

Catalytic Spectrophotometric Determination of Chromium

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The catalytic effect of chromium(III) and chromium(VI) on the oxidation of sulfanilic acid by hydrogen peroxide was studied. The reaction was followed spectrophotometrically by measuring the absorbance of the reaction product at 360 nm. Under the optimum conditions 2 calibration graphs (for chromium(III) up to 100 ng mL^{-1} , and for chromium(VI) up to 200 ng mL^{-1}) were obtained, using the "fixed time" method with detection limits of 4.9 ng mL^{-1} and 3.8 ng mL^{-1} , respectively.

The results suggest that at the reaction conditions chromium(VI) is reduced and chromium(III) is oxidized to an intermediate oxidation state and the catalytic action of chromium is due to the formation of an active complex between oxidant, catalyst and substrate.

A new catalytic spectrophotometric method for the determination of chromium was developed. The proposed method was successfully applied to chromium determination in tap and industrial waters.

Key Words: Chromium, catalytic determination, sulfanilic acid, hydrogen peroxide, tap and industrial waters.

Introduction

Chromium is found throughout the environment in 3 major oxidation states: chromium(0), chromium(III) and chromium(VI). The most stable form, chromium(III), occurs naturally in the environment, while chromium(VI) and chromium(0) are generally produced by industrial processes¹. The trivalent and hexavalent states of chromium are the most biologically significant. Chromium in biologic tissues is almost always trivalent and helps to maintain the normal metabolism of glucose, protein and fat^{1,2}. However, trivalent chromium may be harmful if ingested in large amounts (thousands of micrograms per day). Chromium(VI) is a strong oxidizing agent and highly toxic to humans and animals due to its carcinogenic and mutagenic properties¹.

Hence, the determination of chromium in environmental and biologic samples is of great interest.

There are many sensitive techniques for chromium determination, such as ICP-MS³⁻⁵, ICP-AES^{6,7}, NAA⁸⁻¹⁰, UV-visible^{6,11}, and AAS^{6,12,13}.

On the other hand, the application of kinetic catalytic methods for trace analyses allows one to achieve detection limits and sensitivity comparable with the above-mentioned instrumental techniques and offers simple and low-cost equipment¹⁴. Moreover, catalytic methods for chromium determination take a very small place among the many sensitive methods reported for the determination of chromium. Most catalytic spectrophotometric methods for chromium determination reported so far are based on its catalytic effect on a given redox reaction^{11,15}. The oxidants most frequently used are hydrogen peroxide, chlorate, bromate or ceric ions and most of the substrates used are organic compounds – aromatic amines, phenols and their derivatives^{11,15–19}.

In this study, the catalytic effect of chromium on the oxidation of sulfanilic acid (SA) with hydrogen peroxide was examined. A new catalytic kinetic spectrophotometric method for the determination of chromium was developed. The feasibility of the proposed method was checked by its application to chromium determination in tap and industrial waters.

Experimental

Reagents

All solutions were prepared from analytical-reagent grade chemicals and doubly distilled water. The laboratory glassware was treated with an alkaline solution, rinsed with distilled water and then kept in HCl (1:1) overnight, followed by rinsing with distilled and doubly distilled water.

A stock standard solution of 0.1 mol L⁻¹ Cr(VI) was prepared from potassium dichromate (Fluka). Working solutions were prepared daily by appropriate dilution with 0.01 mol L⁻¹ HCl.

A stock standard solution of 0.1 mol L⁻¹ Cr(III) was prepared from chromium(III) chloride hexahydrate (Merck). Working solutions were prepared daily by appropriate dilution with doubly distilled water.

A 5.0 x 10⁻² mol L⁻¹ water solution of SA (Merck) was also prepared daily.

Water solutions of hydrogen peroxide were prepared from 35% hydrogen peroxide (Merck).

The medium pH was buffered with buffer solutions, prepared by 0.04 mol L⁻¹ acetic acid–boric acid–orthophosphoric acid and brought to the required pH using appropriate volumes of 0.2 mol L⁻¹ solution of sodium hydroxide (Merck).

Potassium cyanide solution (1.0 x 10⁻⁴ mol L⁻¹) was prepared as a masking agent.

Apparatus

Kinetic measurements were performed on a Specol 11 spectrophotometer fitted with 5-cm cells. The spectrophotometer cell compartments were thermostatted by means of circulating water.

Absorption spectra were recorded on a Specord-UV-Vis spectrophotometer using 1-cm quartz cells.

The acidity of the reaction mixture was checked using a pH-meter (Consort R 400).

