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Catalytic–kinetic determination of trace amount of formaldehyde by the spectrophotometric method with a bromate–Janus green system

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Abstract

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 Janus green by bromate in the present of sulfuric acid. The reaction monitored spectrophotometrically by measuring the decrease in absorbance of the reaction mixture at 618 nm. The fixed-time method was used for the first 150 s. For initiation of the reaction, under the optimum conditions, in the concentration range of 0.003–2.5 $\mu g\,ml^{-1}$ formaldehyde can be determined with a limit of detection 0.0015 $\mu g\,ml^{-1}$. The relative standard deviation of five replicate measurements is 2.3% for 1.0 $\mu g\,ml^{-1}$ of formaldehyde. The method was used for the determination of formaldehyde in real samples with satisfactory results.
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Keywords: Janus green; Formaldehyde; Spectrophotometeric; Bromate

1. Introduction

Formaldehyde is one the exceptionally important air pollutants in residential and industrial environments. 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], and spectrophotometry [14–18]. The spectrophotometric methods are most widely used. However, they are not very sensitive and are subject to numerous interferences by phenols, alcohols and cyclohexanone [14–17]. Only few reports have been found for the determination of formaldehyde with kinetic methods [11,18–21]. They are either

not sensitive enough [11] and subject to interference from other compounds [19–21] or have a high limit of detection [11,20,21]. It should be noted that, there are no reports on the use of catalytic effect of formaldehyde for this reaction. Proposed method is a rapid, highly sensitive and selective for the determination of formaldehyde using the Janus green–bromate system. It is suitable for the determination of ultra trace of formaldehyde in real samples. The applications of method to the determination of formaldehyde in melamine-formaldehyde resins and chemical industrial wastewater are reported.

2. Experimental

2.1. Reagents and chemical

All chemical used were of analytical reagent grade and doubly distilled water were used throughout. A 1000 $\mu g\,ml^{-1}$ stock solution of formaldehyde was prepared by diluting 2.5 ml (37%) formaldehyde solution (Merck) to 1000 ml with water and was standardized by using the sulfite method [21]. Formaldehyde working standard solution were prepared daily from the stock standard solution by appropriate dilution with water. Bromate solution (0.25 M) was prepared by dissolving 4.1752 g of $KBrO_3$ (Merck) in water in a 100 ml volumetric flask. Janus green solution (10^{-3} M) was prepared by dissolving 0.051107 g Janus

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green (Aldrich) in water and diluting to 100 ml with water in a volumetric flask. Sulfuric acid solution (2 M) was prepared by diluting the appropriate volume of concentration acid (Merck).

2.2. Apparatus

A photometer (Cary, Model 50 Conc UV–vis) was used to measure the absorbance change at 618 nm. A thermostat water batch (LAUDA, LABSCO, D-6360) was used to keep the reaction temperature at 30 °C.

