

KINETIC DETERMINATION OF GOLD(III) BASED ON ITS INHIBITORY EFFECT IN OXIDIZING HOMOGENOUS REACTION SYSTEM

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ABSTRACT

Development and application of a simple, fast, green analytical kinetic method for the determination of micro-amounts of gold(III) ions, were presented in this paper. The method was based on the inhibitory effect of traces of Au(III) ions on the redox reaction between disodium-6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonate (artificial azo-dye "Sunset Yellow FCF", E110 in further text selected as SY) and hydrogen-peroxide, in alkaline media of borate buffer. All experimental parameters affecting to the determination: reagent concentrations, pH and temperature were investigated and optimised. Working experimental conditions are set according to the highest sensitivity of the proposed kinetic

method for the determination of Au(III) ions. The linearity of the method was obtained within the range 1.97-59.07 µg/mL of Au(III) ions with relative standard deviation of 3.66- 0.43 %, respectively. The influence by possible interference effects by major ions on the determination of Au(III) and their limits are investigated, at the constant Au(III) concentration of 39.39 µg/mL. The results of Au(III) determination in samples obtained by proposed kinetic method and comparative ICP-OES method were statistically agreeable. Obtained results for Au(III) determination in analyzed samples, as well as the development and validation of the proposed analytical procedure have given and discussed.

Keywords: gold(III), kinetic method, sunset yellow.

1. INTRODUCTION

Chemistry of gold is still the subject of research in scientific articles, not only because of its beauty and rarity and usage in jewelry, coinage and economics. Many properties of a gold(III) and gold-nanoparticles as enzyme inhibitor, vehicles for delivery of cancer drugs, antirheumatics based on its coordination and valence state, in many electron transfer processes ((Chandrakant, et al., 2016), (Narkhede et al., 2016), (Yang et al., 2016), (Pyrzyńska et al., 2006). Modern sophisticated techniques such as inductively coupled plasma mass spectrometry (ICP-MS) (Juvonen et al., 2002), flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETA-AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Bulut et al., 2011), and other spectrophotometric methods involving chromogenic reagents such as morin, quercetin (Balcerzak et al., 2006), Spheron (R) and (biphenyl) dimethanethiol, (Behpour et al., 2005) etc. and electroanalytical techniques (square wave voltammetry-SWV, differential pulse voltammetry-DPV etc.) (Bulut et al., 2011) are the most commonly

used techniques in the determination of gold at low levels. UV-Vis spectrophotometric methods ((Chen et al., 2006), (Kamble et al., 2010)) are remarkable for their simplicity and versatility. Other sensitive techniques such as neutron activation analysis (NAA) (Nat et al., 2004) or total reflection X-ray fluorescence spectrometry (TXRF) (Messerschmidt et al., 2000) are less often applied in gold determination due to the complexity and cost of the required instrumentation.

Despite the large number of modern analytical techniques, kinetic methods still are used in real samples in the context of the study of the mechanism and rate of the chemical reactions. Also kinetic methods are preferred in terms of cost the experiment.

In this study simple and fast kinetic-spectrophotometric method was developed, based on inhibitory effect of gold(III). Experimental conditions were optimized as follow: $C_{SY}=4 \cdot 10^{-5}$ mol/L; $CH_2O_2=0.4$ mol/L; $pH=10.5$; $t=25.0 \pm 0.1$ °C. Measurements were done at the wavelength of absorbance maximum of the indicator substance-

artificial color "Sunset Yellow FCF, at $\lambda_{max} = 478.4$ nm.

2. EXPERIMENTAL

2.1. Apparatus

Spectrophotometric measurements were performed on Perkin-Elmer Lambda 15 UV-Vis spectrophotometer, using cylindrical cell thermostated at $25.0 \pm 0.1^\circ\text{C}$. A Julabo MP-5A model thermostatic bath was used to maintain the reaction temperature at $25.0 \pm 0.1^\circ\text{C}$. A pH meter (Hanna pH-210) with a glass electrode was employed for measuring pH values in the aqueous solution. 01 and pH of 4.00 ± 0.01 , were used. iCAP 6000 ICP-OES, Thermo Scientific, Cambridge, United Kingdom.