Calibration procedure

In a 3-compartment reaction vessel (mixer) were placed 0.6 mL of 5.0 x 10⁻² mol L⁻¹ SA solution in the first compartment, 0.6 mL of 7 mol L⁻¹ hydrogen peroxide solution in the second and 0.0–0.6 mL of working chromium solutions in the third. Then 6.3–5.7 mL of buffer solution was divided into 3 approximately equal

aliquots and added to each compartment, so that the overall volume of the reaction mixture (7.5 mL) was roughly the same in each experiment.

The well-closed mixer with reagents was kept for 10 min at 60 °C and then the reagents were mixed by energetic shaking and transferred into a 5 cm constant temperature cell of a Specol 11 spectrophotometer. The absorbance at 360 nm was recorded as a function of time. The reaction rate was calculated from the absorbance-time kinetic curves using the tangent method. When the “fixed time” method was used the absorbance was read 15 min after the mixing.

Procedure for analysis of water samples

Collected samples were analyzed within 24 h of filtration.

In a test tube were placed 0.6 mL of 7 mol L⁻¹ hydrogen peroxide solution, 0.6 mL of standard chromium solution or water sample solution or distilled water, 0.2 mL of 10⁻⁴ mol L⁻¹ potassium cyanide and 5.5 mL of buffer solution (pH 6.6). The test tube was kept at 60 °C in a thermostated water bath for 10 min. Then 0.6 mL of SA (5.0 x 10⁻² mol L⁻¹) was added, the mixture was homogenized by shaking and transferred into a 5 cm constant temperature cell of the spectrophotometer. The absorbances were read at 360 nm 15 min after the addition of SA.

Results and Discussion

The initial experiments showed that both chromium(III) and chromium(VI) possess catalytic activity upon the reaction of oxidation of SA with hydrogen peroxide. That is why the influence of the reaction parameters on the reaction rate was studied in the presence of 2 chromium catalysts – chromium(III) and chromium(VI).

Catalytic action of chromium(III)

Optimum conditions

Figure 1 shows the influence of pH on the initial rate in the presence and absence of chromium(III). The different pH values were obtained by adding 0.2 mol L⁻¹ solution of sodium hydroxide to the 3-component mixture of 0.04 mol L⁻¹ acetic, boric and phosphoric acid. The absorbance was measured first 1 min after mixing and after that at 1-min intervals for 15 min.

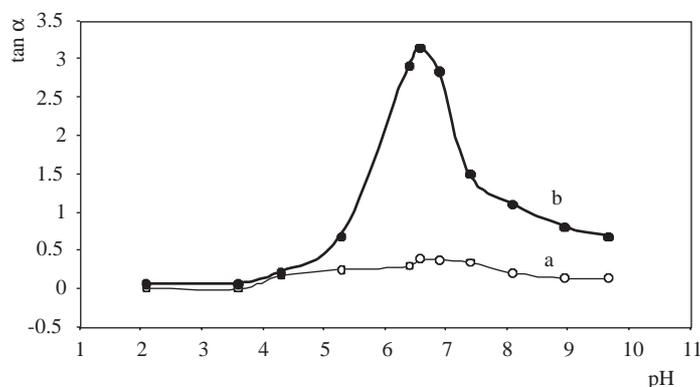


Figure 1. Influence of pH (a) in the absence of the catalyst and (b) in the presence of the catalyst 4 x 10⁻⁷ mol L⁻¹ Cr(III); λ 360 nm; temperature 50 °C; 0.004 mol L⁻¹ SA; 0.56 mol L⁻¹ H₂O₂.

The slope of the curve increased abruptly above pH 5, and the buffer of pH 6.6 provided the highest sensitivity in the determination of chromium(III).

Figure 2 shows the dependence of the initial reaction rate on the SA concentration. We chose 0.004 mol L⁻¹ as the optimal concentration because of the maximum sensitivity.

Figure 3 reflects the influence of the hydrogen peroxide concentration. The concentration of 0.56 mol L⁻¹ was chosen as optimal.

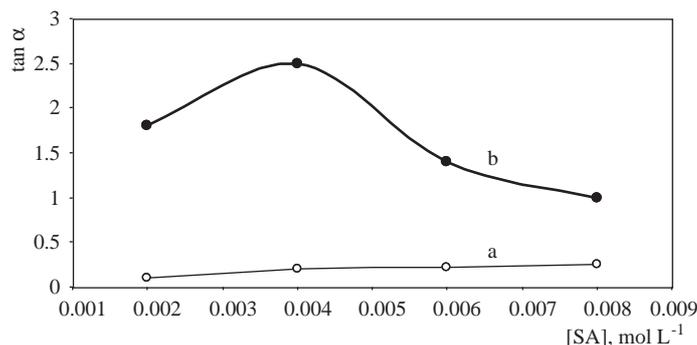


Figure 2. Influence of sulfanilic acid concentration. Other conditions and symbols as in Figure 1.

