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KINETIC SPECTROPHOTOMETRIC DETERMINATION OF MERCURY IN DIFFERENT MATERIALS BASED ON ITS INHIBITORY EFFECT ON THE BRILLIANT GREEN-SULFITE REACTION

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Abstract

A new kinetic method for the determination of Hg(II) based on its inhibitory effect on the Brilliant green-sulfite reaction at pH 6.5 is proposed. The reaction is followed spectrophotometrically at 615 nm by measuring the change in absorbance at the fixed time of 3.5 min after the initiation of the reaction. Both the influence of the reaction variables and the interference of many ions have been studied. Under the selected experimental conditions, Hg(II) was determined in the range 5.0 - 1300 ng.ml^{-1}. The method was applied to the determination of mercury in cleaning solutions for contact lenses and in industrial waste water.

Introduction

Large amounts of mercury enter the environment due to the use of mercury in agriculture and industry. The prolonged intake of even low concentrations of mercury can cause serious toxic effects, hence there has been as increasing interest in the determination of mercury levels in water.

The toxicity of mercury salts and vapors has fostered the development of a number of methods for the determination of the element. Most of these methods have been listed in reviews [1-11]. A significant number of them are based on the catalytic action of Hg(II) [12-16] and the slow redox processes [17-21] or on their inhibitory effect on a catalytic indicator system [22-25].

In an earlier paper we reported on the Brilliant green-sulfite reaction which led us to propose a new kinetic method for the determination of sulfite [26]. The interferences studied showed that mercury exerted a strong inhibitory effect on this reaction, which depended on the mercury concentration.

In this paper, we describe a kinetic method for the determination of Hg(II) based on its inhibitory effect on the Brilliant green-sulfite system at pH 6.5. The procedure has been successfully applied to the determination of mercury in industrial waste water and in pharmaceuticals.

Keywords: Spectrophotometric; Mercury; Green-sulfite

Experimental Section

Reagents

All solutions were prepared from doubly distilled water. The working solutions were all kept in a water-bath at 25°C.

Hg(II) stock solution (1000 μg. ml^{-1}) was prepared by dissolving 0.1708 g of Hg $(NO_3)_2.H_2O$ (Merck) in a 100-ml volumetric flask. Brilliant green solution (1.06×10^{-4} M) was prepared by dissolving 0.0128 g of Brilliant green (Aldrich) in ca. 100 ml ethanol and diluting to 250 ml with water in a 250-ml volumetric flask.

Phosphate buffer solution (pH = 6.5) was used for pH adjustment.

A stock solution (1.0 $mg.ml^{-1}$) of sulfite was prepared daily by dissolving 0.1574 g of anhydrous sodium sulfite (Merck) in freshly boiled water and diluting to 100 ml. This solution was standardized by iodimetric titration [27].

Apparatus

A model 35 spectrophotometer (Perkin-Elmer) with 1.0 cm glass cuvettes was used to measure the absorbance at 615 nm. A thermostat bath (Gallenkamp Griffin, BJL-420-V) was used to keep the reaction temperature at 25°C. A stopwatch was used for recording the reaction time.

Recommended Procedures

The reaction was monitored spectrophotometrically by measuring the change in absorbance at 615 nm. A volume of 2 ml of buffer solution (phosphate buffer, pH = 6.5) and 1.0 ml of 10 $\mu g.ml^{-1}$ sulfite were added to a sample solution containing up to 13 μg of mercury in a 10-ml volumetric flask and the solution was diluted to ca. 8 ml with water. Then the solution was kept in a thermostated water-bath at 25°C for 10 min and 1.0 ml of Brilliant green (1.06×10^{-4} M) previously brought to 25°C was added and the solution was diluted to the mark with water. Time was measured from just after the addition of the Brilliant green solution. The mixture was mixed and a portion of the reaction mixture was transferred into a cell. The reaction was followed by recording the absorbance against water at 615 nm, from 0.5-3.5 min after the initiation of the reaction. Then a calibration graph of the difference between the decrease in absorbance of the blank minus that of the sample ($\Delta A_{blank} - \Delta A_{sample}$) at a fixed time vs. mercury concentration was constructed.

