

## A SENSITIVE KINETIC SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF TUNGSTEN IN SOLUTION BASED ON ITS INHIBITORY EFFECT ON THE DECOLORIZATION REACTION OF POTASSIUM PERMANGANATE

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### ABSTRACT

The present work describes a rapid and sensitive method for the determination of ultramicro amounts of tungsten (VI) based on its inhibitory effect on the oxidation of 4-hidroxicoumarine by potassium permanganate in the presence of hydrochloric acid. The sensitivity of the method is 20 ng/cm<sup>3</sup>. The probable relative error is -4.8-13 % for the W(VI) concentration range 250 to 20 ng/cm<sup>3</sup>, respectively. Kinetic equations for the investigated process which

determine the order of the reactions regarding to each reaction parameter under certain experimental conditions were proposed, and they allowed quantification of the unknown concentrations W(VI) in solution. The detection and quantification limit of the method are 4.5 and 15.1 ng/cm<sup>3</sup>. The effects of certain foreign ions upon the reaction rate were determined for the assessing the selectivity of the method.

**Key words:** Kinetic method, spectrophotometric determination, inhibition, tungsten(VI), 4-hidroxicoumarine.

### 1. INTRODUCTION

Tungsten is a metal which occurs naturally in the lithosphere, usually in small concentrations and it is also found in oceans and sometimes in other groundwaters in trace amounts (Koutsospyros et al., 2006). This metal is biologically active and it can be found in a number of tungsten-containing enzymes (W-enzymes) (L'vov et al., 2002).

Tungsten usually can be found in the most stable oxidation state VI, but it also occurs in the oxidation states III, IV and V. It has the highest melting/boiling points among elements, a tensile strength at high temperature, resistance to corrosion and a high density and hardness. Because of these unique properties, tungsten has various applications in industry. It is used as a filament in incandescent lamps, as steels in magnetos, springs, contact points, spark plugs, and valves and for other products. (Koutsospyros et al., 2006).

In the past, tungsten was considered as less toxic element due to its insolubility and insufficient knowledge about environmental or toxicological effects (Koutsospyros et al., 2006), (Tajima, 2003). Recently, it has been reported that dissolution of metallic tungsten particles may cause adverse environmental effects such as soil acidification as well as direct and indirect toxic effects in plants, and other

living organisms (Strigul a, 2010). Based on these studies, the environmental regulations of tungsten as a “nontoxic” and “environmentally inert” definitely need re-evaluation (Strigul a, 2010), (Strigul b et al., 2010).

It is very difficult to determine tungsten besides the other transition metals, especially in trace levels using chemical methods. It has been determined by different techniques (mostly by spectrophotometric methods (Rohilla et al., 2013), (Masti et al., 2002), ICP-MS (JIS G 1220, 1994), (JIS G 1258, 2000), (Strekopytov et al., 1997) and electrochemical methods (Alvarado-Gómez et al., 2015), (Tanaka et al., 2001), (Zarei et al., 2010).

The kinetic spectrophotometric methods are known as sensitive methods for element quantification (Muller et al., 1980). By studying red-ox reactions of permanganate with organic compounds (Petković et al., 2007), (Micić et al., 2006), it is noticed that tungsten has performed inhibitory effect on the oxidation of 4-hidroxicoumarine by KMnO<sub>4</sub> in the presence of hydrochloride acid (pH 1.2-2). The reaction was recorded spectrophotometrically, based on measuring the decrease in the absorbance of the solution. The aim of this work was to investigate the possibility of sensitive and selective tungsten determination by measuring the rate of change in

absorbance of reaction system (4-hydroxycoumarine by  $\text{KMnO}_4$  in the presence of hydrochloride acid and  $\text{W(VI)}$ ) with time at 525 nm.

## 2. EXPERIMENTAL

### 2.1. Apparatus

The investigated reaction rate was folowed by spectrophotometric method at Perkin-Elmer Lambda 15 spectrophotometer, with thermostated cylindrical cells, length 10 cm. All pH values were measured by the radiometer PHM 29Bb pH-meter and a combined glass-calomel electrode, GK2311C. Before the beginning of the reaction, all solutions were thermostated in water-bath. The optimal wavelength of 525 nm, as a higher absorbance maximum of  $\text{KMnO}_4$ , was applied for kinetic measurements.

