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**ANALYTICAL APPLICATION OF THE REACTION SYSTEM PHENYL FLUORONE-HYDROGEN PEROXIDE FOR THE KINETIC DETERMINATION OF COBALT AND TIN TRACES BY SPECTROPHOTOMETRY IN AMMONIA BUFFER MEDIA**

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## **Abstract**

The present paper describes two new, simple, rapid, selective and sensitive kinetic spectrophotometric methods for Co(II) and Sn(II) determination in solution at room temperature, based on their effect on phenyl fluorone (PF) oxidation by hydrogen peroxide in ammonia buffer. The new method was elaborated for nano amounts of Co(II) determination, based on its catalytic effect on the oxidation of PF by H<sub>2</sub>O<sub>2</sub> in the presence of citric acid (CA) as an activator. Also, the new method for micro amounts of Sn(II) determination was developed based on its inhibitory effect upon the same reaction. Comparison of the results showed that the activated catalytic reaction has better sensitivity than the inhibitory one. Methods were validated by the analyze of chemical substances and results were improved by examining the same samples by AAS method.

PAPER ACCEPTED

## Introduction

The significant reactivity of Co(II) ion in the comparison with Sn(II), and also its ability to form complexes with numerous compounds, caused a development of far more methods for cobalt determination. Although there are published AAS, ASV, ET-LEAFS, FI-PDA, CPE, polarographic, etc. methods, there is no doubt that kinetic and spectrophotometric methods have significant part in cobalt determinations.

Kinetic methods, published in last century, determined Co(II) as the catalyst of various reactions of oxidation with hydrogen peroxide or  $\text{KIO}_4$  as oxidant and different substances like TADAB, FPKH, SPADNS, SPTSQ, SPAQ, cianex, etc., as reductant. Recently, two methods were published: in 2006., the method for Co(II) determination in a reaction of oxidation of red artificial color Ponceau 4R with hydrogen peroxide [1], and the method for Co(II) determination as a catalyst of the reaction of oxidation of Sunset Yellow, by the same oxidant, in 2009. [2]. Also, some kinetic as well as spectrophotometric methods were published for simultaneous determination of cobalt, nickel, copper, zinc and iron in natural waters and laboratory mixtures, without prior separation [3-11]. Karayannis and Pettas suggested a simultaneous kinetic determination of cobalt, nickel and iron in mixtures by coupling stopped-flow techniques and charge coupled device detection [12]. Fernandez *et al.* [13], describe kinetic determination of Co, Cu, Zn and Ni at trace levels by first and second order multivariate calibration. There are interesting kinetic methods for Co(II) determination in the air, natural waters, pharmaceutical products, tea and hair [14-20]. Kinetic methods are also developed for cobalt determination in alloys, oils and ashes [21-24], coal, tobacco, etc. Kamble *et al.* developed a reliable analytical method for synergistic extractive spectrophotometric detection of Co(II) from alloys and nano composite samples [25]. The spectrophotometric method was published for simultaneous

detection of trace amounts of Co, Ni and Cu, after the preconcentration of their 2-aminocyclopentene-1-dithiocarboxylate complexes on microcrystalline naphthalene [26].

Today, tin and organic tin compounds have been increasingly used in a variety of agricultural and industrial applications, as well as ship coats, and have become a serious environmental threat. Aquatic organisms in sea and river waters can effectively accumulate TBT and TPT: fishes, shells, plants and algae and also in marine and river sediments and sludges. Tin is the component of many alloys and it is the material for can production and it can affect the environment by industrial wastewaters. Some biological investigations showed that Sn(II) and Sn(IV) chlorides inhibit growth and chlorophyll content of *Cyanobacterium* cultures under alkaline conditions [27]. Tin content in canned foods, according to the WHO, is not supposed to exceed the concentration of 250 µg/g. In fact, sometimes even the tin concentration of 200 µg/g could cause serious gastrointestinal effects in human organism. Sn(II) forms complexes with compounds like ferrioxalate, rhodamine 6G, catechol, tropolone, chloranilic acid, and propyl gallate, 8-hydroxyquinoline, and bromopyrogallol red, etc. and also spectrophotometric methods were published for tin determination in different samples. Spectrophotometric method for tin determination in canned food was elaborated in 1997. [28], and fluorimetric methods in 1985. [29], and 2006. [30]. Tin was determined in powdered coffee and milk [31], fruit juices [32], biological materials (kidney, liver, heart, muscles) [33], human hair [34], sea water [35], marine sediments [36], river sediments, soils and sludges [37], fly ashes, industrial effluents and alloys [38], etc.

