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Catalytic Spectrophotometric Determination of Formaldehyde Based on Its Catalytic Effect on the Reaction Between Bromate and Cresyl Violet

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A new simple and rapid catalytic kinetic method for the determination of trace amount of formaldehyde is described. The method is based on the catalytic effect of formaldehyde on the oxidation of cresyl violet by bromate in the present of sulfuric acid. The reaction monitored spectrophotometrically by measuring the decrease in absorbance of the reaction mixture at 564 nm. The fixed-time method was used for the first 90 s. For initiation of the reaction, under the optimum conditions, in the concentration range of 0.02-2.00 μg mL^{-1} formaldehyde can be determined with a limit of detection 0.011 μg mL^{-1}. The relative standard deviation of six replicate measurements is 2.5 % for 0.3 μg mL^{-1} of formaldehyde. The method was used for the determination of formaldehyde in water samples with satisfactory results.

Key Words: Catalytic, Cresyl violet, Spectrophotometeric, Bromate, Formaldehyde.

INTRODUCTION

Formaldehyde is a flammable, colourless and readily polymerized gas at ambient temperature. Exposure to formaldehyde has caused intense concern because it is an irritant giving rise to dermatitis, eye irritation, respiratory irritation, asthma and pulmonary edema[1,2]. It has the potential to react with hydrochloric acid to form *bis*(chloromethyl)ether a known carcinogen[3,4]. Industrial exposure to formaldehyde occurs mainly in the woodworking and garment industry using formaldehyde based resins. Because of its widespread use and adverse health effects, Interest in improved analytical methodology for the determination of formaldehyde is high. Various methods have been developed for the determination of formaldehyde including GC[5,6], HPLC[7,8], voltammetry[9,10], chemiluminesence[11], fluorimetry[12,13]. However, they are not very sensitive and are subject to numerous interferences and expensive. Spectrophotometric kinetic analytical methods become important means in trace analysis as various methods have been reported for the determination of trace amount of numerous elements[14-16]. Spectrophotometric catalytic kinetic methods are based on the catalytic effect of the element upon the reactions in coloured (visible) or colourless (UV) solutions[17]. The application of these methods offered some specific advantages such as improved selectivity and high sensitivity. In the past years,

kinetic methods have been widely used in catalytic and non-catalytic determinations of various chemicals. Nevertheless, quite a few methods have been published up to now. They are either narrow linear range[18,19], subject to interference from other compounds[18-21] or have a high limit of detection[22-25]. Here, we report a kinetic method for ultra trace determination of formaldehyde, based on its catalytic effect on the oxidation of cresyl violet by $KBrO_3$ in acidic medium. It should be noted that there are no reports on the use of catalytic effect of formaldehyde for this reaction.

EXPERIMENTAL

Doubly distilled water and analytical reagent grade chemicals were used during all of the experimental studies. Cresyl violet solution 6.22×10^{-4} M was prepared by dissolving 0.020 g of cresyl violet (m.w. = 321.3) in water and solution was diluted to the mark in a 100 mL of volumetric flask. Bromate stock solution 0.015 M, was prepared by dissolving 0.626 g of potassium bromate (M = 167) in water and diluting to 250 mL in a 250 mL volumetric flask. An aqueous formaldehyde stock solution, 1000 μg mL^{-1}, was prepared by diluting 2.5 mL of 37 % w/v stock formaldehyde solution to 1 L with water. Sulfuric acid solution was prepared by appropriate dilution of concentrated sulfuric acid (Merck). Stock solution (1000 μg/mL) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solution. All glassware were cleaned with detergent solution, rinsed with tap water, soaked in dil. HNO_3 solution (2 % v/v), rinsed with water and dried.

