

Determination of Chromium (VI) by a Catalytic Spectrophotometric Method in the Presence of p-Aminobenzoic Acid

[p-Aminobenzoik asit varlığında katalitik spektrofotometrik bir metodla krom (VI) ölçümü]

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ABSTRACT

Chromium (VI) is a strong oxidizing agent and poses a high toxicity to humans and animals due to its carcinogenicity and mutagenicity and therefore the determination of chromium in environmental and biological samples is of great interest.

In the present study, a new catalytic spectrophotometric method for the determination of chromium (VI) is proposed. The method is based on the catalytic effect of chromium (VI) on the oxidation of sulphanilic acid (SA) by hydrogen peroxide in the presence of p-aminobenzoic acid (PABA) as an activator.

The reaction was followed spectrophotometrically by tracing the formation of the reaction product at 360 nm after 15 minutes of mixing the reagents.

The optimum reaction conditions are 4.0×10^{-3} M SA, 0.57 M H_2O_2 , 1×10^{-3} M PABA and 0.04 M acetic acid - boric acid - orthophosphoric acid buffer solution (pH 6.6), at 50 °C.

The linear range of the calibration graph was up to 140 ng/mL and the detection limit was 10 ng/mL. Interferences of Cu (II) and Cr (III) ions were masked. The method was applied to the analysis of Cr (VI) in industrial water with recoveries of 95.2 – 104.5% and RSD of 2.9–5.8%.

Key Words: chromium (VI), catalytic method, sulphanilic acid, p-aminobenzoic acid, industrial water

ÖZET

Krom (VI) kuvvetli bir yükseltgeyici ajandır. Karsinojenite ve mutajenite nedeniyle insan ve hayvanlarda toksik etkisinin yüksek olması, çevresel ve biyolojik örneklerde krom ölçümünü önemli hale getirir.

Bu çalışmada, krom (VI) tayini için yeni bir katalitik spektrofotometrik metod önerilmektedir. Metod, aktivatör olarak p-aminobenzoik asit (PABA) varlığında sülfanilik asitin (SA) oksidasyonu üzerine krom (VI)'nın katalitik etkisine dayanır.

Reaktifler karıştırıldıktan 15 dakika sonra 360 nm'de ürün oluşumu spektrofotometrik olarak izlendi.

Optimum reaksiyon koşulları: 4.0×10^{-3} M SA, 0.57 M H_2O_2 , 1×10^{-3} M PABA ve 0.04 M asetik asit -borik asit- ortofosforik asit tampon çözeltisi (pH 6.6), 50 °C olarak saptandı.

Kalibrasyon eğrisi, 140 ng/mL'ye kadar lineerdi ve ölçüm alt sınırı 10 ng/mL idi. Cu(II) ve Cr(III) iyonlarının interferansı maskelendi. Metod, endüstriyel sudaki Cr(VI) ölçümüne uygulandığında geri kazanım %95.2-104.5 arasında, nisbi standart sapma %2.9-5.8 arasında bulundu.

Anahtar Kelimeler: Krom (VI), katalitik metod, sülfanilik asit, p-aminobenzoik asit, endüstriyel su.

INTRODUCTION

Chromium (VI) is known to be a strong oxidizing agent, posing a high risk to humans and animals due to its carcinogenic and mutagenic properties [1]. That is why the determination of chromium in environmental and biological samples is of great interest.

Various techniques such as NAA, UV-visible, ICP-MS and AAS, with high sensitivity for the determination of chromium reported so far [2-5] need complicated and expensive equipment. Moreover, such techniques are usually not available in most laboratories.

Kinetic catalytic methods have proved to be a cheaper and more reliable alternative to the instrumental analyses for trace determinations [6,7]. Most catalytic methods for chromium determination are based on its effect on the oxidation of organic compounds with a suitable oxidant, most frequently hydrogen peroxide [8-13].