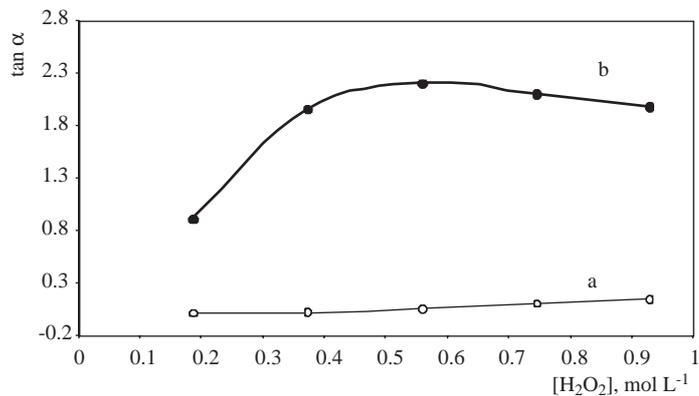


Figure 3. Influence of hydrogen peroxide concentration. Other conditions and symbols as in Figure 1.

The initial rates of the catalyzed and uncatalyzed reactions gradually increased with temperature in accordance with the Arrhenius equation. A temperature of 60 °C was adopted in the procedure to provide high sensitivity and a low blank reading.

Calibration graph

Under the optimal conditions a linear calibration graph up to 100 ng mL⁻¹ of chromium(III) was obtained, using the “fixed time” method. The equation of the calibration graph was $A = 0.079 + 0.010 \text{ Cr}_{(III)}$ with a correlation coefficient $r = 0.9863$, where $\text{Cr}_{(III)}$ is the concentration of chromium(III) expressed in ng mL⁻¹. The detection limit was 4.9 ng mL⁻¹ of chromium.

Catalytic action of chromium(VI)

Optimum conditions

The influence of the reaction parameters (acidity, temperature, reagent concentration) on the reaction rate was studied in the presence and absence of Cr(VI) to establish the optimum reaction conditions.

Figure 4 shows the dependence of the initial reaction rate on the acidity. A pH value of 6.6 was selected as optimum. The influence of the concentrations of SA and hydrogen peroxide was also studied and the results are shown in Figures 5 and 6, respectively. Concentrations of 0.004 mol L^{-1} SA and 0.56 mol L^{-1} hydrogen peroxide were chosen as optimal.

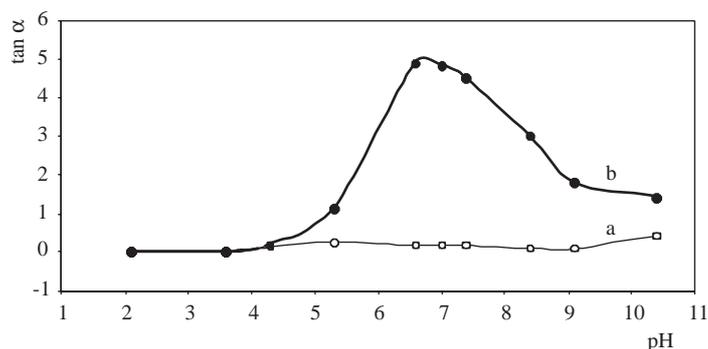


Figure 4. Influence of pH (a) in the absence of the catalyst and (b) in the presence of the catalyst $4 \times 10^{-7} \text{ mol L}^{-1}$ Cr(VI): λ 360 nm; temperature $50 \text{ }^\circ\text{C}$; 0.004 mol L^{-1} SA; 0.56 mol L^{-1} H_2O_2 .

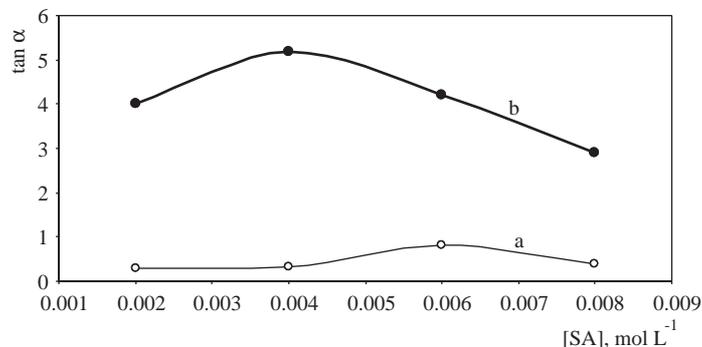


Figure 5. Influence of sulfanilic acid concentration. Other conditions and symbols as in Figure 4.