2.2. Reagents and Solutions

Analytical grade chemicals and deionized water (MicroMed high purity water system, TKA Wasseraufbereitungssysteme GmbH) were used for the preparation all of solutions. The stock Au(III) solution (1×10^{-3} mol/L) was prepared by dissolving $\text{Au}[\text{HCl}_4]$ (Alfa Aeser, A Jonson Matthey Company) in demineralized water. A working solution (1×10^{-5} mol /L) was obtained by diluting the stock solution with water. A solution of SY (provided by the Pharmaceutical laboratory Zdravlje-Actavis, Leskovac, Serbia), of 1×10^{-3} mol/L, was prepared by measuring 0.0226g of substance of analytical grade, and dissolving with deionized water in a volumetric flask of 50 ml. A solution of H_2O_2 of 2 mol/L was prepared by appropriate dilution of 30% H_2O_2 , (Merck) of reagent in volumetric flask of 50 mL with deionized water. The solution of borate buffer was prepared by appropriate mixing a solution of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (0.05 mol/L) and 0.1 mol/L solution of NaOH. All the glassware used was washed with aqueous solution of HCl (1:1) and then thoroughly rinsed with running, distilled water, and then, finally with deionized water.

2.3. Kinetic-Spectrophotometric procedure

Bouderin flask with a four compartment was used for preparing solution (working volume of 5ml) before the start of reaction; a series of standard solution of Au(III) were placed in the first compartment, 0.2 ml of 1×10^{-3} mol/L solution of SY in the second, 2 ml borate buffer pH of 10.5 in the

third and 1 ml of 2 mol/L H_2O_2 in the fourth compartment. The solution was kept at $25.0 \pm 0.1^\circ\text{C}$ in the thermostated bath, before the mixing and beginning of the reaction. After mixing the reaction mixture was put into the spectrophotometric cell with path-length of 1 cm, and the absorbance at 478.4 nm was measured every 30 s during the first period of 6 min from the beginning of the reaction. The reaction rate was monitored spectrophotometrically. Absorbance measurements have been performed at the wavelength of the absorption maximum of SY at 478.4 nm.

Sample preparation. After the preparation of the sample solution injections containing the Au (III) ions in a concentration of 50 mg/0.5mL, based on the weight of the salt of sodium thio-auro-maleate Na_2SAuO_4 , was transferred quantitatively to the volumetric flasks of 50 mL and diluted with demineralized water to line. The concentration of this solution, calculated with respect to the Au (III) ion was 58 mg/mL. From this solution were made series of four different concentrations of Au (III) which are located in the area of the calibration curve: 58.0, 29.1, 14.5, and 4.8 mg/mL.

3. RESULTS AND DISCUSSION

3.1. Optimization of Reaction Variables

Inhibiting effect of Au(III) ion on the rate of reaction oxidation of *di*-sodium-6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphtalenesulfonic acid (artificial color Sunset Yellow FCF, E110) by hydrogen peroxide in borate buffer was observed during kinetic research of this indicator system (Micic et al. 2009, 2014). In order to determine the lowest possible deterable concentration of Au(III), the reaction conditions (the influence of the pH, SY, hydrogen-peroxide concentrations, buffer volume and temperature) were studied for both, non-inhibited and inhibited reactions. The method of tangents was used and the slope of the linear section absorbance-time curve, $dA/dt = t\alpha$, was used as a measure of the reaction rate. In this study, for all parameters investigated, the rates of non-inhibited (indicator) and inhibited reaction were simultaneously measured.