Sn(II) can perform both as the inhibitor of the reactions of oxidation and the catalyst of the reactions of reduction in aqueous medium, but there are only a few kinetic methods published recently for tin determination. The kinetic spectrophotometric method was published for simultaneous determination of Sn(II) and Sn(IV) in water and fruit juices samples without prior

separation steps [39]. Method is based on the difference in the rate of reactions of Sn(II) and Sn(IV) with pyrocatechol violet at pH 4.0. Tin was also determined as the catalyst of the reaction of reduction of chromium blue K in phosphoric acid medium and method was applied for tin determination in geological samples [40].

## Experimental

### *Apparatus*

Spectrophotometric measurements were performed on UV-VIS spectrophotometer Shimadzu UV- VIS 1650 PC (Shimadzu, Japan). AAS measurements were performed on Analyst A300 Perkin Elmer (USA). The cylindrical cells were thermostated at  $20.00 \pm 0.02^\circ\text{C}$  using thermocirculating bath (Julabo MP-5A). The pH measurements were performed using a Hach H260G pH-meter with a non-glass pH probe PH77SS (Hach, USA). Also, stopwatch Agat (Russia) was used.

### *Reagents and Chemicals*

Analytical grade reagents, provided by Merck, Germany, unless indicated otherwise and deionised water (Micro Med high purity water system, TKA Wasseraufbereitungs system GmbH) or ammonia buffer were utilized for solutions preparation. Ammonia buffers were prepared by mixing  $\text{NH}_3(\text{aq})$  and  $\text{NH}_4\text{Cl}$  solutions ( $0.2 \text{ mol dm}^{-3}$ ) and their pH values were checked using pH-meter. A stock Co(II) solution ( $1 \cdot 10^{-3} \text{ g cm}^{-3}$ ) was prepared by dissolving the exactly measured  $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$  in deionised water. The concentration of the stock solution was checked electrogravimetrically. Basic Sn(II) solution ( $1 \cdot 10^{-3} \text{ g cm}^{-3}$ ) was prepared by dissolving 1.00 g of metallic tin (99.999%) in  $100 \text{ cm}^3$  of concentrated HCl. Solution was diluted to  $1 \text{ dm}^3$  by

deionised water and its concentration was checked by iodometric titration. The concentrations of  $\text{H}_2\text{O}_2$  solutions were verified by  $\text{KMnO}_4$  titration. The phenyl fluorone basic solution was prepared by dissolving the exactly measured dry substance in ammonia buffer. All the polyethylene containers and the glassware were washed by diluted hydrochloric acid (1:1), solution of potassium hydroxide in ethanol and then repeatedly well rinsed by tap distilled and deionized water. All concentrations described here are the initial concentrations in the reaction mixture at time zero after mixing. Each kinetic result is the average of five determinations.

### *Procedure*

In order to obtain good mechanical and thermal stability, the instruments were run for ten minutes before the first measurement. Selected volumes of reactants and deionized water were poured separately in the reaction mixture vessel with four compartments (Budarin vessel) up to a predetermined total volume of  $10\text{ cm}^3$ . The solution of  $\text{Co(II)}$ , during cobalt determination, and  $\text{Sn(II)}$ , during tin determination, was measured in one compartment of Budarin vessel for catalytic, *e.g.* inhibitory reaction, and the same volume of deionized water was measured for non-catalytic and non-inhibitory reaction. After thermostating for ten minutes, the reagents were mixed and simultaneously the stopwatch was turned on. To properly rinsed spectrophotometer cell with a path length of 10 cm, the solution was immediately added and absorbance was measured every 15 seconds, starting from the 45<sup>th</sup> second of reaction, up to ten minutes of the reaction.

The reaction was tested by examination the influence of each component of the reaction mixture upon the reaction rate of catalytic and non-catalytic reaction for cobalt method development and inhibitory and non-inhibitory reaction for tin method development. The concentration of each

component was changing consecutively, while the concentration of other components, as well as the working temperature, were kept constant.

## Results and Discussion

Until the reaction goes on, the initial red color of solution fades and the colorless reaction product is forming. The exact mechanism of reaction and the nature of reaction products were not the main interest of our investigation. All spectrophotometric measurements were performed at the wavelength of absorption maximum of phenyl fluorone in ammonia buffer (493.6 nm, Fig. 1).

Fig. 1.

The logarithm of absorbance-time curves are linear during the first five to ten minutes of reaction for different Co(II) and Sn(II) concentrations, so all kinetic results were treated by the integral variant of tangent method [41]. The rate of reaction was obtained using the slope of the kinetic curves of the absorbance-time plot.

According to the our preliminary investigations, kinetic catalytic reaction of Co(II) is faster in the the presence of citric acid, so citric acid was added in the reaction mixture as an activator, during cobalt method investigations.