Our preliminary experiments showed that chromium (VI) could be determined due to its catalytic action on the reaction of oxidation of sulfanilic acid by hydrogen peroxide with moderate sensitivity and detection limit.

One of the most effective determinant of the sensitivity of a kinetic catalytic reaction is the usage of activators [7]. In order to improve the analytical parameters of the above reaction, different activators were tested and the most significant activating effect was found using p-aminobenzoic acid.

In this study, a new catalytic spectrophotometric method for the determination of chromium (VI) is proposed. The method is based on the catalytic effect of chromium (VI) on the oxidation of sulphanic acid (SA) by hydrogen peroxide in the presence of p-aminobenzoic acid (PABA) used as an activator.

MATERIALS AND METHODS

Reagents

All solutions were prepared from analytical-reagent grade chemicals and with double distilled water. Stock standard solutions of 0.1 M potassium dichromate (Fluka) (diluted as necessary), 0.05 M sulfanilic acid (SA) (Merck), 7 M hydrogen peroxide (Merck) and 0.015 M p-aminobenzoic acid (PABA) (Merck) were used.

A 10% aqueous ammonia solution was prepared from a 25% aqueous ammonia solution (Merck). The medium pH was controlled using buffers prepared by using 0.04 M acetic acid, boric acid and orthophosphoric acid and adjusted to the pH needed by using 0.2 M sodium hydroxide (Merck).

Apparatus

Absorbance measurements were made on a Specol 11 spectrophotometer (Carl Zeiss Jena, Germany) fitted with 5 cm cells. The spectrophotometer cell compartments were thermostated by means of circulating water. A TB 120 thermostat (VEB Prüfgeräte-Werk, Medingen, Germany) was used to control the temperature.

Absorption spectra were obtained using a Specord-UV-Vis spectrophotometer (Carl Zeiss Jena, Germany).

Procedure for the Kinetic Spectrophotometric Determination of Chromium (VI)

The reaction parameters were studied by following the reaction rate, which was determined by following the formation of the colored reaction product as a function of time, and calculating $\tan \alpha = \Delta A / \Delta \tau$ for the rectilinear portions of the kinetic curves (absorbance (A) vs. time (τ)).

The following reactants were introduced to a special, three-compartment glass reaction vessel - mixer as follows: in the first compartment - 0.6 mL sulfanilic acid (50 mM); in the second - 0.6 mL H₂O₂ (7 M) and in the third - 0.0 – 1.0 mL of potassium dichromate (10 μ M) and 0.5 mL of PABA (15mM). Buffer (4.8-5.8 mL, pH 6.6) was added to each compartment divided into three approximately equal aliquots, so the overall volume of the reaction mixture (7.5 mL) was the same in each experiment.

The mixer with reagents was placed into the thermostat for 10 min at 50 °C, and after that the reaction was started by rapid inverting of the well-closed vessel. The mixture was transferred into a 5 cm constant temperature cell of a Specol 11 spectrophotometer and the changes in absorbances with time were measured at 360 nm.

The saturation in the kinetic curves obtained allowed using the "fixed time" method [7, 14], which is technically more convenient. In this case the reaction vessel was returned to the thermostat after the reagents were mixed and the absorbances were measured at a fixed time of 15 min after mixing.

Procedure for Analysis of Water Samples

The following reactants were placed: 0.6 ml of 7 M hydrogen peroxide solution; 0.5 mL of PABA (15 mM) and 0.6 ml of standard chromium (VI) solution, or aqueous sample, or distilled water; 0.1 ml of 10% ammonia solution and 5.1 ml of buffer solution (pH 6.6). The contents of the test tube was kept at 50 °C in a thermostated water bath for 10 min. Then 0.6 ml of sulfanilic acid (50 mM) were added, the mixture was thoroughly mixed by shaking and then transferred into a 5 cm constant temperature cell of the spectrophotometer. The absorbances were measured at 360 nm 15 min after adding sulfanilic acid.