2.3. Recommended procedure

All solution was kept in a 30 °C thermostat water batch for 30 min before initiation of the reaction. To a series of 10 ml volumetric flasks, 0.3 ml of 10^{-3} M Janus green solution, 1 ml of 2 M sulfuric acid and different amounts of formaldehyde were added. Then 1 ml of 0.25 M bromate solution was added and the solution diluted to the mark with double distillated water. After shaking, the solution was transferred in to 10 mm cell of the spectrophotometer and the zero time was taken as the moment at which the last drop of bromate solution had been added. The variation in absorbance of dye ($\lambda_{max} = 618$ nm) versus time (for a during of 150 s) was started to be measured 30 s after addition of bromate solution. The absorption spectra of Janus green in the studied system, was given in (Fig. 1). The spectra showed that the absorption of dye in 618 nm was reduced with the formaldehyde addition in the different times. The measured kinetic parameter was "net absorbance versus time", the difference between blank and sample absorbance versus time at initial time was obtained
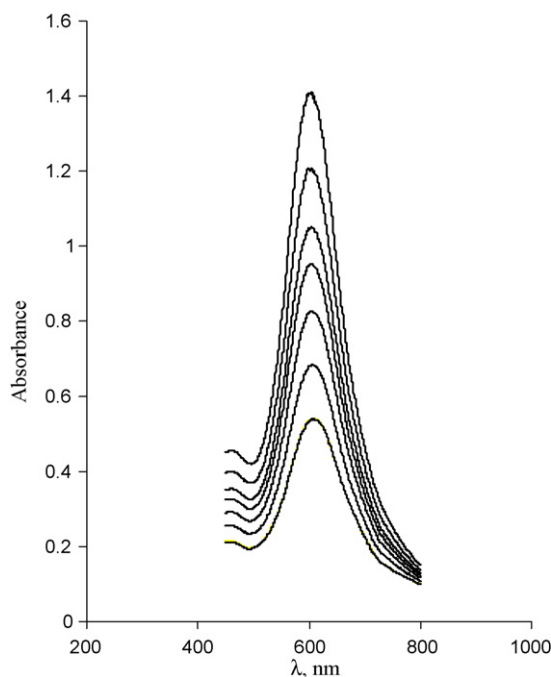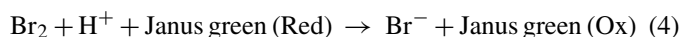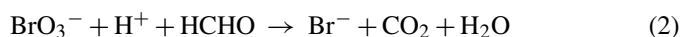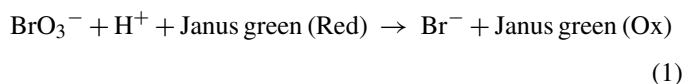
for different catalyst concentrations in order to prepare a calibration graph.

3. Results and discussion

Janus green is a dye that can be oxidized with strong oxidizing agents at slow reaction. Formaldehyde can increasing rate this reaction at ultra-trace level. The possible mechanism of the Janus green reaction may be contributed to the following reactions in its simplest form:

$$BrO_3{}^- + H^+ + Janus\ green\ (Red) \rightarrow Br^- + Janus\ green\ (Ox) \tag{1}$$

$$BrO_3{}^- + H^+ + HCHO \rightarrow Br^- + CO_2 + H_2O \tag{2}$$

$$BrO_3{}^- + H^+ + Br^- \rightarrow Br_2 + H_2O \tag{3}$$

$$Br_2 + H^+ + Janus\ green\ (Red) \rightarrow Br^- + Janus\ green\ (Ox) \tag{4}$$

where Red is reduced form and Ox is the oxidized form reaction. Because reaction (1) is very slow [22], in the absence of formaldehyde, $BrO_3{}^-$ oxidized Janus green to produce weak reduce in absorbance of dye. When formaldehyde was added to this system, reactions (2) and (3) were very fast. Because the Br_2 generated in situ in this system was a nascent oxidant [23].

For finding the optimum experimental conditions, the effect of temperature, sulfuric acid concentration, bromate concentration, ionic strength and concentration of Janus green on the reaction rate were studied by fixed-time method.

3.1. Effect of sulfuric acid concentration

The effect of various acid types with the same concentration such as sulfuric acid, hydrochloric acid, phosphoric acid and nitric acid was studied. The results show that sulfuric acid gives greater sensitivity. That effect of sulfuric acid concentration on obtaining maximum sensitivity was investigated with 2.0×10^{-5} M Janus green and 3.75×10^{-3} M bromate for catalyzed and uncatalyzed reaction in 30 °C (Fig. 2). The results show that by increasing the acid concentration up 0.24 M the sensitivity increased. On the other hand, higher acid concentration, cause a small decrease of the sensitivity ($\Delta A_s - \Delta A_b$). This is due to the fact that at presence of higher acid concentrations, the blank reaction becomes faster and thus (ΔA_b) become larger and ($\Delta A_s - \Delta A_b$) smaller. Therefore 0.24 M of sulfuric acid was used for the study.

3.2. Effect of Janus green concentration

The effect of Janus green concentration in the reaction rate was studied with 0.24 M sulfuric acid and 3.75×10^{-3} M bromate at 30 °C. The results show that by increasing the Janus green concentration up to 3.5×10^{-5} M the sensitivity ($\Delta A_s - \Delta A_b$) increases, whereas a greater amount of reagent dose not effect it (Fig. 3). Thus 3.5×10^{-5} M Janus green was selected throughout the study.