Keeping all other experimental parameter constant, the influence of the pH in borate buffer on the rate of the reactions in the range of 8.0 – 11.5 were studied, under concentration of gold(III) of 39.4 $\mu\text{g/mL}$. The

influence of pH on the reaction rates were separately measured with the same method by varying the pH. The best results were obtained for the value pH of 10.5 (Fig. 1), and this value was selected for further work. The order for both reactions, are variable in investigated interval regarding to pH. In order to obtain the rate of reactions regarding to C_{H^+} the dependence $-\log \text{tga} / -\log C_{H^+}$ within interval of pH 9.5-10.5 were constructed. Based on the slope of this dependence the order of the reactions were calculated. Its value for non-inhibited reaction is -0.9 and for inhibited is -0.5. (Fig. 3 and 4). The dependence of the reaction rates for both reactions, on the volume of borate buffer was also studied. The optimum difference between the rate of the non-inhibited and inhibited reactions is for volume of 2.0 mL of borate buffer, Fig. 4. The dependence of the reaction rates on the concentration of H_2O_2 were investigated over the range 0.1–0.8 mol/L, Fig. 5. For further work, a concentration of H_2O_2 of 0.4 mol /L was selected as the suitable. The dependence of reaction rates on the concentration of SY was investigated over the range 1.0×10^{-5} – 6×10^{-5} mol/L. The optimum difference between the rates of the non-inhibited and inhibited reactions occurred for concentration of 4.0×10^{-5} mol/L of SY, Fig.6. At higher concentration of SY absorbance significantly increases ($A > 1.0$), when error of spectrophotometric measurement becomes higher (area of Beer's law validity). The influence of temperature on the reaction rate was studied in the range 22°C – 28°C . The rate of reaction as expected increases with temperature. Although higher sensitivity could be obtained at the higher reaction temperature, for practical reasons measurement were done at $25 \pm 0.1^\circ\text{C}$. On the basis of dependence of rates of reactions on the concentration of each reactant, kinetic equations for non-inhibited (1) and inhibited reactions can be derived as follows:

$$-\left(\frac{dC}{dt}\right) = k_0 \cdot C_{H^+}^{-0.9} \cdot C_{SY} \quad (1)$$

$$-\left(\frac{dC}{dt}\right) = k \cdot C_{H^+}^{-0.5} \cdot C_{SY} \cdot C_{Au(III)}^{-1} \quad (2)$$

Where k_0 is constant which is proportional to the constant rate of non-inhibited reaction, and k is constant which is proportional to the constant of inhibited reaction. Based on kinetic equations (1) and (2) rate constants were calculated for non-inhibitory

and inhibitory reactions in the temperature range of 22 – 25°C (295 – 301K), and obtained results are shown in Table 1.

Based on the Arrhenius's equation for non- inhibitory and inhibitory reactions Arrhenius's plot has obtained (Fig.7., 8.) the activation energy (E_a^*) were calculated by following equation, for both process, non-inhibited and inhibited:

$$E_a^* = -R \left[\frac{\partial \ln k}{\partial (1/T)} \right]_p \quad (3)$$

Based on its value and thermodynamics equations for change of Gibbs's energy, enthalpy (H) and entropy (S) can calculated for both processes. Based on this results mechanism of examined redox reactions can be discussed under given experimental conditions- concentration of reaction parameters, at room temperature and atmospheric pressure in examined redox system.

Table 1. Rate constants.

T(K)	$k_0 \cdot 10^8 (\text{mol/l})^{1-n} \text{S}^{-1}$	$k \cdot 10^8 (\text{mol/l})^{1-n} \text{S}^{-1}$
295	3.55	1.41
298	6.65	4.22
301	7.98	13.4

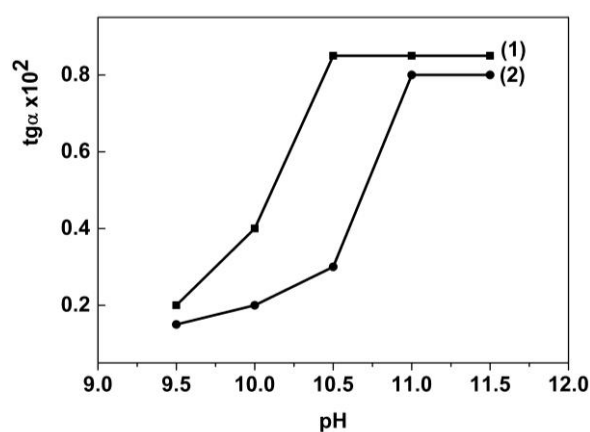


Fig. 1 The influence of pH.