Absorption spectra were recorded with a CECIL model 7500 spectrophotometer with a 1.0 cm quartz cell. A model 2501 CECIL Spectrophotometer with 1.0 cm glass cuvettes was used to measure the absorbance at a fixed wavelength of 564 nm. A thermostat water bath (Gallen Kamp Griffin, BGL 240 V) was used to keep the reaction temperature at 27 °C. A stopwatch was used for recording the reaction time.

Recommended procedure: All the solutions and distilled water were kept in a thermostated water bath at 27 °C for 20 min for equilibration before starting the experiment. An aliquot of the solution containing 0.2-20 μg mL^{-1} formaldehyde was transferred into a 10 mL volumetric flask and then 2 mL 5 M H_2SO_4 and 3 mL 6.22×10^{-4} M cresyl violet were added to the flask.The solution was diluted to *ca.* 7 mL with water. Then, 1.8 mL of 0.015 M bromate was added and the solution was diluted to the mark with water. The solution was mixed and a portion of the solution was transferred to the spectrophotometer cell. The reaction was followed by measuring the decrease in absorbance of the solution against water at 564 nm for 0.5-2.0 min from initiation of the reaction. This signal (sample signal) was labeled as ΔA_s. The same procedure was repeated without addition of formaldehyde solution and the signal (blank signal) was labeled as ΔA_b. Time was measured just after the addition of last drop of bromate solution. Analytical signal was difference between blank signal and sample signal (ΔA_s-ΔA_b).

RESULTS AND DISCUSSION

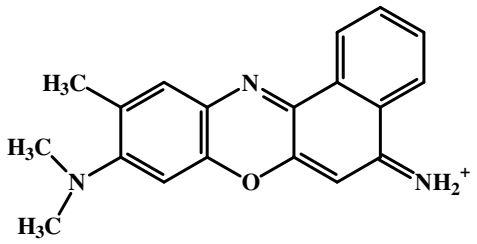
Cresyl violet (**I**) is a dye that can be oxidized with strong oxidizing agents at slow reaction. It is found that trace amount of formaldehyde have a catalytic effect on the oxidation of cresyl violet by bromate in acidic medium.Therefore, by measuring the decrease in absorbance of cresyl violet for a fixed time of 0.5-2.0 min initiation of the reaction, the formaldehyde contents in the sample can be measured, this reaction rate is sharply increased by addition of trace amounts of formaldehyde. The rate equation of the catalyzed reaction is:

$$\text{Rate} = -d[\text{cresyl violet}]/dt$$
$$= K[\text{formaldehyde}][\text{cresyl violet}]^m[BrO_3^-]^n \quad (1)$$

where k is the rate constant. because $[BrO_3^-] >> [\text{cresyl violet}]$, BrO_3^- can be considered to be constant and m was found to be 1. By integration of eqn. 1 and by incorporating Beer's law, we obtain the final expression:

$$\Delta A = K[\text{formaldehyde}]t \quad (2)$$

where t is the reaction time.



Structure of cresyl violet (**I**)

There are many methods, such as fixed-time, initial rate, rate constant and variable time methods for measuring the catalytic species. Among these, the fixed-time method is the most conventional and simplest, involving the measurement of ΔA at 564 nm (Fig. 1).

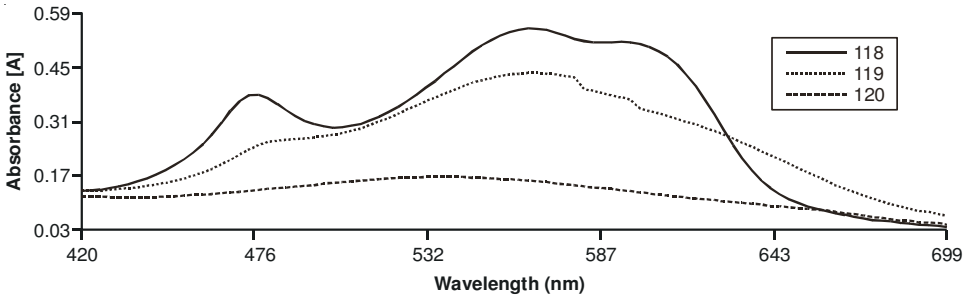


Fig.1. Absorption spectrum for the formaldehyde-cresyl violet-BrO_3-system with time. Conditions: H_2SO_4, 1 M; cresyl violet, 1.87×10^{-4} M; BrO_3^- 2.7×10^{-3} M; formaldehyde 0.4 μg/mL, temperature, 27 °C; interval time for each scan, 0.5, 1.5, 2.5 and 3.5 from initiation of the reaction