Fig. 1. Variation of absorbance spectra with time. *Condation*—formaldehyde: 1 μg ml^{-1}; Janus green: 2×10^{-5} M; BrO$_3{}^-$: 3.75×10^{-3} M; H$_2$SO$_4$: 0.5 M; time interval (s): 30, 60, 90, 120, 150, 180 and 210 s; temperature: 30 °C.

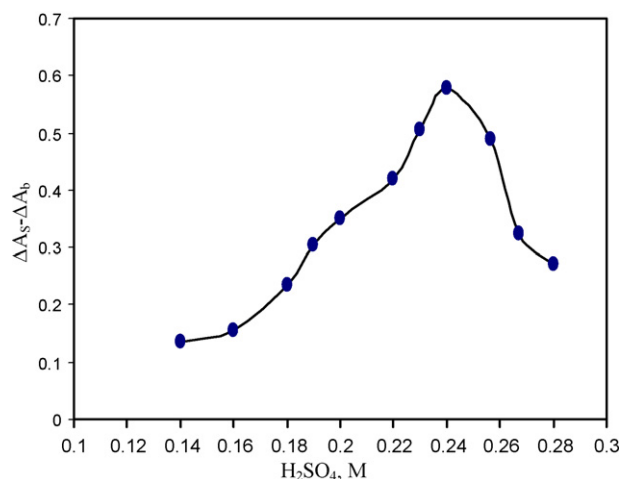Fig. 2. Effect of sulfuric acid concentration on the reaction rate. *Condition*—formaldehyde: 1 µg ml^{-1}; Janus green: 2×10^{-5} M; BrO$_3^-$: 3.75×10^{-3} M; temperature: 30 °C.

3.3. Effect of bromate concentration

The influence of bromate concentration on the reaction rate was studied in the range of 5.5×10^{-3} to 3×10^{-3} M with 0.24 mol l^{-1} sulfuric acid and 3.5×10^{-5} M Janus green at 30 °C (Fig. 4). The results show that by increasing the bromate concentration up to 4.5×10^{-3} M the sensitivity increased, whereas grater amounts of the bromate cause decreasing sensitivity. This effect is due to the fact that blank reaction becomes faster and sensitivity ($\Delta A_s - \Delta A_b$) decreased. Therefore 4.5×10^{-3} M bromate concentration was selected for the study.

3.4. Effect of temperature

The influence of temperature on the sensitivity ($\Delta A_s - \Delta A_b$) was studied in the range of 10–50 °C with the optimum reagent concentrations. The results show that with increasing temperature of 30 °C the net reaction rate increased. A temperature of
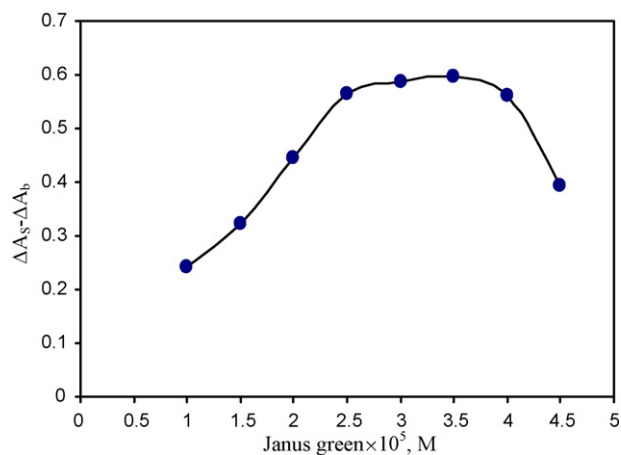