The influence of the pH value of selected ammonia buffers on the rate of both the catalytic and non-catalytic reaction for cobalt method development was examined in the pH interval from 10 to nearly 12. Within this range, both reactions showed complex dependence on the pH value of ammonia buffer (Fig. 2). The value of 11.7 was selected as the most appropriate one, because it

provides the adequate difference of the reaction rates of the catalytic and non-catalytic reaction. So, the ammonia buffer pH 11.7 was used in all subsequent investigations.

Fig. 2.

The influence of pH value of ammonia buffer upon the rate of both inhibitory and non-inhibitory reaction for tin method development was examined in pH interval from nearly 9.0 to nearly 11.5. In this range, both reactions show complex dependence of pH value of ammonia buffer (Fig.3). The ammonia buffer 10.4 was used in all following investigations.

Fig. 3.

The rates of both catalytic and non-catalytic reactions, for cobalt method investigation, are of the first order dependence on the reductant concentration (Fig.4) within the range of  $1.8 \cdot 10^{-5}$  to  $7.3 \cdot 10^{-5}$  mol dm<sup>-3</sup>. Consequently, a concentration of  $7.3 \cdot 10^{-5}$  mol dm<sup>-3</sup> was selected as optimal for the subsequent measurements.

Fig. 4.

In the range of PF concentration from  $1.0 \cdot 10^{-5}$  to  $6.0 \cdot 10^{-5}$  mol dm<sup>-3</sup>, the rates of both inhibitory and non-inhibitory reaction, for tin method investigation, are in the first order dependence upon the reductant concentration (Fig. 5). The concentration of  $4.0 \cdot 10^{-5}$  mol dm<sup>-3</sup>, was selected as optimal for next measurements.



Fig. 5.

The dependence of the rate of the catalytic and non-catalytic reaction on the oxidant concentration was monitored within the concentration range of about 1.0 to about 3.2 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>. Within this interval, the rate of catalytic reaction (in the presence of Co(II)) shows a complex dependence, whereas the non-catalytic one is of the zero order dependence within the concentration range of about 1.0 to about 2.0 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> (Fig. 6.). As optimal, a concentration of 1.3 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> was selected.

Fig. 6.

Dependence of inhibitory and non-inhibitory reaction rate on the oxidant concentration for tin method was followed for the concentration range of about 2.4 to about 4.4 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>. In this interval, both reactions show the first order dependence of H<sub>2</sub>O<sub>2</sub> concentration (Fig. 7). The concentration of 2.94 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub> was selected for further investigations.

Fig. 7.

The influence of the concentration of activator was examined only for catalytic and non-catalytic reaction for cobalt method development (Fig. 8). Inside the investigated concentration range of citric acid of nearly 4.5·10<sup>-3</sup> to nearly 27.0·10<sup>-3</sup> mol dm<sup>-3</sup>, the catalytic reaction exhibited a complex dependence, while the non-catalytic reaction showed zero order dependence. Citric acid concentration of 4.5·10<sup>-3</sup> mol dm<sup>-3</sup> was selected for further work.

Fig. 8.

Hence, the optimal conditions for performing the reaction for cobalt determination were found to be: pH 11.7,  $c_{PF} = 7.3 \cdot 10^{-5} \text{ mol dm}^{-3}$ ,  $c_{H_2O_2} = 1.3 \text{ mol dm}^{-3}$ ,  $c_{CA} = 4.5 \cdot 10^{-3} \text{ mol dm}^{-3}$ . In addition, the optimal conditions for performing the reaction for tin determination were found to be pH 10.4,  $c_{PF} = 4.0 \cdot 10^{-5} \text{ mol dm}^{-3}$ ,  $c_{H_2O_2} = 2.94 \text{ mol dm}^{-3}$ .

Under the selected conditions, the dependence of catalytic reaction rate on the Co(II) concentration was observed at  $20 \pm 0.02^\circ\text{C}$ . The linear dependence of calibration curve falls within the range of  $5 \cdot 10^{-9}$  to  $18 \cdot 10^{-8} \text{ g cm}^{-3}$  Co(II).

The adequate equation of calibration curve for  $20 \pm 0.02^\circ\text{C}$ , is:

$$\text{Slope} = (0.00253 \pm 0.00001) \cdot c + (0.00178 \pm 0.00008) \quad (1)$$

where:  $c$  is Co(II)  $\cdot 10^{-8}$  concentration in  $\text{g cm}^{-3}$ .

Under selected conditions, dependence of inhibitory reaction rate on the Sn(II) concentration at  $20.00 \pm 0.02^\circ\text{C}$  was tested. The linear range of calibration curve was found to be 0.4 to  $4.0 \mu\text{g cm}^{-3}$  Sn(II).