Determination of Mercury in Pharmaceuticals and Water

For the determination of Hg(II) in a cleaning solution for contact lenses, samples of 5-10 ml were treated with 1 ml of concentrated H_2SO_4 and 10 ml of concentrated HNO_3. The mixture was heated until persistent white fumes appeared, it was then mixed with 3 M NaOH solution (ca. to neutralize) and made up to volume with water in a 250-ml volumetric flask. The mercury was determined by the recommended procedure.

For the analysis of waste water, 50 ml samples were first filtered through fine filter-paper and the recommended procedure was applied directly to the sample after passing through a cation exchanger resin (Dowax 50) [28].

Results and Discussion

Effects of Variables

The decrease in the absorbance of Brilliant green with and without mercury was studied in the pH range 6-8 for 1.0×10^{-5} M Brilliant green and 1.0 $\mu g.ml^{-1}$ sulfite in the presence of 0.50 $\mu g.ml^{-1}$ Hg(II) and the following results were obtained: In the pH range 6.5 - 8.0, the rate of decrease in absorbance is less in the presence of mercury than when compared with the blank (Fig. 1). Above pH 8, the reaction rate was not tested owing to the fact that the Brilliant green undergoes decomposition due to the formation of a carbinol [28]. From these results the pH of 6.5 was chosen as the optimum working pH.

The influence of the concentration of each reagent on the rate of both sample and blank reaction was studied. The effect of sulfite concentration on the rate of reaction with and without Hg(II) was studied. The concentration of sulfite was varied from 0.100 -1.400

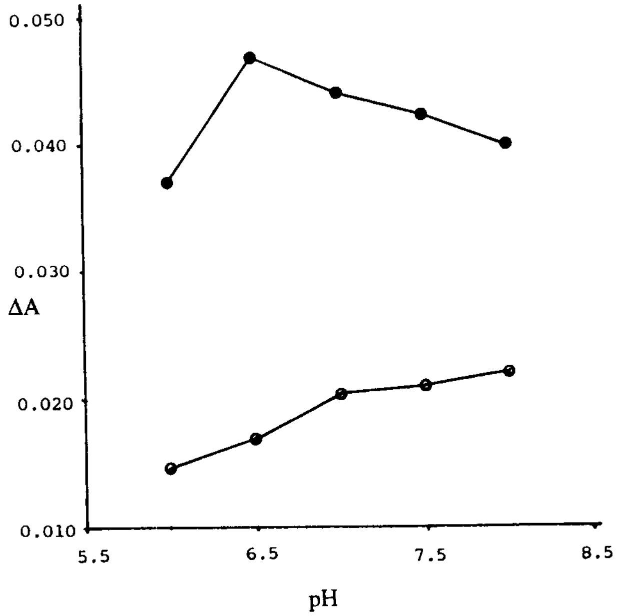

Figure 1. Effect of pH on the rate of inhibitory effect of mercury with (∘) and without (•) mercury. Conditions: Brilliant green, 1.0×10^{-5} M; interval time, 0.5-3.5 min, temperature, 25°C and Hg(II), 0.500 μg/ml.

µg.ml^{-1}. The results are shown in Figure 2. From the results, 1.0 mg.ml^{-1} sulfite was chosen as the optimum working sulfite concentration.

The effect of Brilliant green concentration on the rate of reaction with and without Hg(II) is shown in Figure 3. The concentration of Brilliant green was varied from 3.18×10^{-6} to 2.12×10^{-5} M, a limited range owing to the high molar absorptivity of the reagent. From these results, 1.0×10^{-5} M of Brilliant green was selected.