### 2.2. Reagents

The  $\text{KMnO}_4$  solution ( $0.02 \text{ mol/dm}^3$ ) was prepared from an ampoule produced by „Merck“. The 4-hydroxycoumarine  $1 \cdot 10^{-3} \text{ mol/dm}^3$  solution was made by direct weighing of the solid substance. The HCl solution ( $0.2 \text{ mol/dm}^3$ ) was prepared from 37% concentrated HCl solution. The basic  $\text{W(VI)}$  solution  $1000 \text{ ng/cm}^3$  was prepared by dissolving 1.7942 g  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (analytical grade) in deionized water with conductivity less than  $0.5 \mu\text{S}$ . The exact concentration was determined volumetrically. Analytical grade reagents, deionized water and polyethylene vessels were used throughout.

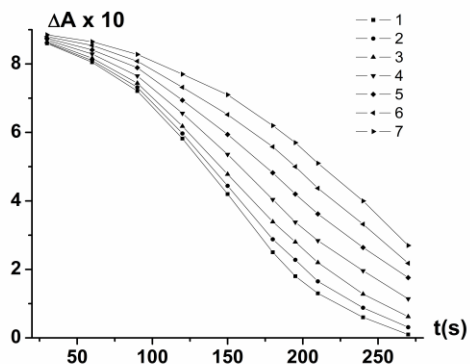
### 2.3. Procedure

Inhibited reaction was followed spectrophotometrically by monitoring the change in absorbance at 525 nm. The initial concentrations of each of the reactants were varied in turn systematically (Muller et al., 1980), (Alekseev, 1973), while the initial concentrations of the other reactants were being kept constant. The same procedure as in previous works (Petković et al., 2007), (Micić et al., 2006) was used in experiments. The selected volumes of the reactants were put into a  $20 \text{ cm}^3$  standard flask, in order: 4-hydroxycoumarine, HCl, inhibitor and water to make up the exact predetermined volume. The flask was kept in the thermostat for 10 min, and then the solution was filled up with  $\text{KMnO}_4$  to the mark and vigorously shaken. The cell of the photometer was rinsed well and filled with the solution. The

absorbance was measured every 15 s, for 3–6 min the time has been measured at the moment of  $\text{KMnO}_4$  addition. The initial concentrations of the reagent solutions after dilution to  $20 \text{ cm}^3$  were:  $1 \cdot 10^{-5} - 4 \cdot 10^{-5} \text{ mol/dm}^3$  4-hydroxycoumarine,  $1.5 \cdot 10^{-5} - 4.5 \cdot 10^{-5} \text{ mol/dm}^3$   $\text{KMnO}_4$ ,  $1.0 \cdot 10^{-2} - 5.62 \cdot 10^{-2} \text{ mol/dm}^3$   $\text{H}_3\text{O}^+$  ions;  $10 - 250 \text{ ng/cm}^3$   $\text{W(VI)}$ .

## 3. RESULTS AND DISCUSSION

The determination of ultramicro amounts of tungsten(VI) is based on its inhibitory effect on the oxidation of 4-hydroxycoumarine by  $\text{KMnO}_4$  in the presence of hydrochloric acid in strong acidic solution - pH less then 2. It is interesting that above the value of  $\text{pH}=2$ ,  $\text{W(VI)}$  influences catalytically on the same reaction. Catalitic effect of  $\text{W(VI)}$  on mention reaction can used for determination of  $\text{W(VI)}$  in acetate buffer, but selectivity of the method is much lower than in proposed method with inhibitory effect. On the basis of the results obtained by investigation of the indicatory reaction kinetics for the determination of  $\text{W(VI)}$  nanogram amounts, the kinetic method was elaborated for  $\text{W(VI)}$  trace determination within the range from 20 to  $250 \text{ ng/cm}^3$   $\text{W(VI)}$ .