RESULTS AND DISCUSSION

Optimum conditions

The influence of the reaction parameters (absorption spectra, acidity, temperature, reagent concentration) on the reaction rate was studied in the presence and absence of chromium (VI) to establish the optimum reaction conditions. The systems studied were optimized by altering each variable in turn while keeping all the others unchanged.

The absorption spectra of the reaction products showed only one absorption maximum at 360 nm, and this was chosen as the measurement wavelength.

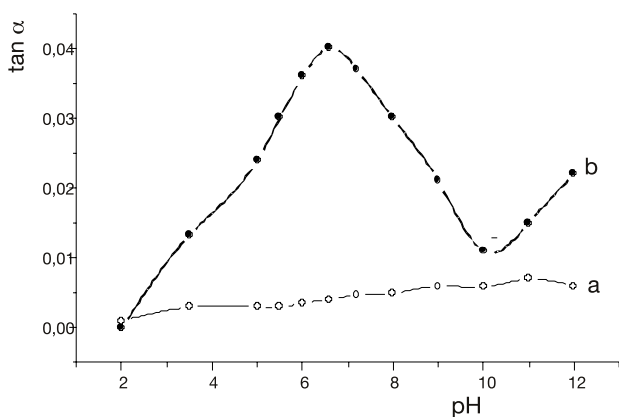


Figure 1. Influence of pH on the initial reaction rate in the absence of the catalyst (a) and in the presence of the catalyst $\text{Cr(VI)} 4 \times 10^{-6} \text{ M}$ (b) $\lambda 360 \text{ nm}$; temperature 50°C ; 0.004 M SA ; $0.57 \text{ M H}_2\text{O}_2$; 0.001 M PABA

It has been established by UV, IR and NMR spectroscopy after chromatography that the products of oxidation of sulfanilic acid are mainly azobenzene-4,4'-disulfonic acid ($\lambda_{\text{max}} = 325$ and 446 nm) and o-benzoquinone-4-sulfonic acid ($\lambda_{\text{max}} = 250$ and 368 nm) [15]. Thus, the absorption spectra obtained indicates that the main product of the proposed reaction is o-benzoquinone-4-sulfonic acid.

Figure 1 shows the dependence of the initial reaction rate on the acidity in the presence of the catalyst. pH value of 6.6 was selected because it presented the highest sensitivity provided.

The influence of the temperature was studied between 20 and 70°C (Fig. 2). The initial rates of the catalyzed and uncatalyzed reactions increased exponentially with temperature. 50°C was provided a moderate sensitivity and because of its convenience it was chosen for the operations.

The influence of the activator concentration on the initial reaction rate is shown in Fig. 3, from which it can be seen that the optimum concentration is $1 \times 10^{-3} \text{ M PABA}$.

Fig. 4 reflects the influence of the sulfanilic acid concentration on the initial reaction rate. The sensitivity

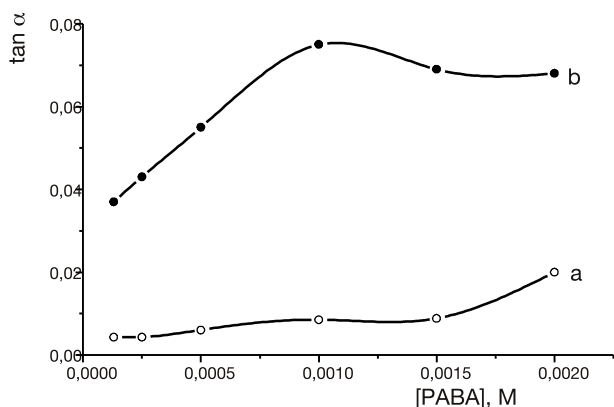


Figure 3. Influence of PABA concentration on the initial reaction rate in the absence of the catalyst (a) and in the presence of the catalyst $\text{Cr(VI)} 4 \times 10^{-6} \text{ M}$ (b) $\lambda 360 \text{ nm}$; pH 6.6; temperature 50°C ; 0.004 M SA ; $0.57 \text{ M H}_2\text{O}_2$