Influence of variables: In order to take full advantage of the procedure, the reagent concentrations must be optimized. The effect of sulphoric acid concentration, cresyl violet concentration, bromate concentration and temperature on analytical signal was studied.

The effect of sulfuric acid concentration on the analytical signal was studied in the range of 0.7-1.2 M (Fig. 2). The results show that the analytical signal increases with increasing sulphuric acid concentration up to 1 M and decreases at higher concentrations. Therefore, a sulfuric acid concentration of 1 M was selected for further study.

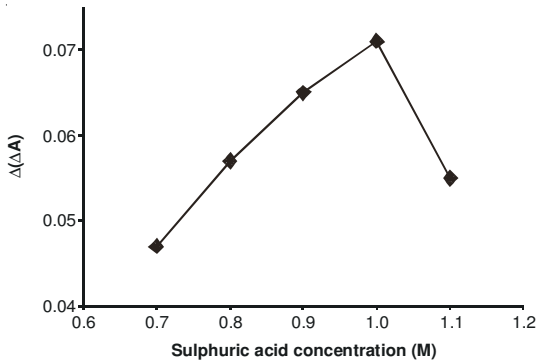


Fig. 2. Effect of H_2SO_4 concentration on the analytical signal, conditions: cresyl violet, 1.2×10^{-4} M; BrO_3^- 3.0×10^{-3} M; formaldehyde 0.4 µg/mL, temperature, 27 ºC and time of 1.5 min from initiation of the reaction

The influence of cresyl violet concentration on the analytical signal was studied in the concentration range of $9.95 \times 10^{-5} - 2.1 \times 10^{-4}$ M (Fig. 3). The results show that analytical signal increases with increasing cresyl violet concentration up to 1.87×10^{-4} M and decreases at higher concentrations. Therefore, a cresyl violet concentration of 1.87×10^{-4} M was selected for further study.

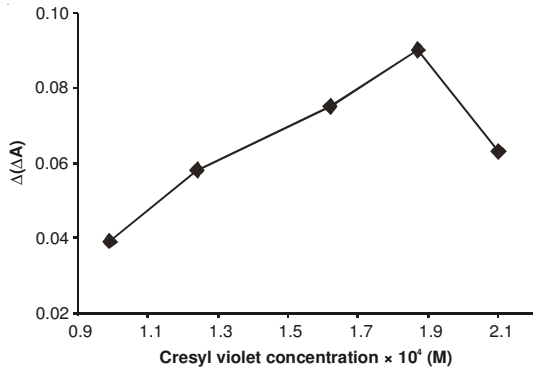


Fig. 3. Effect of cresyl violet concentration on the analytical signal, conditions: H_2SO_4, 1 M; BrO_3^-, 3.0×10^{-3} M, formaldehyde 0.4 µg/mL, temperature, 27 ºC and time of 1.5 min from initiation of the reaction

Fig. 4 shows the effect of the bromate concentration on the analytical signal for the range of $2.1 \times 10^{-3} - 3.3 \times 10^{-3}$ M. This analytical signal increases with increasing bromate concentration up to 2.7×10^{-3} M and decreases at higher concentrations. Therefore, a final concentration of 2.7×10^{-3} M of bromate was selected as the optimum concentration.