Fig. 3. Effect of Janus green concentration on the reaction rate. *Condition*—formaldehyde: 1 µg ml^{-1}; H$_2$SO$_4$: 0.24 M; BrO$_3^-$: 3.75×10^{-3} M; temperature: 30 °C.
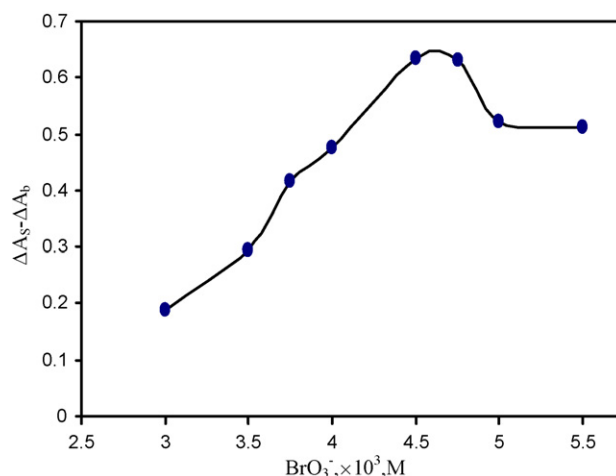

Fig. 4. Effect of bromat concentration on the reaction rate. *Condition*—formaldehyde: 1 µg ml^{-1}; Janus green: 3×10^{-5} M; H$_2$SO$_4$: 0.24 M; temperature: 30 °C.

30 °C was selected due to the simplicity of application and its reproducibility.

3.5. Effect of ionic strength

The effect off ionic strength on the net reaction rate ($\Delta A_s - \Delta A_b$) was studied in the range of 0.05–0.35 M Na$_2$SO$_4$ solution and optimum reagent concentration. The results show that a change in ionic strength has little effect in the sensitivity.

4. Calibration graph and precision

The calibration graphs were obtained by applying the fixed-time method. By fixed-time method, formaldehyde concentration under optimum condition was varied from 0.0 to 3.0 µg ml^{-1} by running five replicate measurements for each concentration. The calibration graph was linear in the range of 0.003–0.100 and 0.100–2.5 µg ml^{-1} of formaldehyde concentration. The calibration graph in the range of 0.003–0.100 µg ml^{-1} of formaldehyde concentration in the present of the optimum conditions with a regression equation $\Delta A = 0.0102 + 0.0053 C_{formaldehyde}$ ($r^2 = 0.993$, $n = 5$), and the calibration graph in the range of 0.1–2.5 µg ml^{-1} of formaldehyde concentration have a regression equation $\Delta A = 0.089 + 0.0036 C_{formaldehyde}$ ($r^2 = 0.9985$, $n = 5$), where ΔA is ($\Delta A_s - \Delta A_b$) and C is the concentration of formaldehyde in ng ml^{-1} the experimental limit of detection (defined as three times the standard deviation of the blank divided by the slope of the calibration graph, $3S_b/m$) is equal to 0.022 µg ml^{-1} formaldehyde concentration. The relative standard deviation for five replicate measurement of 100, 1000, 2000 ng ml^{-1} of formaldehyde were 2.8, 2.3, 1.2%, respectively.

5. Interference study

For analytical application of the catalytic reaction, the fixed-time method is recommended. The influences of several organic

Table 1
Interference study for the determination of formaldehyde

Species	Tolerable concentration ratio ($W_{substance}/W_{formaldehyde}$)
Cd^{2+}, Mg^{2+}, Na^+, K^+, Mn^{2+}, Al^{3+}, La^{3+}, NH_4^+, NO_3^-, SO_4^{2-}, CO_3^{2-}, CH_3COO^- benzene, acetone, toluene	1000
Ca^{2+}, ethanol, methanol	750
Acetaldehyde, benzaldehyde	500
Zn^{2+a}	100
Cl^-, Br^-, I^{-b}	10

[a] Masking with 0.1% EDTA solution.
[b] Removed by addition of $5\,mol\,l^{-1}$ nitric acid as well as boiling the solution.