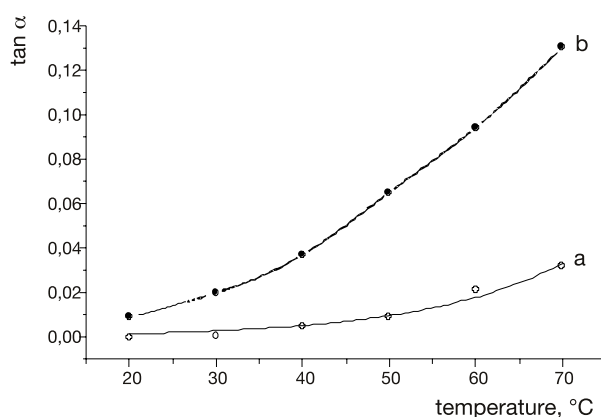


Figure 2. Influence of temperature on the initial reaction rate in the absence of the catalyst (a) and in the presence of the catalyst $\text{Cr(VI)} 4 \times 10^{-6} \text{ M}$ (b) $\lambda 360 \text{ nm}$; pH 6.6; 0.004 M SA ; $0.57 \text{ M H}_2\text{O}_2$; 0.001 M PABA

remained constant above $3.0 \times 10^{-3} \text{ M}$ of SA. Therefore, $4.0 \times 10^{-3} \text{ M}$ of sulfanilic acid was chosen as the optimal concentration.

Fig. 5 shows the influence of the hydrogen peroxide concentration. As can be seen the slope of the curve, representing catalyzed reaction, increased to a constant value above $0.5 \text{ M H}_2\text{O}_2$. That is why we chose $0.57 \text{ M H}_2\text{O}_2$ as the optimal concentration.

Based on the results of the investigations made, the optimum reaction conditions were established as:

$4.0 \times 10^{-3} \text{ M SA}$, $0.57 \text{ M H}_2\text{O}_2$, $1.0 \times 10^{-3} \text{ M PABA}$ and 0.04 M acetic acid – boric acid – orthophosphoric acid buffer solution (pH 6.6), at 50°C .

Calibration graph

Under the optimum conditions, a linear calibration graph up to 140 ng/mL chromium (VI) was obtained using “fixed time” method [7, 14]. The regression equation of the calibration graph was:

$A_{360} = 0.019 C + 0.22$, where C is concentration (ng/mL) and the correlation coefficient was 0.994. The proposed method yields a relative standard deviation of 2.8% for 10 determinations of 30 ng/mL of chromium (VI). The

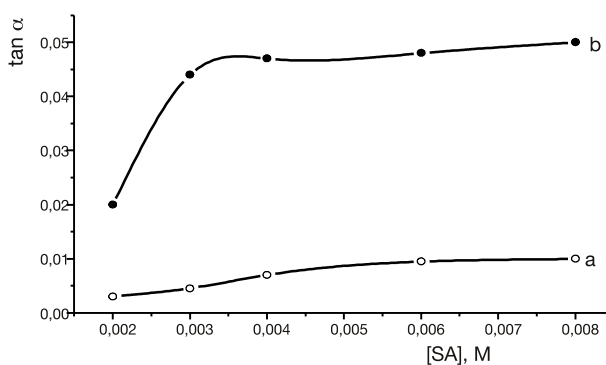


Figure 4. Influence of SA concentration on the initial reaction rate in the absence of the catalyst (a) and in the presence of the catalyst $\text{Cr(VI)} 4 \times 10^{-6} \text{ M}$ (b) $\lambda 360 \text{ nm}$; pH 6.6; temperature 50°C ; $0.57 \text{ M H}_2\text{O}_2$; 0.001 M PABA