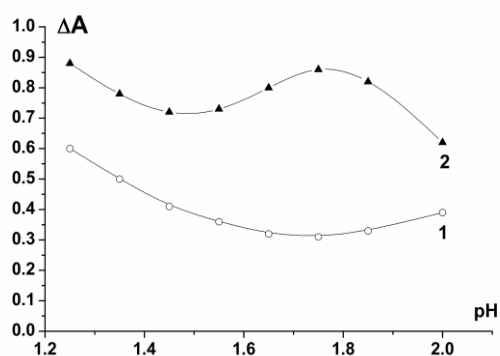
**Fig.1.** Change of absorbance ( $\Delta A$ ) for different concentrations  $\text{W(VI)}$  ( $\text{ng/cm}^3$ ),  $T = 298 \text{ K}$ ,  $l = 10 \text{ cm}$ ; **1**-0.0; **2**-20; **3**-50; **4**-100; **5**-150; **6**-200; **7**-250;  $C_{\text{KMnO}_4} = 3.6 \cdot 10^{-5}$ ;  $C_{4\text{-OHcoum}} = 2.75 \cdot 10^{-5} \text{ mol/dm}^3$

Based on the shape of the curves obtained by mesuring absorbance for different concentrations of  $\text{W(VI)}$  depending of time (Fig. 1), the differential time method for processing the kinetic data was selected (Muller et al., 1980). The maximum difference between non-catalytic and catalytic reactions occurred at 195 s and this time is selected as optimal and fixed in further experiments.

### 3.1. Effect of pH

The effect of pH on non-inhibited and inhibited reaction rates is shown in Fig. 2. It appears that there is a complex relationship between pH and the reaction rate, i.e. a reaction order is variable with respect to hydrogen-ion concentration for the range of studied concentrations. For further work, pH = 1.74 was selected for quantitative applications.

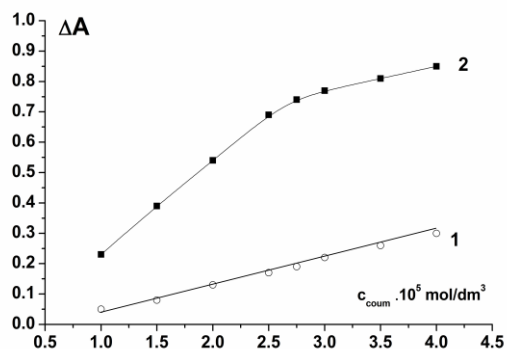
It is important to notice that W(VI) could be separated from Mo(VI) (which also shows inhibiting effect on permanganate reaction with coumarine), by monitoring the change in absorbance at 525 nm on pH lower than 1.2.



**Fig. 2.** Dependence of the reaction rate on pH. Initial conditions:  $3.6 \cdot 10^{-5}$  mol/dm<sup>3</sup> KMnO<sub>4</sub>;  $2.75 \cdot 10^{-5}$  mol/dm<sup>3</sup> 4-hydroxycoumarine; 200 ng/cm<sup>3</sup> W(VI); temperature  $25 \pm 0.1$  °C; 1-inhibited reaction; 2-non-inhibited reaction.

### 3.2. Effect of 4-hydroxyl coumarine concentration

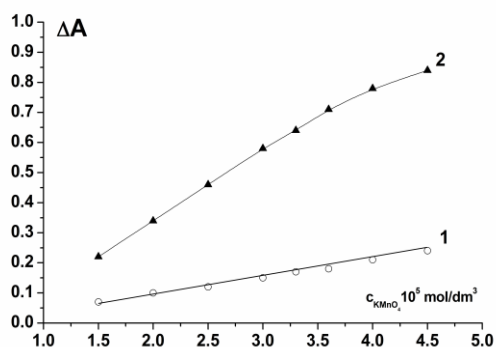
The dependence of  $\Delta A$  on the 4-hydroxycoumarine concentration is shown in Fig. 3. The maximum difference between the rates of inhibited and non-inhibited reactions has been observed for 4-hydroxycoumarine concentration of  $2.75 \cdot 10^{-5}$  mol/dm<sup>3</sup>. The inhibited reaction is the first-order in the full range of examined concentrations, while the basic non-inhibited reaction is the first-order for the concentrations of 4-hydroxycoumarine less than  $2.75 \cdot 10^{-5}$  mol/dm<sup>3</sup>.



