



J. Serb. Chem. Soc. 74 (8–9) 977–984 (2009)
JSCS–3892

Journal of
the Serbian
Chemical Society

JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS

UDC 546.873+543.23+543.4/.5+542.97

Short communication

SHORT COMMUNICATION

Kinetic spectrophotometric determination of Bi(III) based on its catalytic effect on the oxidation of phenylfluorone by hydrogen peroxide

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(Received 1 December 2008, revised 15 April 2009)

Abstract: A new reaction was suggested and a new kinetic method was elaborated for determination of Bi(III) in solution, based on its catalytic effect on the oxidation of phenyl-fluorone (PF) by hydrogen peroxide in ammonia buffer. By application of spectrophotometric technique, a limit of quantification (LQ) of 128 ng cm⁻³ was reached, and the limit of detection (LD) of 37 ng cm⁻³ was obtained, where LQ was defined as the ratio signal:noise = 10:1 and LD was defined as signal 3:1 against the blank. The *RSD* value was found to be in the range 2.8–4.8 % for the investigated concentration range of Bi(III). The influence of some ions upon the reaction rate was tested. The method was confirmed by determining Bi(III) in a stomach ulcer drug (“Bicit HP”, Hemofarm A.D.). The obtained results were compared to those obtained by AAS and good agreement of results was obtained.

Keywords: kinetic method; catalytic reaction; Bi(III) determination.

INTRODUCTION

The most important methods of bismuth determination are kinetic, spectrophotometric and atomic absorption spectroscopy (AAS) methods.^{1–21} An interesting electrothermal atomic absorption spectroscopy (ET AAS) method was published for the determination of bismuth traces in sea water.²² Some photometric, chromatographic (HPLC) and flow-injection analysis (FIA) methods are also reported.^{23–25} There are relatively small number of kinetic methods for Bi(III) determination, compared to a great number of spectrophotometric ones based on its ability to form complexes, mainly colored, with organic and inorganic compounds.

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doi: 10.2298/JSC0909977R

An interesting kinetic method, described by Murty, points out the catalytic effect of Bi(III) in the molybdenum phosphorous acid reduction by ascorbic acid,¹ although a new method, employing the same reaction system, but with better sensitivity, was also reported.² The method was used to determine the traces of Bi(III) in alloys. A method based on the catalytic effect of Bi(III) ions is employed in the oxidation of hematoxylin (HT) by H₂O₂ in a strong acid solution.³ Kinetic catalytic method for bismuth determination in strong acid medium with KIO₄ as the oxidant and dibrom-nitro-arsenazo (DBN-arsenazo) as the reductant was used for bismuth determination in drinking water.⁴ Another kinetic method employed for the determination of Bi(III) in alloys and drinking water⁵ is based on the catalytic effect of bismuth on the oxidation of carboxyazo I by KIO₄. The inhibitory effect of Bi(III) on the fading reaction of crystal violet oxidized by H₂O₂ in the acetate buffer solution was followed by kinetic spectrophotometric method.⁶ Of all reported kinetic methods, only the method reported by Sanz et al. was used to determine bismuth in drugs.⁷

The aim of this communication is to present the results obtained in a new kinetic spectrophotometric determination of Bi(III) using its catalytic effect in the oxidation of phenylfluorone (PF) by hydrogen peroxide in ammonia buffer. The method is employed for the determination of Bi(III) in a stomach ulcer drug.

EXPERIMENTAL

Apparatus

The spectrophotometric measurements were performed on a Perkin-Elmer UV-Vis Lambda 15 spectrophotometer. The cylindrical cells were thermostated at 20±0.1 °C using a thermocirculating bath. The pH measurements were performed using a Radiometer PHM 29 b pH-meter with a combined glass-calomel electrode GK 2311 C.

Reagents

All solutions were prepared by dissolving p.a. quality "Merck" reagents in deionized water (0.4–0.8 μS cm⁻¹) and ammonia buffer. Adequate polyethylene vessels were used for storage of the solutions. Ammonia buffers were prepared by mixing NH₃(aq) and NH₄Cl solutions (0.2 mol dm⁻³)²⁶ and their pH values were checked using pH-meter. A stock Bi(III) solution (1.0×10⁻³ g cm⁻³) was prepared by dissolving 1.00 g of metallic bismuth (99.999 %) in a minimal volume of HNO₃ (1:1) and diluting it to 1 dm³ with 2 % HNO₃ solution. The concentration of the stock solution was checked by EDTA titration.²⁷ The concentrations of H₂O₂ solutions were verified by KMnO₄ titration. The phenylfluorone solution was prepared by dissolving the exactly measured amount of dry substance in ammonia buffer (pH 10.4).