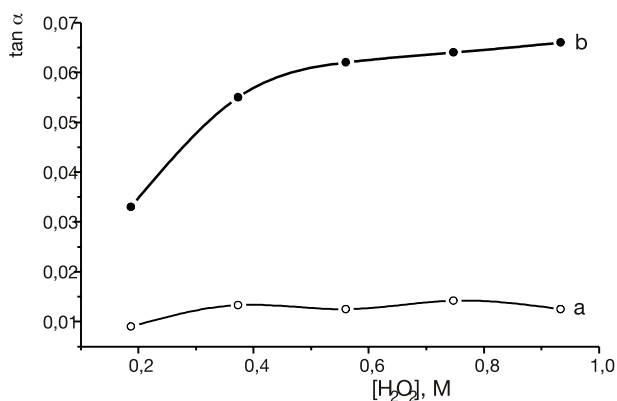


Figure 5. Influence of hydrogen peroxide concentration in the absence of the catalyst (a) and in the presence of the catalyst Cr(VI) 4×10^{-6} M (b) λ 360 nm; pH 6.6; temperature 50°C; 0.004 M SA; 0.001 M PABA

Table 1 Effect of foreign ions on the determination of chromium (VI) (60 ng/mL)

Foreign ion	Tolerated ratio [ion] : [Cr (VI)]
K^+ , Na^+ , NH_4^+ , BO_3^{3-} , PO_4^{3-} , CH_3COO^-	>1000
Ca^{2+} , Ba^{2+} , Mg^{2+} , Zn^{2+} , Hg^{2+} , Al^{3+} , EDTA, SO_4^{2-} , Cl^-	100
Cd^{2+} , Ni^{2+} , Ag^+ , Mo^{VI}	25
Fe^{2+} , Fe^{3+} , Co^{2+} , Pb^{2+} , SCN^- , CN^- , citrate	15
Cr^{3+}	5
Cu^{2+}	0.2

detection limit was 10 ng/mL, calculated as three times the standard deviation of the blank.

Study of Interferences

In order to assess the potential analytical applications of the proposed kinetic reaction, the influence of 28 foreign ions on the determination of chromium (VI) was investigated. The tolerated limits for the ions assayed are

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Table 2 Analytical recovery of the method for chromium (VI) determination in industrial water

Sample (AAS)	Chromium (VI) concentration, ng/mL		Relative standard deviation, %	Recovery, %
	Added	Found (mean±standard deviation) (n=6)		
15.6	-	15.4±0.89	5.8	-
	15.0	30.0±1.29	4.3	97.3
	20.0	36.3±1.16	3.2	104.5
37.2	-	37.7±1.55	4.1	-
	25.0	61.5±2.40	3.9	95.2
	30.0	68.4±3.28	4.8	102.3
53.8	-	54.9±1.59	2.9	-
	40.0	93.1±3.63	3.9	95.5
	50.0	104.2±4.27	4.1	98.6

shown in Table 1 (with relative errors less than 5%). As can be seen, most ions were tolerated at high concentrations. The interferences of Cu (II) and Cr (III) ions were eliminated by the addition of ammonia, as given in the procedure for the analysis of water samples.

Application

The usefulness of the proposed method was tested by determining the chromium concentration in samples of circulating industrial water from a glass factory, previously certified by atomic absorption spectrometry.

Chromium concentration was determined by applying the calibration curve and standard addition methods [7, 14]. Recovery tests for the analyzed samples were satisfactory (about 95.2 – 104.5%) with relative standard deviations of 2.9 – 5.8 % (Table 2).

The proposed catalytic method possesses a low detection limit satisfactory for given application, high precision and simple instrumentation, and can be applied for determination of chromium (VI) in industrial and waste waters polluted with chromium, thereby broadening the scope of application of catalytic methods for chromium determination.

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