**Fig. 3.** Dependence of the reaction rate on 4-hydroxycoumarine concentration. Initial conditions:  $3.6 \cdot 10^{-5}$  mol/dm<sup>3</sup> KMnO<sub>4</sub>; pH = 1.74; 200 ng/cm<sup>3</sup> W(VI); temperature  $25 \pm 0.1$  °C; 1-inhibited reaction; 2-non-inhibited reaction

### 3.3. Effect of potassium permanganate concentration

The dependence of the reaction rates on the concentration of KMnO<sub>4</sub> is shown in Fig. 4.

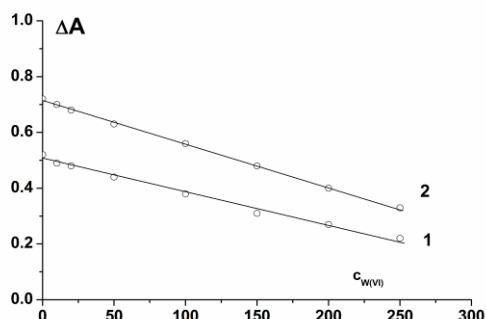


**Fig. 4.** Dependence of the reaction rate on KMnO<sub>4</sub> concentration. Initial conditions:  $2.75 \cdot 10^{-5}$  mol/dm<sup>3</sup> 4-hydroxycoumarine; pH = 1.74; 200 ng/cm<sup>3</sup> W(VI); temperature  $25 \pm 0.1$  °C; 1-inhibited reaction; 2-non-inhibited reaction.

It is obviously from Fig. 3 that the inhibited reaction is the first-order in the all range of presented concentrations, while the basic non-inhibited reaction is the first-order for the concentrations less than  $3.6 \cdot 10^{-5}$  mol/dm<sup>3</sup>.

### 3.4. Effect of tungsten (VI) concentration

Under optimal conditions  $3.6 \cdot 10^{-5}$  mol/dm<sup>3</sup> KMnO<sub>4</sub>;  $2.75 \cdot 10^{-5}$  mol/dm<sup>3</sup> 4-hydroxycoumarine pH = 1.74, the tungsten (VI) concentration has been varied from 10 to 250 ng/cm<sup>3</sup>. Fig. 5 shows the calibration line which can be used for determination of W(VI) in the interval of concentration mentioned above at temperatures  $20 \pm 0.1$  °C (1) and  $25 \pm 0.1$  °C (2).



**Fig. 5.** Dependence of the reaction rate on W(VI) concentration. Initial conditions:  $3.6 \cdot 10^{-5}$  mol/dm<sup>3</sup> KMnO<sub>4</sub>;  $2.75 \cdot 10^{-5}$  mol/dm<sup>3</sup> 4-hydroxycoumarine; pH = 1.74; 1-temperature  $20 \pm 0.1$  °C; 2-temperature  $25 \pm 0.1$  °C.

Based on calibration line (2), at 25°C, the unknown concentration of W(VI) can be determined by following equation:

$$c_{W(VI)} = \frac{0.72 - \Delta A}{0.00152} (=) \text{ng/cm}^3 \quad (1)$$

where  $\Delta A$  is the change of absorbance for indicator substance (KMnO<sub>4</sub>) after 195 s from the beginning of the reaction.

The limits of detection (LOD) and quantitation (LOQ) were found to be 4.5 and 15.1 ng/cm<sup>3</sup> and they are evaluated using the following equations:

$$\text{LOD} = 3.3 S / b \quad (2)$$

$$\text{LOQ} = 10 S / b \quad (3)$$

where  $S$  is the residual standard deviation of the calibration line and  $b$  is the slope of the calibration line.

The relationship between the reaction rates and the concentrations of the reacting components can be explained by the following kinetic equations (at constant pH):

For the inhibited reaction ( $C_{\text{coum}} \leq 4 \cdot 10^{-5}$  mol/dm<sup>3</sup>;  $C_{\text{MnO}_4^-} \leq 4.5 \cdot 10^{-5}$  mol/dm<sup>3</sup> and  $20 \leq C_{\text{W(VI)}} \leq 250$  g/cm<sup>3</sup>):

$$-\left(\frac{dc}{dt}\right) = k \cdot c_{\text{coum}} \cdot c_{\text{MnO}_4^-} \cdot c_{\text{W(VI)}}^{-1} \quad (4)$$

where  $k$  is the constant which is proportional to the constant rate of inhibited reaction.