The adequate equation of calibration curve for  $20.00 \pm 0.02$ , is:

$$\text{Slope} = (-0.00276 \pm 0.00002) \cdot c + (0.01192 \pm 0.00017) \quad (2)$$

where:  $c$  is Sn(II)  $\cdot 10^{-6}$  concentration in  $\text{g cm}^{-3}$ .

The accuracy and precision of the methods were checked for three different Co(II) and Sn(II) concentrations within the range of adequate calibration curves. Five repeated measurements were performed for each concentration. Satisfactory results were obtained for both methods. For Co(II)

concentrations of  $64 \text{ ng cm}^{-3}$ ,  $91 \text{ ng cm}^{-3}$ , and  $108 \text{ ng cm}^{-3}$ , RSD values were found to be 5.9%, 3.6%, and 1.5%, respectively. For Sn(II), concentrations of  $1.0$ ,  $2.5$  and  $3.5 \text{ } \mu\text{g cm}^{-3}$ , RSD was found to be 6.2% , 4.2% and 1.3% , respectively.

The selectivity of both methods was established by interference studies: selected ions were separately added in the reaction mixture. The tolerance limit was estimated as the concentration of the added ion that gives up to a 3% relative error in the determination of cobalt and tin. Cations were added as chlorides or nitrates and anions were added as sodium or potassium salts. Each ion was added in six known concentration ratios (0.01:1, 0.1:1, 1:1, 10:1, 100:1 and 1000:1) against the constant Co(II) concentration of  $91.0 \text{ ng cm}^{-3}$ , for cobalt method investigation and constant Sn(II) concentration of  $2.0 \text{ } \mu\text{g cm}^{-3}$ , for tin method investigation. The measurements were performed at  $20 \pm 0.02^\circ\text{C}$ , and about 30 most frequently used cations and anions were tested ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$ , acetates, tartarates, oxalates, molybdates, wolframates,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ) and  $\text{Sn}^{2+}$  in cobalt method investigation and  $\text{Co}^{2+}$  in tin method investigation. The results presented in Table 1. reveal that proposed methods for cobalt and tin determination have a very good selectivity.

Table 1.

As it could be noticed, only the presence of  $\text{Ni}^{2+}$ , in the ratio 1000:1 and  $\text{Bi}^{3+}$  and  $\text{Cd}^{2+}$ , in the ratio 10:1, catalyzes the determination of cobalt, while  $\text{Sn}^{2+}$ , in the ratio 10:1, inhibits the determination of cobalt by this method. The method for tin determination also has very good selectivity because only the presence of  $\text{Mg}^{2+}$ , in the ratio 100:1 and wolframates, in the ratio 1:1, interferes the tin determination.  $\text{Co}^{2+}$  and  $\text{Bi}^{3+}$ , both in the ratio 0.1:1 to the tin concentration,

have the catalytic effect to the tin determination by this method. The ions that interfere determination of cobalt and tin can be easily removed by standard analytical methods like masking, precipitation, etc., depending of different samples nature.

The new developed methods were successfully applied to cobalt and tin determination in chemical substances: Co(II) determination in  $\text{KNO}_3$  and tin determination in zinc powder.

Solutions containing a known quantity of cobalt were prepared by dissolving the substance in deionised water. The solutions were analyzed by application of both the presented kinetic method and AAS method. The results are shown in Table 2. A good agreement between the results of both methods can be seen.

Table 2.

The solution for tin determination was prepared by dissolving the zinc powder with addition of  $\text{HNO}_3$  (1:1) and the small volume of  $\text{H}_2\text{SO}_4$  (1:3). Solution was vaporized to dry and the residue was dissolved in adequate volume of deionized water. The analysis was performed by applying both kinetic and AAS method. The final results are shown in Table 3.

Table 3.

## Conclusions

The limit of quantification (LQ) of  $1.1 \text{ ng cm}^{-3}$  was reached, and the limit of detection (LD) of  $0.3 \text{ ng cm}^{-3}$  was obtained for Co(II) determination. The optimized conditions yielded the LD value of  $31.2 \text{ ng cm}^{-3}$  for Sn(II) determination, while LQ was found to be  $107.1 \text{ ng cm}^{-3}$ . LQ was defined as the ratio  $\text{signal:noise}=10:1$  and LD was defined as  $\text{signal } 3:1$  against the blank. The

RSD value was found to be in the range 1.5-5.9% for the investigated concentration range of Co(II) and 1.3% to 6.2% for the investigated concentration range of Sn(II) determination. The methods allow the determination of Co(II) over the concentration range of 5.0-180.0 ng cm<sup>-3</sup> and 0.4-4.0 µg cm<sup>-3</sup> for Sn(II). The influence of about 30 selected ions upon the reaction rate was tested in order to assess the selectivity of both methods. The results were validated statistically and through recovery studies. The both methods were confirmed by determination in chemical substances: Co(II) was determined in KNO<sub>3</sub> and Sn(II) was determined in zinc powder. The obtained results were in a good agreement with results obtained by AAS method.