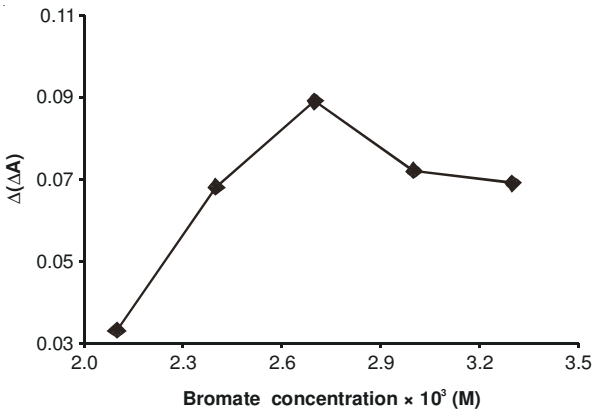


Fig. 4. Influence of BrO_3^- concentration on the analytical signal, conditions: H_2SO_4, 1 M; cresyl violet 1.87×10^{-4} M formaldehyde 0.4 µg/mL; temperature, 27 ºC and time of 1.5 min from initiation of the reaction

The effect of the temperature on the analytical signal was studied in the range 20-40 °C with the optimum of the reagents concentrations. The results showed that, as the temperature increases up to 27 °C, the analytical signal increases, whereas higher temperature values decrease the analytical signal ($\Delta A = \Delta A_s - \Delta A_b$). Therefore, 27 °C was selected for further study.

Calibration graph, precision and limit of detection: Calibration graph were obtained using the fixed-time method. This method was applied to the change in absorbance over an interval of 0.5-2.0 min from intiation of the reaction because it provided the best regression and sensitivity. Under the optimum conditions described above, a linear calibration range 0.020-2.0 µg/mL of formaldehyde. The equation of the calibration graph is $\Delta A = 0.1335C + 0.029$ ($n = 11$, $r = 0.9997$). The calibration graph was constructed by plotting of ΔA_s at a fixed-time method *versus* formaldehyde concentration. The experimental 3 δ limit of detection was 0.011 µg/mL.

The relative standard deviation for six replicate determinations of 0.3 and 1 µg/mL resorcinol was 2.5 and 2.9 %, respectively.

Interference study: In order to assess the application of the proposed method to synthetic samples, the effect of various ions on the determination of 0.6 µg/mL resorcinol was studied. The tolerance limit was defined as the concentration of a added ions causing a relative error less than 3 % in Table-1. The results show that method is relatively selective for formaldehyde determination.

TABLE-1
EFFECT OF FOREIGN IONS ON THE DETERMINATION
OF 0.6 μg/mL FORMALDEHYDE

Species	Tolerance limit ($w_{ion}/w_{formaldehyde}$)
Na^+, K^+, NH_4^+, Rb^+, Cs^+, Se^{4+}, Al^{3+}, Ni^{2+}, Cd^{2+}, HSO_4^-, CO_3^{2-}, HCO_3^-, PO_4^{3-}, BO_3^{3-}, tatarate	1000
Ethanol, methanol, ethanolamine	400
$S_2O_3^{2-}$, SO_3^{2-}, I^-	100
Br^-	1

Sample analysis: In order to evaluate the applicability of the proposed method, water samples were analyzed to determine formaldehyde contents. The results are presented in Table-2. Good recoveries with precise results show good reproducibility and accuracy of the method.

TABLE-2
DETERMINATION OF FORMALDEHYDE IN SYNTHETIC SAMPLES

Sample	Formaldehyde added (ng/mL)	Formaldehyde found (ng/ml)	Recovery (%)	RSD (n = 4)
Well water	–	–	–	–
Well water	60	64	106.6	2.1
Well water	300	291	97.0	2.9

Conclusion

The catalytic-spectrophotometric method developed for the determination of formaldehyde is inexpensive, uses readily available reagents, allows rapid determination at low operating costs and shows simplicity, adequate Selectivity, low limit of detection and good precision and accuracy compared to other kinetic procedures.

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