For the non-inhibited reaction ( $C_{\text{coum}} \leq 2.75 \cdot 10^{-5}$  mol/dm<sup>3</sup>;  $C_{\text{MnO}_4^-} \leq 3.6 \cdot 10^{-5}$  mol/dm<sup>3</sup>):

$$-\left(\frac{dc}{dt}\right) = k_0 \cdot c_{\text{coum}} \cdot c_{\text{MnO}_4^-} \quad (5)$$

where  $k_0$  is the constant which is proportional to the constant rate of non-inhibited reaction.

Accuracy and precision are presented in Table 1. The probable relative error ranges from 13 to - 4.8 % for W(VI) concentration from 20 to 250 ng/cm<sup>3</sup>

Table 1. Accuracy and precision of tungsten W(VI) determination

Taken ( $\mu$ ) (ng/cm <sup>3</sup> )	Found ( $\bar{x}$ ) (ng/cm <sup>3</sup> )	$n$	$\frac{100 \cdot t \cdot S}{\bar{x} \sqrt{n}}$ (%)	$\frac{\bar{x} - \mu}{\mu} \cdot 100$ (%)
20	23	5	9.61	13.0
50	54	5	4.64	8.0
100	104	5	3.12	4.0
250	238	5	2.80	-4.8

$\bar{x}$  – mean value ;  $\mu$  – true value;  $S$ – standard deviation;

$t$  – Student's test for 95% confidence;

$\frac{100 \cdot t \cdot S}{\bar{x} \sqrt{n}}$  – precision;  $\frac{\bar{x} - \mu}{\mu} \cdot 100$  – accuracy.

### 3.5. Interference study

To access the selectivity of the method, influences of some foreign ions on the inhibited reaction rates were studied, at the constant W(VI) concentration of 200 ng/cm<sup>3</sup>. The method has relative good selectivity . The results are presented in Table 2.

Table 2. Influence of interfering ions for determination of W(VI) by proposed method \* W(VI) concentration of 200 ng/cm<sup>3</sup>.

Tolerance limit Foreign ion/W(VI)*	Ion added	Comment
10 <sup>4</sup>	Cl <sup>-</sup> , Na <sup>+</sup> , K <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Mg <sup>2+</sup> , Sr <sup>2+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup>	does not interfere
400	Hg <sup>2+</sup> , Cd <sup>2+</sup> , Sn <sup>2+</sup> , Pb <sup>2+</sup> , Ni <sup>2+</sup>	does not interfere
200	Al <sup>3+</sup> , Co <sup>2+</sup> , Cu <sup>2+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup> , Pd <sup>2+</sup> , Pt <sup>4+</sup>	does not interfere
100	Zn <sup>2+</sup> , Zr <sup>4+</sup> , Ti <sup>3+</sup> , AsO <sub>4</sub> <sup>3-</sup> , Sb <sup>3+</sup> , Bi <sup>3+</sup> ,	practically does not interfere
50	PO <sub>4</sub> <sup>3-</sup> , SCN <sup>-</sup> , C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> and citrate	have a slightly inhibiting effect
40	Ag <sup>+</sup>	have a slightly catalytic effect
10	VO <sup>2+</sup>	inhibit the reaction
5	MoO <sub>4</sub> <sup>2-</sup>	inhibit the reaction
1	Mn <sup>2+</sup> , Au <sup>3+</sup>	catalyze the reaction

#### 4. CONCLUSION

This work describes kinetic method for the determination of trace amounts of tungsten (VI), which is based on the inhibitory effect on the oxidation of 4-hydroxycoumarine by KMnO<sub>4</sub> at pH=1.74. The optimal conditions for this kinetic spectrophotometric method are found and equation which allowed determination of unknown concentration of tungsten by measuring the absorbance after 195 s from the beginning of the reaction, at 525 nm, is evaluated. The interference study suggests a relative good selectivity, indicating possibility of successful determination in complex matrix of a real sample. Statistic calculations based on obtained results for five times repeated determinations under the same conditions show good accuracy and precision.