The activated catalytic reaction (PF, H<sub>2</sub>O<sub>2</sub>, Co(II), CA) in ammonia buffer media shows better sensitivity for cobalt determination than inhibitory reaction for tin determination (PF, H<sub>2</sub>O<sub>2</sub>, Sn(II)) at room temperature.

The new kinetic method for Co(II) nano amounts determination is very sensitive one and provides rapid and easy performance at room temperature, with precise, reproducible results and good selectivity. On the grounds of the obtained results, the method is recommendable for the determination of Co(II) in chemical substances of high purity grade. It could also be a good basis for further investigations in the area of kinetic methods for cobalt determination in different samples.

The new kinetic method for Sn(II) micro amounts determination is one of very few known kinetic methods for tin determination in solution. It is inexpensive, rapid, selective and simple to perform. Based on the obtained results, method is recommendable for determination of Sn(II) in chemical substances as well as in wastewater samples and the other environmental solutions. It could be used as a good basis for further investigations in the area of kinetic methods for tin determination.

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## Izvod

# ANALITIČKA PRIMENA REAKCIONOG SISTEMA FENIL FLUORON-VODONIK PEROKSID ZA KINETIČKO ODREĐIVANJE TRAGOVA KOBALTA I KALAJA SPEKTROFOTOMETRIJSKI U AMONIJAČNOM PUFERU

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(Naučni rad)

Pri određivanju Co(II), ostvarena je granica određivanja (LQ) od 1.1 ng cm<sup>-3</sup> i granica detekcije (LD) od 0.3 ng cm<sup>-3</sup>. Pod optimalnim uslovima, nađeno je da LD, pri određivanju Sn(II), iznosi 31.2 ng cm<sup>-3</sup>, a LQ je 107.1 ng cm<sup>-3</sup>, pri čemu je LQ definisan kao odnos signal:šum=10:1, a LD kao signal 3:1 u odnosu na slepu probu. RSD se, pri određivanju kobalta kreće u rasponu od 1.5-5.9%, za ispitivani interval koncentracija Co(II), odnosno u rasponu od 1.3% to 6.2%, za ispitivani interval koncentracija Sn(II). Novom metodom je moguće određivanje Co(II) u opsegu od 5.0-180.0 ng cm<sup>-3</sup>, kao i određivanje Sn(II) u opsegu od 0.4-4.0 μg cm<sup>-3</sup>. Radi utvrđivanja selektivnosti novih metoda, ispitan je uticaj dodatka tridesetak različitih jona na brzinu, kako katalizovane, tako i inhibirane reakcije i utvrđena je njihova dobra selektivnost. Rezultati su statistički obrađeni i komentarisani. Metode su proverene određivanjem kobalta i kalaja u hemijskim supstancama: Co(II) je određivan u KNO<sub>3</sub>, a Sn(II) u cinku u prahu. Dobijeni rezultati pokazuju dobro slaganje s rezultatima dobijenim ispitivanjem istih uzoraka AAS metodom.

**Keywords:** Co(II) determination, Sn(II) determination, kinetic spectrophotometric method,

**Ključne reči:** određivanje Co(II), određivanje Sn(II) , kinetičko spektrofotometrijska metoda

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### **Table captions**

Table 1. Selected results of interference studies for cobalt and tin determination

Table 2. Co(II) determination in  $\text{KNO}_3$

Table 3. Sn(II) determination in zinc powder

### **Naslovi tabela**

Tabela 1. Izabrani rezultati ispitivanja uticaja stranih jona pri određivanju kobalta i kalaja

Tabela 2. Određivanje Co(II) u  $\text{KNO}_3$

Tabela 3. Određivanje Sn(II) u cinku u prahu

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## Figure captions

Fig. 1. Absorption spectra of PF in ammonia buffer. Initial conditions:  $1.5 \cdot 10^{-5}$  mol dm<sup>-3</sup> PF;  $20.00 \pm 0.02^\circ\text{C}$ ; pH: 1) 10.2, 2) 10.6; 3) 11.9. C

Fig. 2. Dependence of the reaction rate on pH for cobalt method development. Initial conditions:  $9.1 \cdot 10^{-3}$  mol dm<sup>-3</sup> CA;  $7.3 \cdot 10^{-5}$  mol dm<sup>-3</sup> PF;  $1.8$  mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>;  $1.8 \cdot 10^{-7}$  g cm<sup>-3</sup> Co(II);  $20 \pm 0.02^\circ\text{C}$ ; 1-catalytic reaction, 2-non-catalytic reaction.