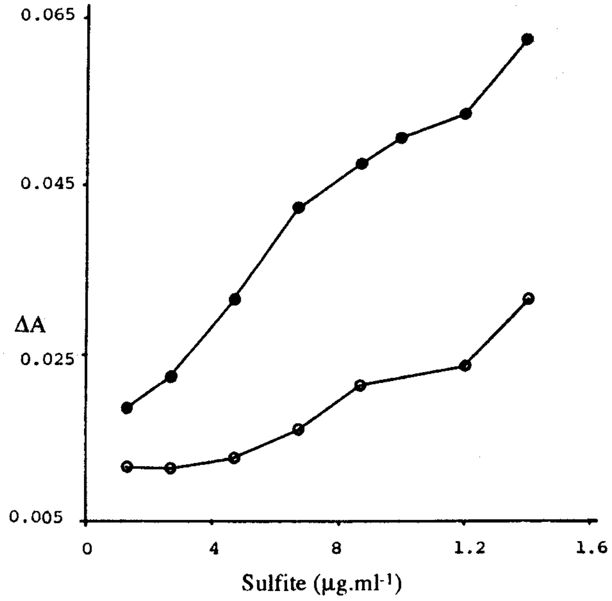

Figure 2. Effect of sulfite concentration on the rate of reaction with (∘) and without (•) mercury. Conditions: Brilliant green, 1.0×10^{-5} M; Hg(II), 0.500 µg/ml; pH, 6.5 and temperature, 25°C.

The effect of ionic strength on the rate of reaction was investigated. The rate of reaction decreased very slightly with an increase of ionic strength up to 1.0 M (3 M $NaNO_3$ solution was used).

Effect of Temperature

The effect of the reaction temperature was studied in the range of 5-40°C at the optimum conditions. Figure 4 shows that the rate of reaction with and without Hg(II) decreased with temperature. The decrease in the rate of reaction may be due to the instability of sulfite at higher temperatures. A temperature of 25°C was selected as the working temperature.

Calibration

Under the optimum conditions described above, the fixed time method was applied for the change in absorbance over an interval of 0.5 - 3.5 min, which gives the best sensitivity and regression. The change in absorbance with Hg(II) concentration was linear from 0.005 to 1.300 µg.ml^{-1}. The linear equation for

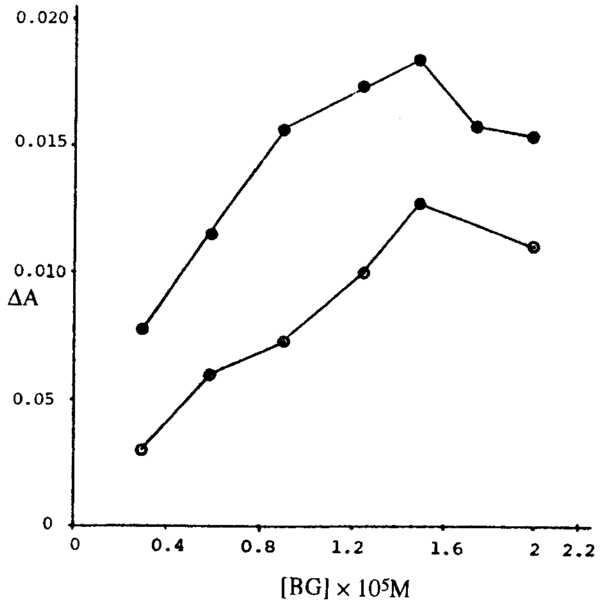

Figure 3. Effect of Brilliant green concentration on the rate of reaction with (∘) and without (•) Hg(II). Conditions: Sulfite, 1.0 µg.ml; Hg(II), 0.500 µg/ml: pH, 6.5 and temperature 25°C.

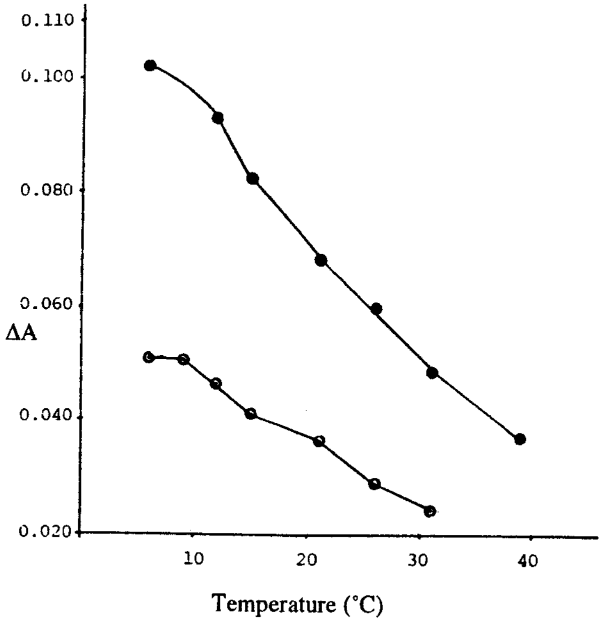

Figure 4. Effect of temperature on the rate of reaction with (∘) and without (•) Hg(II). Condition: Brilliant green, 1.0×10^{-5} M; SO_3^{2-}, 1.0 µg/ml; Hg(II), 0.500 µg/ml and pH, 6.5 and temperature 25°C.

