-IR[8], gas chromatography-mass spectrometry (GC-MS)[9] and flow injection analysis (FIA)[10, 11] have also been used for the determination of formaldehyde. However, some of these methods are not sensitive enough or require complicated and expensive instruments.

In this paper we wish to report a simple and sensitive kinetic spectrophotometric method for the determination of formaldehyde based on its catalytic effect on the oxidation of neutral red by bromate ion in acidic media.

EXPERIMENTAL

Reagents

All chemicals were of highest purity available and used without further purification. Double distilled water was used throughout the experiment.

A stock solution of formaldehyde (1000 μg mL^{-1}) was prepared by diluting 2.5 mL of 37% formaldehyde solution (Merck) to 1 L with water. This solution was standardized using the sulfite method[12, 13]. Further dilutions were made using the stock solution when needed. Potassium bromate (4.4×10^{-2} mol L^{-1}) solution was prepared by dissolving 1.8420 g of $KBrO_3$ (Merck) in water and diluting to 250 mL. Neutral red (5.0×10^{-4} mol L^{-1}) solution was prepared by dissolving 0.1444 g of neutral red (Merck) in water and diluting to 1000 mL.

Absorption spectra were recorded on a JASCO model 7850 UV-visible spectrophotometer and the absorbance measurements were made using a Milton Roy 20 spectrophotometer. A Galenkamp BJH-400-01 OD thermostat in which the temperature could be maintained to ± 0.1°C was used.

Recommended Procedure

An appropriate amount of standard formaldehyde solution was transferred into a 10 mL flask so that the final concentration would be in the range of 25–600 ng mL^{-1} or 0.6–6.0 μg mL^{-1}. Then 1 mL of 5×10 mol L^{-1} solution of neutral red, 1 mL of 1 mol L^{-1} solution of sulfuric acid and enough water for diluting the solution to *ca.* 8 mL, were added. The solution was kept in a water bath at 33°C for 15 min, and then 1 mL of 4.4×10^{-2} mol L^{-1} solution of potassium bromate was added and diluted exactly to the mark. The zero time was taken as the moment at which the last drop of bromate solution has been added. A portion of the solution was transferred into a glass cell immediately for the absorbance measurements and the time (t) required for the absorbance (at λ_{max} = 524 nm) to decrease to 0.30 was measured. A blank solution was also prepared in the same way using distilled water instead of formaldehyde solution and $\Delta(1/t)$ was calculated.

RESULTS AND DISCUSSION

It was found that bromate oxidizes neutral red only slowly in acidic media, but trace amount of formaldehyde catalyzes the reaction so that it will proceed much faster.

Fig. 1 shows the catalytic effect of formaldehyde on neutral red-bromate reaction with time. This catalyzed redox reaction was monitored spectrophotometrically by measuring the time required for the absorbance to decrease to 0.3 (variable time method).

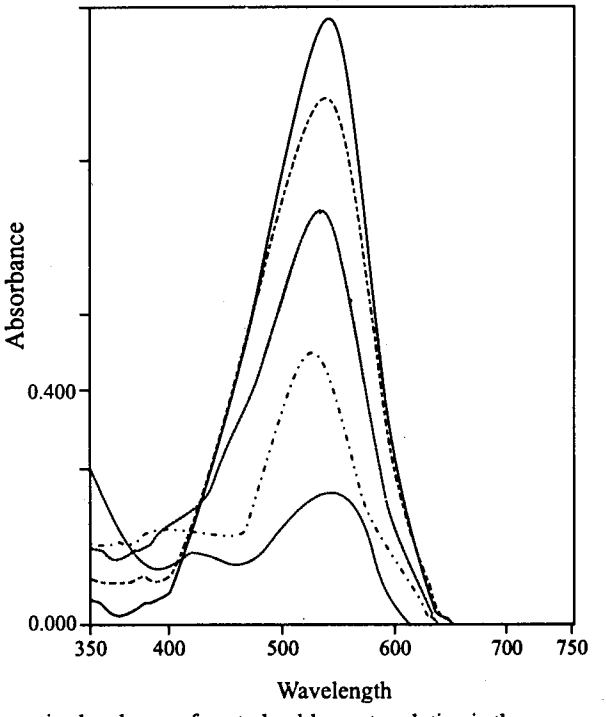

Fig. 1. Decrease in absorbance of neutral red-bromate solution in the presence of 2 μg mL^{-1} of formaldehyde, time interval 30 sec.

Effect of variables

The effect of acidity on the reaction rate was studied both in the presence and absence of formaldehyde by the addition of sulfuric acid to the test solution. The results shown in Fig. 2 indicate that the optimum concentration of sulfuric acid is 0.1 mol L^{-1} in the final solution.

The influence of bromate concentration was also studied in the concentration range of 2.0×10^{-3}–12.1×10^{-3} mol L^{-1} and the highest $\Delta(1/t)$ was obtained when concentration of bromate was 4.4×10^{-3} mol L^{-1} in the final solution.

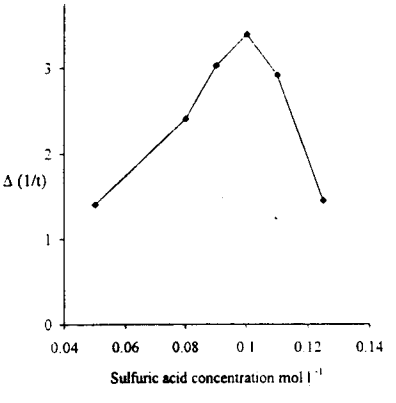

Fig. 2. The effect of sulfuric acid concentration on the absorbance changes of neutral red-bromate solution.