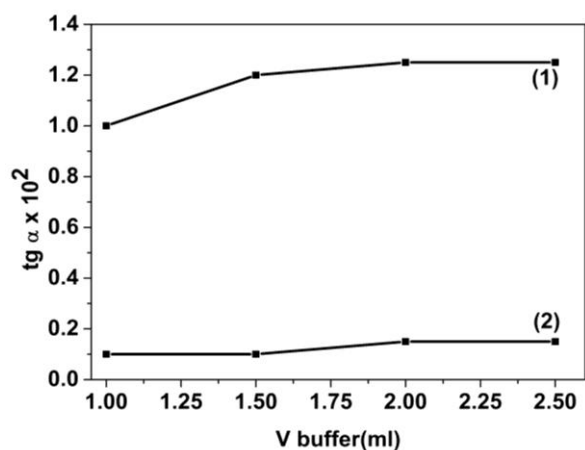


Fig. 2 The influence of borate buffer.

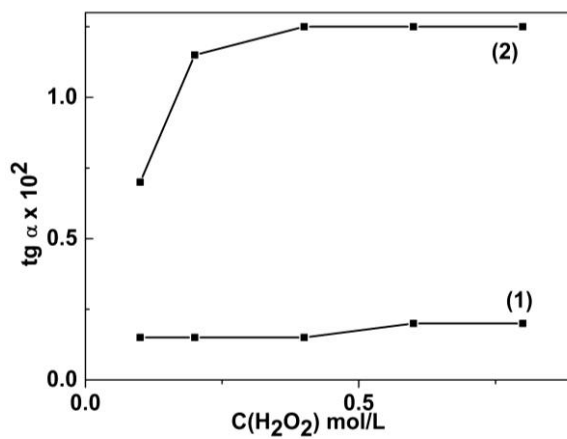


Fig. 5 The influence of H₂O₂.

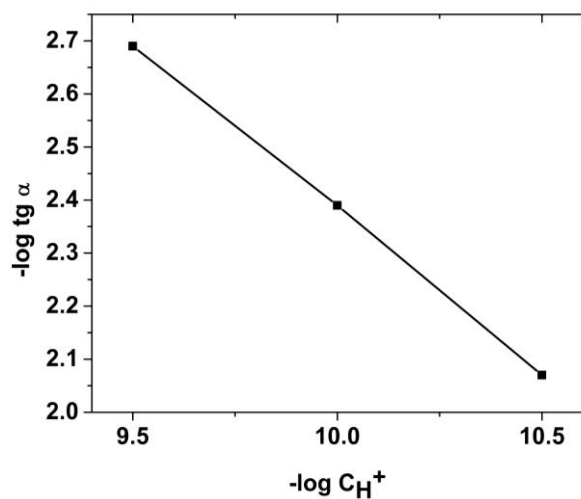


Fig. 3 Dependence $-\log \text{tg } \alpha / -\log C_{\text{H}^+}$ -non-inhibited.

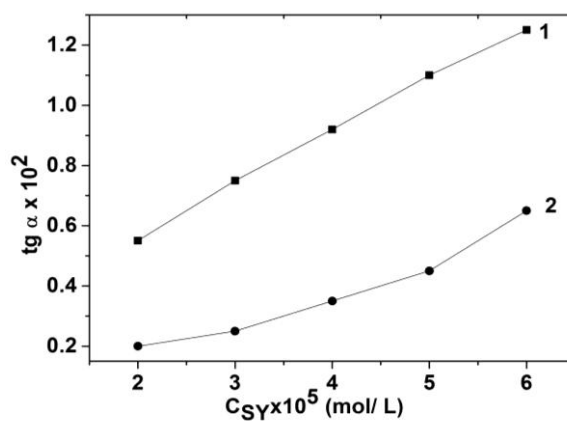


Fig. 6 The influence of SY.