Fig. 3. Dependence of the reaction rate on pH for tin method development. Initial conditions:  $5.0 \cdot 10^{-5}$  mol dm<sup>-3</sup> PF;  $3.92$  mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>;  $2.5$  μg cm<sup>-3</sup> Sn(II);  $20.00 \pm 0.02^\circ\text{C}$ ; 1-inhibitory reaction, 2-non-inhibitory reaction.

Fig. 4. Dependence of the reaction rate on PF concentration for cobalt method development. Initial conditions:  $9.1 \cdot 10^{-3}$  mol dm<sup>-3</sup> CA;  $1.8$  mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>;  $1.8 \cdot 10^{-7}$  g cm<sup>-3</sup> Co(II); pH-11.7;  $20 \pm 0.02^\circ\text{C}$ ; 1-catalytic reaction, 2-non-catalytic reactio.

Fig. 5. Dependence of the reaction rate on PF concentration for tin method development. Initial conditions:  $3.92$  mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>;  $2.5$  μg cm<sup>-3</sup> Sn(II); pH-10.4,  $20.00 \pm 0.02^\circ\text{C}$ ; 1-inhibitory reaction, 2-non-inhibitory reaction.

Fig. 6. Dependence of the reaction rate on H<sub>2</sub>O<sub>2</sub> concentration for cobalt method development. Initial conditions:  $9.1 \cdot 10^{-3}$  mol dm<sup>-3</sup> CA;  $7.3 \cdot 10^{-5}$  mol dm<sup>-3</sup> PF;  $1.8 \cdot 10^{-7}$  g cm<sup>-3</sup> Co(II); pH-11.7;  $20 \pm 0.02^\circ\text{C}$ ; 1-catalytic reaction, 2-non-catalytic reaction.

Fig. 7. Dependence of the reaction rate on H<sub>2</sub>O<sub>2</sub> concentration for tin method development. Initial conditions:  $4.0 \cdot 10^{-5}$  mol dm<sup>-3</sup> PF;  $2.5$  μg cm<sup>-3</sup> Sn(II); pH-10.4;  $20.00 \pm 0.02^\circ\text{C}$ ; 1-inhibitory reaction, 2-non-inhibitory reaction.

Fig. 8. Dependence of the reaction rate on CA concentration for cobalt method development.

Initial conditions:  $7.3 \cdot 10^{-5}$  mol dm<sup>-3</sup> PF; 1.3 mol dm<sup>-3</sup> H<sub>2</sub>O<sub>2</sub>;  $1.8 \cdot 10^{-7}$  g cm<sup>-3</sup> Co(II); pH-11.7;

20±0.02°C; 1-catalytic reaction, 2-non-catalytic reaction.

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Table 1.

Added ion	Ion ratio:Co(II)	Cobalt determination	Ion ratio:Sn(II)	Tin determination
Ni(II)	1000	catalyzes	100	–
Cd(II)	10	catalyzes	1	–
Mg(II)	100	–	100	interferes
Bi(III)	10	catalyzes	0.1	catalyses
Co(II)			0.1	catalyses
Sn(II)	10	inhibits		
WO <sub>4</sub> <sup>2-</sup>	1000	–	1	interferes

Table 2.

Measured ng cm <sup>-3</sup>	Kinetic determination <sup>a</sup> ng cm <sup>-3</sup>	Recovery %	AAS determination <sup>a</sup> ng cm <sup>-3</sup>	Recovery %
10.0	12.6±1.8	126.0	10.5±0.2	105.0
30.0	31.2±1.6	104.0	29.8±0.2	99.3
50.0	50.6±1.0	101.2	50.2±0.2	100.4

<sup>a</sup>The mean value of five measurements±2SD

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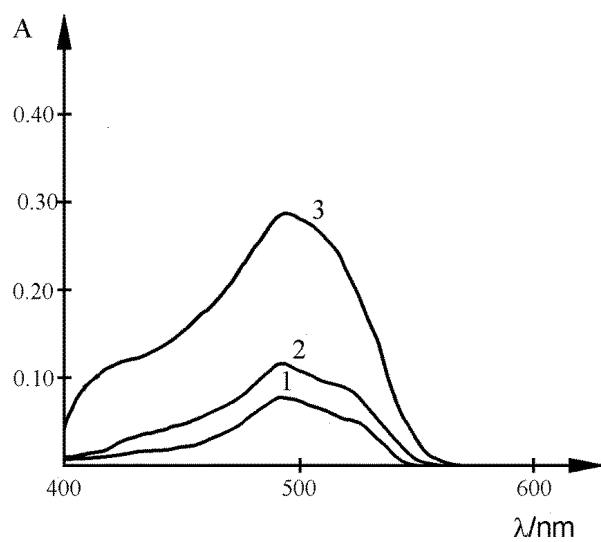
Table 3.