Procedure

Selected volumes of reactants and deionized water were poured separately into four-legged Budarin vessel up to a predetermined total volume of 10 cm³. The solution of Bi(III) was measured into one leg of Budarin vessel for catalytic reaction and the same volume of deionized water was measured for the non-catalytic reaction. After thermostating for 10 min the reagents were mixed and absorbance was measured in 15 s intervals 45 s after beginning of the reaction. Absorbance measurements were performed at 20±0.1 °C.

RESULTS AND DISCUSSION

While the reaction proceeds, the initial red color of solution fades and a colorless reaction product is formed. Neither the exact mechanism of reaction nor the chemical nature of the products was of major interest in this investigation. The spectrophotometric measurements were performed at the wavelength of the absorption maximum of phenyl fluorone in ammonia buffer (493.6 nm, Fig. 1). The logarithm of absorbance-time curves are linear during the first 5–10 min of reaction for different Bi(III) concentrations. The rate of the reaction was obtained using the slope of the kinetic curves of the absorbance–time plot.²⁸

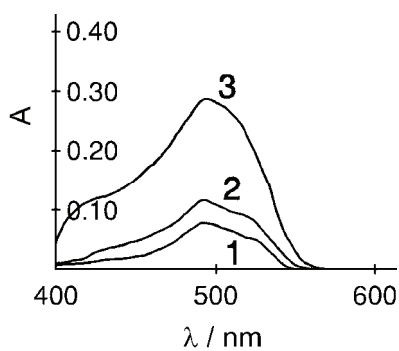


Fig. 1. Absorption spectra of PF in ammonia buffer. Initial conditions: 1.5×10^{-5} mol dm⁻³ PF; 20 ± 0.1 °C; pH: 1) 10.2, 2) 10.6; 3) 11.9.

According to the previous results,²⁹ borate and phosphate buffers are inadequate for this reaction. Hence, the influence of the pH value of selected ammonia buffers on the rate of both the catalytic and non-catalytic reaction was examined in pH interval of about 9 to about 11. Within this range, the non-catalytic reaction showed zero order dependence on the pH value of the ammonia buffer, while the catalytic reaction exhibited a complex dependence (Fig. 2). The value of 10.4 was selected as the most appropriate one, because it provides the largest difference of the reaction rates of the catalytic and non-catalytic reaction.

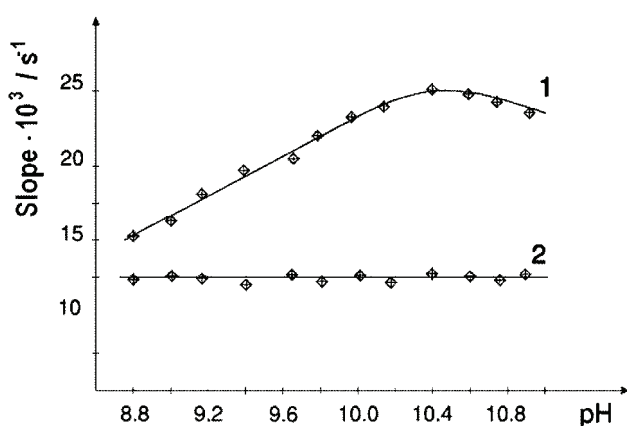


Fig. 2. Dependence of the reaction rate on pH. Initial conditions: 4×10^{-5} mol dm⁻³ PF; 3.9 mol dm⁻³ H₂O₂; 2.5 μg cm⁻³ Bi(III); 20 ± 0.1 °C; 1 – catalytic reaction, 2 – non-catalytic reaction.

Hence, the ammonia buffer pH 10.4 was used in all subsequent investigations.

The rates of both reactions are of the first order dependence on the reductant concentration (Fig. 3) within the range of 1.0×10^{-5} to 4.0×10^{-5} mol dm⁻³. Consequently, a concentration of 3.0×10^{-5} mol dm⁻³ was selected as optimal for the subsequent measurements.