#### REFERENCES

Alekseev, V.N. 1973. Kurs kachestvenogo polumikro analiza. Moscow: Khimya.  
 Alvarado-Gómez, A.L., Alonso-Lomillo, M.A., Domínguez-Renedo, O., & Arcos-Martínez, M.J. 2015. A chronoamperometric screen printed carbon biosensor based on alkaline phosphatase inhibition for W(IV) determination in water, using 2-phospho-L-ascorbic acid trisodium salt as a substrate. *Sensors (Basel)*, 15(2), pp. 2232-43. pmid:25621602.

-JIS G 1220. 1994. Iron and steel: Methods for determination of tungsten content. Tokyo: Japanese Industrial Standards Committee.  
 -JIS G 1258. 2000. Iron and steel: Methods for inductively coupled plasma atomic emission spectrometry (Amendment 1). Tokyo: Japanese Industrial Standards Committee.  
 Koutsospyros, A., Braidia, W., Christodoulatos, C., Dermatas, D., & Strigul, N. 2006. A review of tungsten: From environmental obscurity to scrutiny. *J. Hazard. Mater.*, 136, pp. 1-19.  
 L'vov, N.P., Nosikov, A.N., & Antipov, A.N. 2002. Tungsten-containing enzymes. *Biochemistry Mosc.*, 67(2), pp. 196-200. pmid:11952415. doi:10.1023/A:1014461913945  
 Masti, S.P., Seetharamappa, J., & Melwanki, M.B. 2002. Extractive Spectrophotometric Determination of Tungsten(VI) in Alloy Steels Using Ethopropazine Hydrochloride. *Analytical Sciences*, 18(8), pp. 913-915. doi:10.2116/analsci.18.913  
 Micić, R.J., Simonović, R.M., & Petković, B.B. 2006. Kinetic Spectrophotometric Determination of Traces of Manganese(II) by Its Catalytic Effect on Oxidation of 4-Hydroxycoumarine with Potassium Permanganate in River Water Samples. *Analytical Letters*, 39, pp. 425-433.  
 Muller, H., Oto, M., & Werner, G. 1980. Katalytische Methoden in der Spurenanalyse. Leipzig: Akademische Verlagsgesellschaft Geest und Portig K. G..  
 Petković, B.B., Simonović, R.M., & Micić, R.J. 2007. Determination of Ultramicroquantities of Au(III) by Its Catalytic Effect on 4-Hydroxyl Coumarone

- Oxidation with Potassium Permanganate. *J. Anal. Chem.*, 62, pp. 697-700.
- Rohilla, J., Baweja, R.K., & Kumar, S. 2013. Spectrophotometric determination of tungsten (VI) after extraction of its 6-chloro-3-hydroxy-2-phenyl-4-oxo-4H-1-benzopyran complex into chloroform. *Arch. Appl. Sci. Res.*, 5, pp. 81-89.
- Strekopytov, S.V., & Dubinin, A.V. 1997. Determination of Zr, Hf, Mo, W and Th in standard reference samples of ocean sediments by inductively coupled plasma mass spectrometry. *J. Anal. Chem.*, 52, pp. 1171-1174.
- Strigul, N. 2010. Does speciation matter for tungsten ecotoxicology. *Ecotoxicol. Environ. Saf.*, 73, pp. 1099-1113.
- Strigul, N., Koutsospyros, A., & Christodoulatos, C. 2010. Tungsten speciation and toxicity: Acute toxicity of mono- and poly-tungstates to fish. *Ecotoxicol. Environ. Saf.*, 73, pp. 164-171.
- Tajima, Y. 2003. 'The effects of tungstophosphate and tungstosilicate on various stress promoters transformation', *Escherichia Coli. J. Inorg. Biochem.*, 94, pp. 155-160.
- Tanaka, T., Sakairi, Y., & Ishiyama, T. 2001. Determination of Tungsten in Iron and Steel by Adsorptive Stripping Voltammetry. *Anal. Sci.*, 17, pp. 949-952.
- Zarei, K., Atabati, M., & Shoari, R. 2010. Catalytic adsorptive stripping voltammetry determination of ultratrace amount of tungsten using factorial design for optimization. *J. Anal. Chem.*, 65, pp. 518-524.

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