The effect of neutral red concentration on the reaction rate was investigated in the concentration range of 2.5×10^{-5}–7.5×10^{-5} mol L^{-1}. As shown in Fig. 3 optimum concentration was found to be 5×10^{-5} mol L^{-1} of neutral red.

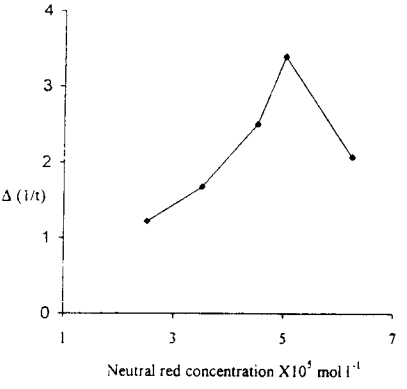

Fig. 3. The influence of neutral red concentration on the reaction rates.

The rate of the oxidation reaction in the presence and absence of formaldehyde was found to increase by increasing the temperature. A temperature of 33 ± 0.1°C was used for further work.

Effect of ionic strength on the reaction rate was also studied. The ionic strength of the solution varied from 0.01 to 0.35 mol L^{-1} using Na_2SO_4 and KNO_3 solutions. The results showed that ionic strength has no considerable effect on the reaction rate.

Analytical Parameters

The calibration graph was obtained using recommended procedure under the optimum condition. The method shows two linear calibration graphs in the concentration ranges of 25–600 ng mL^{-1} and 0.6–6.0 μg mL^{-1} of formaldehyde. The correlation coefficient of both graphs is 0.9990. The regression equation for the concentration range of 25–600 ng mL^{-1} is $\Delta(1/t) \times 10^2 = 3.487 + 0.0068C$ where C is in ng mL^{-1} of formaldehyde and that of concentration range of 0.6–6.0 μg mL^{-1} is $\Delta(1/t) \times 10^2 = 6.55 + 1.7C$, where C is in μg mL^{-1} of formaldehyde. The limit of detection obtained by the equation LOD $= KS_b/m$, is 23 ng mL^{-1} (K = 3, m is slope of the calibration graph for the range of 25–600 ng mL^{-1} and S_b is standard deviation of the blank). The relative standard deviation for eight replicate measurements of 1 μg mL^{-1} of formaldehyde is 0.93%.

Effect of foreign ions

In order to study the effect of various species on the determination of formaldehyde, a fixed amount of formaldehyde (1 μg mL^{-1}) was taken with different amounts of foreign species and the recommended procedure was followed. A relative error of 3% was considered tolerable. The results are

summarized in Table-1. As it is seen, a large number of cations and anions and some organic compounds have no considerable effect on the determination of formaldehyde. Some of the aldehydes tested were tolerated at concentrations 25 times more than formaldehyde. The interference of I^-, CN^-, SCN^- and SO_3^{2-} was eliminated using Hg^{2+}.[14] The interfering cations can successfully be removed by passing the solution through a column containing a strongly acidic cation exchanger.

TABLE-1
TOLERANCE LIMITS OF DIVERSE SPECIES ON THE DETERMINATION OF 1 μg mL^{-1} FORMALDEHYDE

Species	Tolerated ratio of foreign species formalhedyde
K^+, Na^+, NO_3^-, NH_4^+, Mg^{2+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, Al^{3+}, Cd^{2+}, F^-, PO_4^{3-}, CO_3^{2-}, acetone, acetic acid, formic acid, CH_3COO^-, IO_3^-, ClO_4^-	1000
Ethanol, methanol	20
Acetaldehyde, isobutyraldehyde, benzaldehyde, propionaldehyde	25
Cl^-, Br^-, Mo^{6+}, Cu^{2+}, Ag^+, Fe^{2+}, Fe^{3+}, I^-, CN^-, SCN^-, SO_3^{2-}	1

Application

The method was applied to the determination of free formaldehyde present in commercial melamine formaldehyde resin. About 0.1 g of the resin was exactly weighed and suspended in water. The free formaldehyde was separated by steam distillation and 250 mL of the distillate was collected. The concentration of formaldehyde in the distillate solution was determined by the proposed method and a standard method using chromotropic acid and sulfite procedure[12, 13]. As it is shown in Table-2, there is a good agreement between the results obtained by the proposed method and the standard method.

TABLE-2
RESULTS OF FORMALDEHYDE DETERMINATION IN COMMERCIAL MELAMIN FORMALDEHYDE RESIN BY THE PROPOSED METHOD AND STANDARD METHOD

Method	Average concentration of formaldehyde (n = 5) μg mL^{-1}	RSD (n = 5)
Kinetic	5.19	0.93
Standard	5.22	0.76

Conclusion

The method described provides a simple and sensitive means for the determination of trace amounts of formaldehyde in the presence of large amounts of other species. The method offers a wider dynamic range than many previously reported methods. The detection of the method is also low compared to the other methods[5, 11] and does not require sophisticated instruments[9] or time consuming pre-concentration procedures. The method could easily be applied to the determination of formaldehyde in real samples with good accuracy and precision.

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