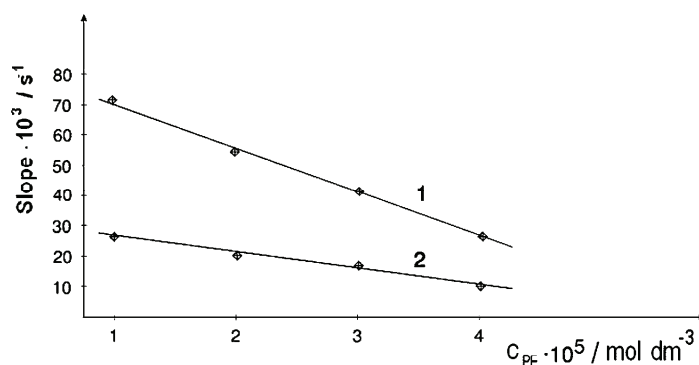


Fig. 3. Dependence of the reaction rate on the PF concentration. Initial conditions: $3.9 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$; $2.5 \mu\text{g cm}^{-3} \text{ Bi(III)}$; $20 \pm 0.1 \text{ }^\circ\text{C}$; 1 – catalytic reaction, 2 – non-catalytic reaction.

Based on the previous investigations,²⁹ the dependence of rate of the catalytic and non-catalytic reaction on the oxidant concentration was monitored within the concentration range of about 2.0 to about $4.0 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$. Within this interval, the catalytic reaction rate increases with oxidant concentration, whereas the non-catalytic one does not depend on oxidant concentration (Fig. 4). As optimal, a concentration of $3.9 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$ was selected, because at this concentration (in the investigated range) the difference between the reaction rates of catalytic and non-catalytic reaction was the greatest.

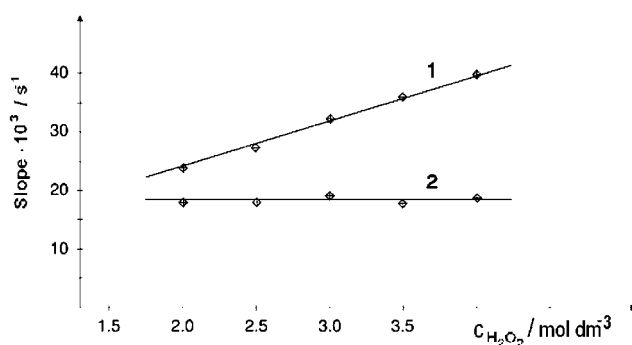


Fig. 4. Dependence of the reaction rate on the H_2O_2 concentration. Initial conditions: $3 \times 10^{-5} \text{ mol dm}^{-3} \text{ PF}$; $2.5 \mu\text{g cm}^{-3} \text{ Bi(III)}$; $20 \pm 0.1 \text{ }^\circ\text{C}$; 1 – catalytic reaction, 2 – non-catalytic reaction.

Hence, the optimal conditions for performing the reaction were found to be: pH 10.4, $c_{PF} = 3.0 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{H_2O_2} = 3.9 \text{ mol dm}^{-3}$.

Under the selected conditions, the dependence of catalytic reaction rate on the Bi(III) concentration was observed at three temperatures: 20 ± 0.1 , 23 ± 0.1 and 25 ± 0.1 °C. The linear dependence of calibration curves falls within the range of 6.0×10^{-7} to $3.0 \times 10^{-6} \text{ g cm}^{-3}$ Bi (III) (Fig. 5).

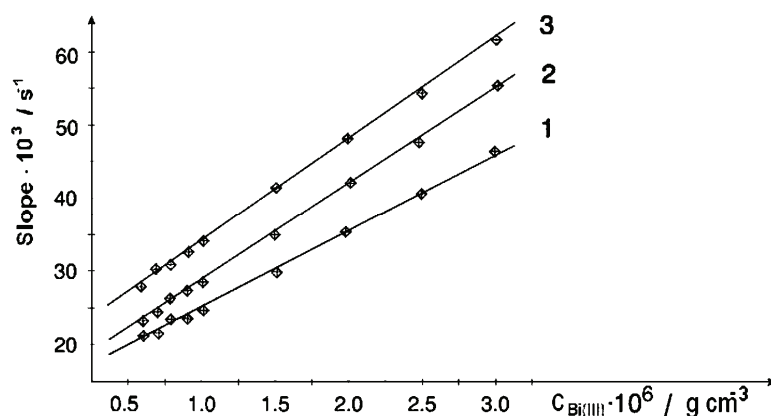


Fig. 5. Calibration curve at different temperatures: 1 – 20 ± 0.1 , 2 – 23 ± 0.1 and 3 – 25 ± 0.1 °C.

The adequate equations of calibration curves for 20 ± 0.1 , 23 ± 0.1 and 25 ± 0.1 °C, were calculated as follows:

$$\text{Slope} = (0.01027 \pm 0.00001)c + (0.01495 \pm 0.00017) \quad (1)$$

$$\text{Slope} = (0.01234 \pm 0.00003)c + (0.01811 \pm 0.00015) \quad (2)$$

$$\text{Slope} = (0.01325 \pm 0.00002)c + (0.02246 \pm 0.00011) \quad (3)$$

where c is the Bi(III) concentration in $\mu\text{g cm}^{-3}$.