Kinetic determination <sup>b</sup> g cm <sup>3</sup> · 10 <sup>7</sup>	Recovery %	AAS determination <sup>b</sup> g cm <sup>3</sup> · 10 <sup>7</sup>	Recovery %
4.06±0.10	101.5	4.01±0.02	100.2

<sup>b</sup> The mean value of five measurements±2SD

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Fig 1.



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Fig. 2.

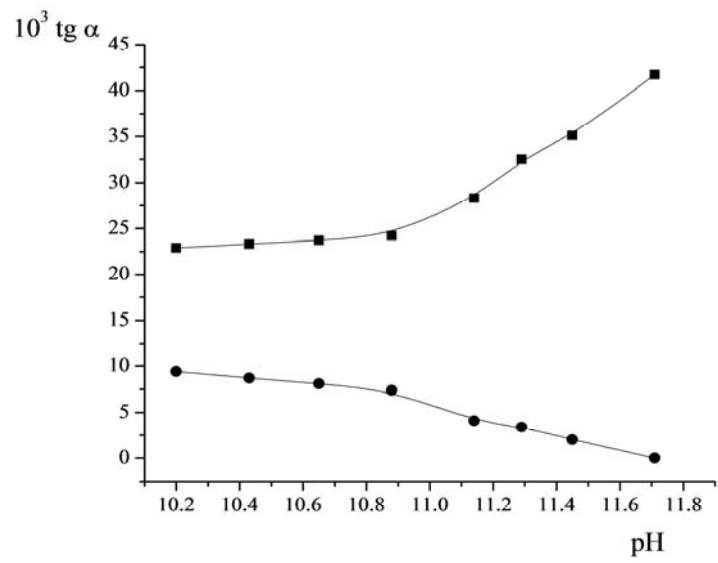


Fig. 3.

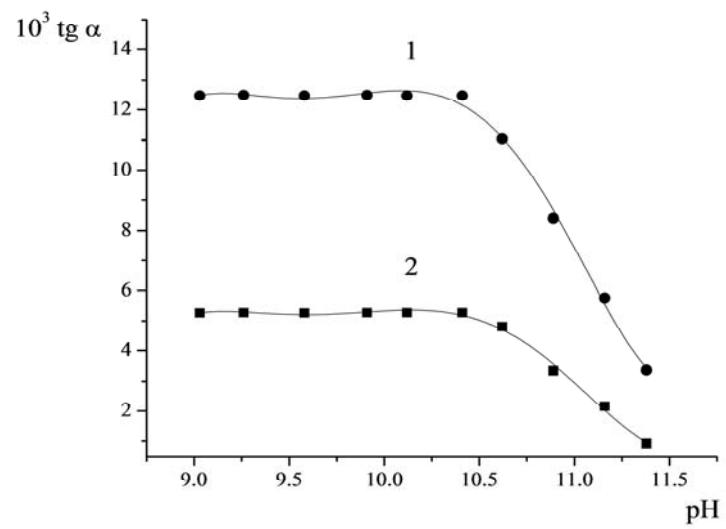


Fig. 4.

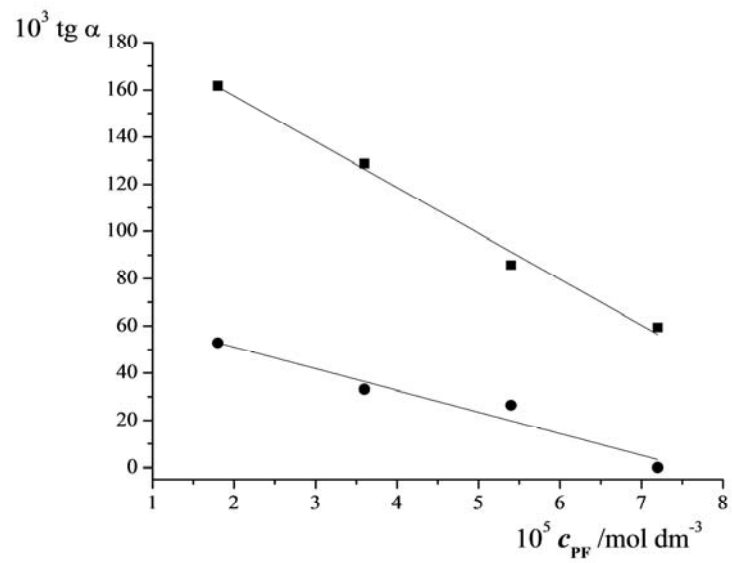


Fig. 5.