the calibration graph is $\Delta A = 2.2 \times 10^{-3} + 0.565C$ with a correlation coefficient of 0.9995 (n = 5), where C is the $\mu g.ml^{-1}$ of Hg(II) and ΔA is equal to the ΔA_{blank} minus ΔA_{sample}.

The limit of detection, defined as the average of the blank signal value plus three times its standard deviation [29] was 1.0 $ng.ml^{-1}$. The relative standard deviation for ten replicate determinations for 10, 50 and 250 $ng.ml^{-1}$ of Hg(II) is 1.5%, 1.3% and 1.1%.

Interferences

During the optimization of the kinetic spectrophotometric determination of mercury, the possibility of interferences from some cations and anions was investigated according to the recommended procedure. The maximum amount of the substance causing an error of less than 3% (two times the maximum relative standard deviation) was taken as the tolerance limit. The results are shown in Table 1. No interference was observed from chlorate, borate, sulfate, perchlorate, nitrate, carbonate, phosphate, fluoride, tartarate, chloride, Mn(II), Ni(II), Cr(III), Ca(II), Mg(II), Hf(IV), W(VI), Na^+, K^+ and Zr(IV). However, when a cation exchanger resin [28] was used, the tolerance for Fe(III) and Cu(II) ions was increased 500-fold (molar ratio to mercury) in the presence of mercury (0.100-100.0 $\mu g.ml^{-1}$) with a 94%-103% recovery range.

Applications

The proposed method was satisfactorily applied to the determination of mercury in a cleaning solution for contact lenses, where it is present as phenylmercury nitrate or sodium ethylmercurithiosalicylate thiomersal.

Table 1. Effect of diverse species on the determination of 0.400 μg/ml Hg(II)

Species	Tolerance limit (molar ratio to mercury)
NH_4^+, NO_3^-, CO_3^{2-}, $SO_4^{=2-}$, BrO_3^- PO_4^{3-}, ClO_4^-, ClO_3^-, $B_4O_7^{2-}$, F^- Tartarate, Citrate, Ni(II), Mn(II), Ca(II), Mg(II), Hf(IV), U(VI), Na^+, K^+, Cl^-	2000*
Zr(IV), Br^-, Zn(II), Th(IV), SCN^-,	1000
In(III), Rh(III), La(III), Cd(II), CO(II)	500
$S_2O_3^{2-}$, Ce(III), Pb(II), Fe(III), Ag(I)	100
V(V), I^-, CN^-, Sn(II), Cu(II)	0.5

*: 2000 was the maximum concentration of the ions tested.

In addition, the method was also applied to the determination of mercury in a sample of industrial waste water. The results were compared with a standard method for the determination of mercury [30]. The results for both samples are given in Table 2.

Table 2. Determination of mercury in real samples

Sample	Mercury found by the		
	proposed method (n = 5)	RSD%	standard method (n = 5)
Phenylmercury nitrate* (cleaner solution no. 1)	0.0033%	1.7%	0.0033%
Sodium ethylmercurithio-salicylate** (cleaner sol. no. 2)	0.0040%	1.5%	0.0040%
Chemical industrial waste water	0.010 μg/ml	2.3%	0.011 μg/ml

*: Certifide content 0.0033%
**: Certifide content 0.0040%

Conclusion

The suitability of the Brilliant green-sulfite system for the development of a kinetic method for determining ultra traces of mercury as low as 0.005 $\mu g.ml^{-1}$ has been demonstrated. This method is found to be sensitive, precise, rapid and relatively selective. The procedure was applied to various real samples to evaluate its effectiveness (Table 2).

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