The accuracy and precision of the method were checked for three different Bi(III) concentrations within the range of calibration curve. Five repeated measurements were performed for each concentration. Satisfactory results were obtained since the Bi(III) concentrations of 1.0, 2.0 and $3.0 \mu\text{g cm}^{-3}$ gave the RSD values of 4.8, 3.6 and 2.8 %, respectively.

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The selectivity of reaction was established by separately adding the selected ions to the reaction mixture. Each ion was added in six known concentration ratios (0.001:1, 0.01:1, 1:1, 10:1, 100:1 and 1000:1) to the constant Bi(III) concentration ($2.0 \mu\text{g cm}^{-3}$). The measurements were performed at 20 ± 0.1 °C,

and 30 most frequently used cations and anions were tested (Na^+ , K^+ , Ag^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , Ni^{2+} , Co^{2+} , Hg^{2+} , Sn^{2+} , Fe^{3+} , Al^{3+} , As^{3+} , Sb^{3+} , acetate, tartarate, oxalate, molybdate, wolframate, bromide, iodide, chloride, nitrate, sulphate, carbonate, phosphate). The method was found to have extremely good selectivity. Only the presence of As(III), Sb(III), Hg(II), molybdate and wolframate, in the ratio 1:1, interferes the determination of bismuth; Sn(II) in the ratio 1:1 inhibits the determination, and Co(II) in the ratio 0.01:1 catalyzes the determination of Bi(III) by this method.

The method was successfully applied to the determination of Bi(III) in stomach ulcer drug "Bicit HP" (Hemofarm A.D.). This drug contains bismuth in the form of subcitrate. Solutions containing a known quantity of bismuth were prepared by dissolving the drug in deionized water. The solutions were analyzed by application of both the presented kinetic method and the AAS method. The results are given in Table I, from which the good agreement between the results of both methods can be seen.

TABLE I. Bi(III) determination in a drug

| Measured $\mu\text{g cm}^{-3}$ | Kinetic determination ^a $\mu\text{g cm}^{-3}$ | RSD % | Determined by AAS ^a $\mu\text{g cm}^{-3}$ | RSD % |
|-----------------------------------|---|----------|---|----------|
| 1.0 | 1.16±0.18 | 4.6 | 1.05±0.02 | 1.0 |
| 2.0 | 2.08±0.13 | 3.7 | 2.01±0.02 | 0.9 |
| 3.0 | 2.93±0.10 | 2.6 | 3.00±0.02 | 0.6 |

^aThe mean value of five measurements $\pm 2SD$

CONCLUSIONS

A new method for the determination of Bi(III) was developed, providing rapid and easy performance at room temperature, giving precise, reproducible results and exhibiting exceptional selectivity. On the grounds of the obtained results, the method is highly recommendable for the determination of Bi(III) in drug solutions. It could also be a good basis for further investigation in the area of kinetic methods for the determination of bismuth.

ИЗВОД

КИНЕТИЧКО СПЕКТРОФОТОМЕТРИЈСКО ОДРЕЂИВАЊЕ Bi(III) НА ОСНОВУ ЊЕГОВОГ КАТАЛИТИЧКОГ ДЕЈСТВА НА ОКСИДАЦИЈУ ФЕНИЛФЛУОРОНА ВОДОНИК-ПЕРОКСИДОМ

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Предложена је нова реакција и развијена нова кинетичка метода за одређивање Bi(III) у раствору, на основу његовог каталитичког дејства на оксидацију фенилфлуорона (PF) водоник-пероксидом у амонијачном пуферу. Применом спектрофотометријске методе, под

оптimalним условима, постигнута је граница одређивања (LQ) од 128 ng cm⁻³ и остварена граница детекције(LD) од 37 ng cm⁻³. LQ је дефинисана као однос сигнал:шум = 10:1, а LD као сигнал 3:1 према слепој проби. RSD се креће од 2,8 до 4,8 % у испитиваном интервалу концентрација Bi(III). Испитан је и утицај присуства других јона у реакционој смеши на брзину основне реакције. Метода је примењена за одређивање бизмута у леку за чир на желуцу, ("Bicit HP", Хемофарм А.Д.). Добијени резултати показују добро слагање с резултатима добијеним ААС методом која је коришћена као референтна метода.

(Примљено 1. децембра, ревидирано 15. априла 2009)

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