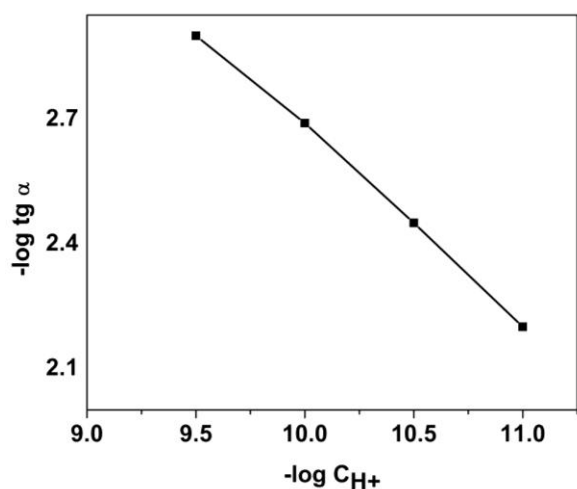


Fig. 4 Dependence $-\log \text{tg } \alpha / -\log C_{\text{H}^+}$ -inhibited.

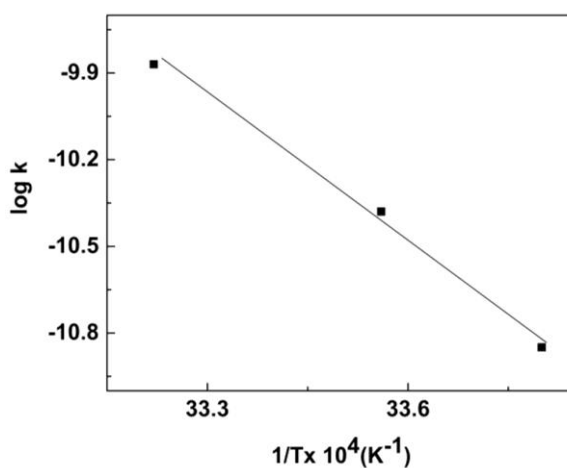


Fig. 7 Arrhenius' plot for inhibited reaction.

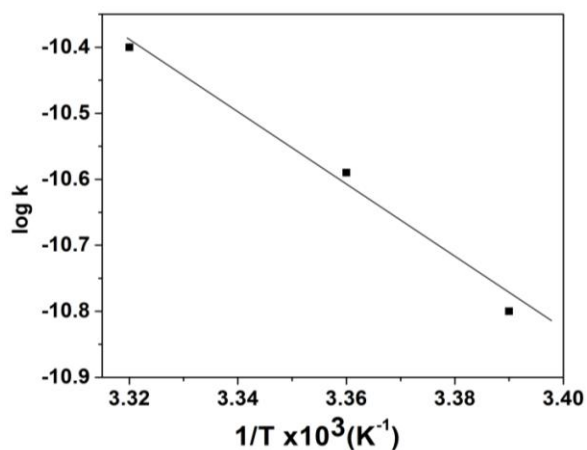


Fig. 8 Arrhenius' plot for non-inhibited reaction.

3.2. Validation of the proposed method

The calibration graph was constructed under the established optimal conditions regarding on sensitivity and reproducibility of the method as follows: $C_{SY}=4 \times 10^{-5} \text{ mol/L}$; $C_{H_2O_2}=0.4 \text{ mol/L}$; $\text{pH}=10.5$; $t=25.0 \pm 0.1^\circ\text{C}$, $\lambda_{max}=478.4 \text{ nm}$. The linearity was obtained within the range 1.97-59.07 $\mu\text{g/mL}$ of Au(III). Obtained analytical and statistical data of the calibration graph at $25.0 \pm 0.1^\circ\text{C}$ were presented in Table 2. In order to assess the precision and accuracy of the proposed kinetic method, measurements were done in five replicate determinations at each of four different Au(III) concentrations. Obtained results are shown in Table 3.

Table 2. Analytical and statistical data.