Table 2
Determinetion of formaldehyde in real samples

Sample	Formaldehyde found ($\mu g\,ml^{-1}$)	
	Proposed method ($n = 5$)	Standard method ($n = 5$)
Melamine-formaldehyde resin	$6.5 \pm 0.71\%$	$6.3 \pm 0.21\%$
Chemical industerial wastewater	$0.70 \pm 0.01\%$	$0.71 \pm 0.1\%$

and inorganic compounds were tested using the standard solution of formaldehyde ($1.00\,\mu g\,ml^{-1}$). The results are given in Table 1. This table shows that the metal cation that seriously interference is Zn^{2+} above $100\,\mu g\,ml^{-1}$. The interference of Zn^{2+} can be greatly diminished by addition of 0.1% EDTA solution. Iodide, bromide, and chloride interference at concentration greater than $10\,\mu g\,ml^{-1}$. The interference of iodide, bromide and chloride can be greatly diminished by addition of 5 M nitric acid as well as boiling the solution [24].

6. Application

The free formaldehyde in melamine-formaldehyde resin was determined using a simple calibration graph and also by the standard addition method. Similar results were obtained by both methods. This shows that a simple calibration graph is adequate for determination of formaldehyde in the resin (Table 2). The proposed method was also applied to the determination of formaldehyde in a sample of chemical industrial wastewater. The results were compared with a standard method for the determination of formaldehyde [25].

7. Conclusion

The proposed method kinetic–catalytic photometric method is simple, rapid and sensitive for the determination of formaldehyde in real samples. The results, given in Table 2 shows that the method is accurate and gives good recoveries of added formaldehyde.

Acknowledgement

References

[1] M. Agathos, H.A. Bernecker, Derm. Beruf. Umwelt. 30 (1982) 43.
[2] D.W. Cockcroft, V.H. Hoeppner, Dolvovich. J. Chest. 82 (1982) 49.
[3] L.S. Frankel, K.S. McCallum, L. Collier, Environ. Sci. Technol. 8 (1974) 356.
[4] G.L. Kallos, R.A. Solomon, Am. Ind. Hyg. Assoc. J. 34 (1973) 469.
[5] E.R. Kennedy, R.H. Hill, Anal. Chem. 54 (1982) 1739.
[6] V. Neitzert, W. Seiler, Geophys. Res. Lett. 8 (1981) 79.
[7] K. Fung, D. Grosjean, Anal. Chem. 53 (1981) 168.
[8] L.J. Salas, H.B. Singh, Atoms. Environ. 20 (1986) 1301.
[9] J.C. Septon, J.C. Ku, Am. Ind. Hyg. Assoc. J. 43 (1982) 845.
[10] W. Li, X. Chen, Z. Cheng, Huanjing Huaxue 7 (1988) 53.
[11] L. Xiaohu, L. Minggang, Y. Fang, Anal. Lett. 25 (1992) 2073.
[12] P. Bisgaard, L. Molhave, B. Rietz, P. Wilhardt, Anal. Lett. 16 (1983) 1457.
[13] S. Dong, P.K. Dasgupta, Environ. Sci. Technol. 21 (1987) 581.
[14] R.C. Schothorst, M.V. Son, G.D. Beof, Anal. Chim. Acta 162 (1984) 1.
[15] W. Huber, Z. Fresenus, Anal. Chem. 309 (1981) 386.
[16] M.H. Ho, ACS. Symp. Ser. 316 (1986) 107.
[17] D.C. Hakes, G.D. Johnson, J.S. Marhevka, Am. Ind. Hyg. Assoc. J. 45 (1984) 274.
[18] A.A. Ensafi, S. Abbasi, Fresenius J. Anal. Chem. 363 (1999) 376.
[19] K. Takeuchi, H. Takeuchi, S. Kutsuna, Bunseki Kagaku 42 (1993) 439.
[20] A. Safavi, A.A. Ensafi, Anal. Chim. Acta 252 (1991) 167.
[21] P.M. Mavia, F.G. Rueda, M.P. Luis, Analyst 114 (1989) 1469.
[22] S. Wang, L. Du, A. Zhang, Chin. J. Anal. Chem. 28 (2000) 628.
[23] X. Zheng, M. Yang, Z. Zhang, Acta Chim. Sin. 59 (2001) 945.
[24] A.A. Ensafi, S. Abbasi, Anal. Lett. 31 (1997) 327.
[25] G. Schlesinger, S.L. Miller, J. Am. Chem. Soc. 95 (1973) 3729.