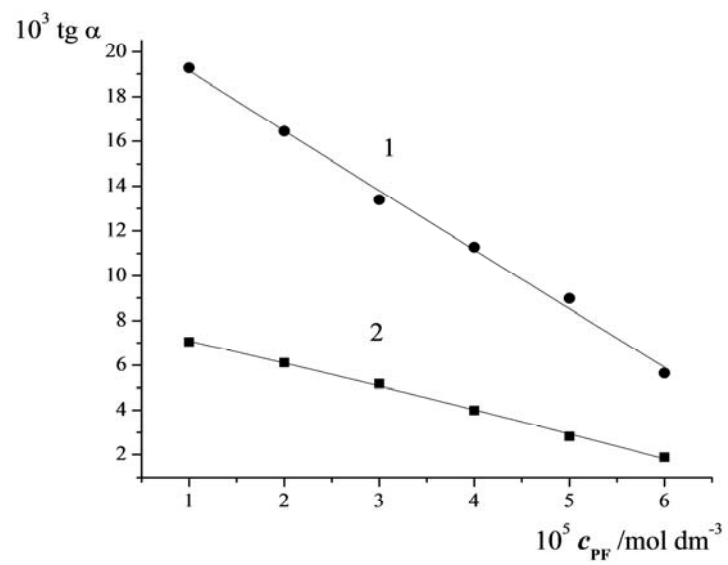
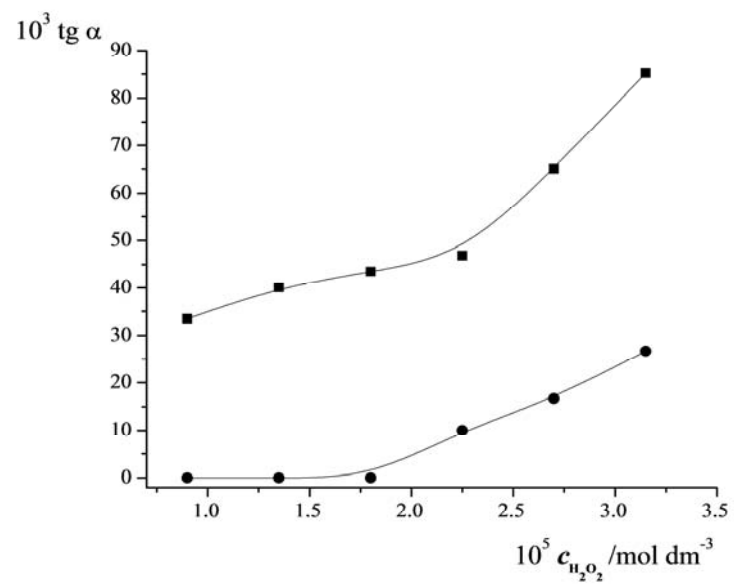




Fig. 6.



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Fig. 7.

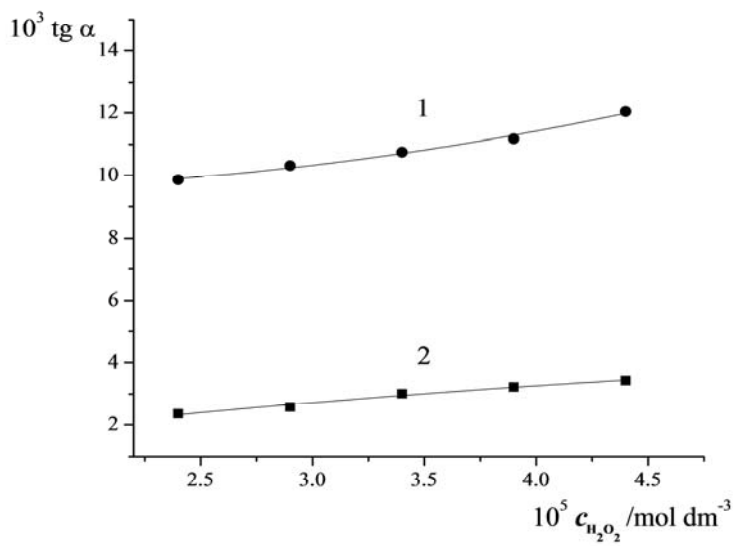


Fig. 8.