Analytical and Statistical Data	Temperature $25.0 \pm 0.1^\circ\text{C}$
	Dynamic range 1.97-59.07 ($\mu\text{g/mL}$)
Number of points	9
Limit of detection $\mu\text{g/mL}$	0.12
Limit of quantification $\mu\text{g mL}^{-1}$	0.36
Slope $\times 10^2$	-0.0126
Intercept $\times 10^2$	0.8948
Correlation Coefficient	-0.9997
Standard error of the slope	1.217×10^{-4}
Standard error of the intercept $\times 10^2$	0.00382
Standard deviation of the Fit $\times 10^2$	0.00382
Analytical frequency, h^{-1}	10

The robustness of proposed method is a measure of its capacity to remain unaffected by small, but deliberate variations in the method parameters and provides an indication of its reliability during usage. The most significant variables of the system (temperature and concentration of SY, hydrogen peroxide) were modified in range $\pm 10\%$ (excluding pH, which was modified in range $\pm 5\%$) from their optimum values. Errors lower than 5% were observed in all cases.

Table 3. Accuracy and precision of the method.

Added ($\mu\text{g mL}^{-1}$)	Found ^a ($\mu\text{g mL}^{-1}$)	RSD ^b (%)	$(\bar{x}-\mu)/\mu \cdot 100^c$
1.9	1.9 ± 0.07	3.7	-3.1
19.7	19.9 ± 0.6	3.2	+1.1
39.4	38.8 ± 0.4	1.0	-1.5
59.1	58.8 ± 0.2	0.4	-0.4

^amean value \pm standard deviation (n=5) ^brelative standard deviation; ^c – accuracy.

To assess the selectivity of the method, the influence of major foreign ions on the inhibited reaction rate was studied, under the reaction conditions mentioned above, at a constant Au(III) concentration of $C_{Au(III)}=39.39 \mu\text{g/mL}$. The results are summarized in Table 4.

Table 4. Selectivity of the proposed method.

Ratio $C_{\text{other ion}}/C_{Au(III)}$	Other ions
100	$\text{Na}^+, \text{K}^+, \text{Cl}^-$
10	$\text{F}^-, \text{Li}^+, \text{Zn}^{2+}, \text{Al}^{3+}, \text{Mg}^{2+}, \text{V}^{5+}, \text{As}^{3+}, \text{As}^{5+}, \text{SO}_3^{2-}, \text{NH}_4^+, \text{CH}_3\text{COOH}, \text{Sn}^{2+}, \text{Sr}^{2+}, \text{I}^-, \text{CO}_3^{2-}$
1	$\text{Mo}^{6+}, \text{Cr}^{6+}, \text{Ba}^{2+}, \text{Cd}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Al}^{3+}, \text{Ca}^{+2}, \text{NO}_3^-, \text{SO}_4^{2-}, \text{C}_2\text{O}_4^{2-}$
0.1	$\text{Fe}^{3+}, \text{Co}^{2+}, \text{Hg}^{2+}$

3.3 Application of the proposed method

In order to evaluate of proposed procedure this kinetic method was applied to the determination of Au(III) ions in pharmacological samples, ampoules Tauredon® with Au(III) ions concentration of 50 mg/0.5 mL, (Na_2SAuO_4). Obtained results are given in

Table 5. As can see results obtained by proposed kinetic and comparable ICP-OES method are in good agreement.

Table 5. Application in ampules *Tauredon*®.

Added (µg/mL) <i>Tauredon</i> ®	Found ^a (µg/mL)	RSD ^b (%)	ICP-OES Found ^a (µg/mL)	F-test
4.8	4.8±0.2	3.1	4.8±0.2	1.0
14.5	14.4±0.5	3.6	14.5±0.4	1.6
29.1	28.8±0.6	2.2	29.0±0.3	0.4
58.1	57.2±0.8	1.3	59.1±0.3	0.7

4. CONCLUSION

In this work fast, simple cost-effective, green analytical kinetic method for gold(III) determination was given. Application of the method was demonstrated in pharmacological ampoules *Tauredon*®. Method has good analytical performance and could be useful for trace determination of Au(III) ions in different kind of real samples. Thus, the proposed method was found to be robust for routine determination of Au(III) in different real samples.

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