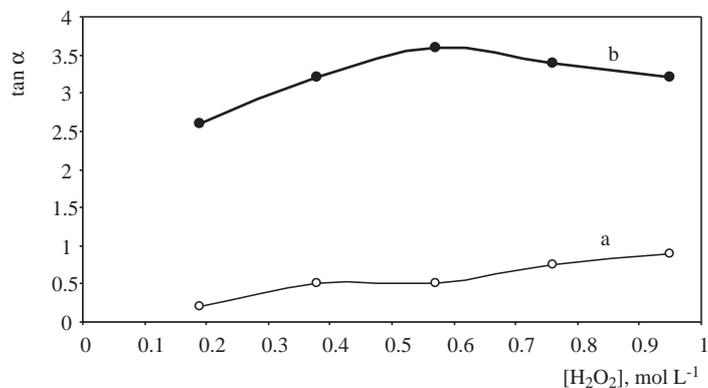


Figure 6. Influence of hydrogen peroxide concentration. Other conditions and symbols as in Figure 4.

The influence of temperature was studied between 20 and 70 °C. Increasing the initial rate of both catalyzed and uncatalyzed reactions satisfied the Arrhenius equation. A temperature of 60 °C was chosen because of the higher sensitivity and lower background.

Calibration graph

The calibration curve up to 200 ng mL⁻¹ of chromium(VI) was obtained by the “fixed time” method. The equation of the calibration graph was $A = 0.080 + 0.0167 \text{ Cr}_{(VI)}$ with a correlation coefficient $r = 0.9941$, where $\text{Cr}_{(VI)}$ is the concentration of chromium(VI) expressed in ng mL⁻¹. The detection limit was 3.8 ng mL⁻¹ of chromium.

On the mechanism of the catalytic action of chromium

Studies of the catalytic action of chromium on the reaction of oxidation of SA by hydrogen peroxide showed that, irrespective of the analyte's valency, Cr(III) or Cr(VI) as a catalyst, the optimum conditions found were the same, namely pH 6.6, 0.004 mol L⁻¹ SA, 0.56 mol L⁻¹ hydrogen peroxide and temperature 60 °C.

As seen in Figure 7, the absorption spectra of the reaction products for chromium(III) and chromium(VI) catalyzed reactions are similar. That is why we supposed that in both cases chromium acts as a catalyst in one and the same oxidation state.

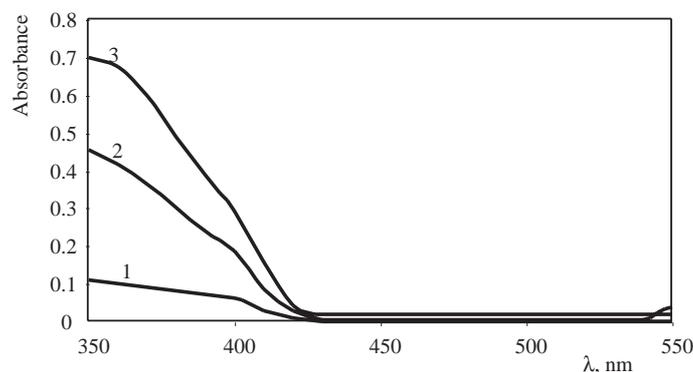


Figure 7. Absorption spectra of the reaction product (1) in the absence of the catalyst; (2) in the presence of 20 ng mL⁻¹ of Cr(III); (3) in the presence of 20 ng mL⁻¹ of Cr(VI). Conditions: 0.004 mol l⁻¹ SA; 0.56 mol l⁻¹ H₂O₂; pH 6.6; time 15 min, and temperature 60 °C.

We tried to stabilize the chromium(VI) oxidation state by dissolving potassium dichromate in a 0.18 mol L⁻¹ solution of sulfuric acid. No reaction was observed. Moreover, when we used a water solution of potassium dichromate, the reaction proceeded very slowly, and only when we dissolved potassium dichromate in a 0.01 mol L⁻¹ solution of hydrochloric acid was the catalytic action of chromium found. Thus we supposed that chromium(VI) is reduced at the reaction conditions to a lower oxidation state.

On the other hand, the concentration of hydrogen peroxide at the reaction conditions is approximately 10⁶ times higher than the chromium(III) concentration; thus we could consider that chromium(III) is oxidized by hydrogen peroxide to a higher oxidation state.

Analogous kinetic dependencies showed that the catalytic cycle in the process of oxidation of SA by hydrogen peroxide in the presence of chromium(III) and chromium(VI) is identical.

Probably during the proposed reaction chromium(VI) is reduced and chromium(III) is oxidized to chromium (IV) or chromium(V) and the catalytic action of chromium is due to the formation of an intermediate ternary complex between oxidant, catalyst and substrate – {H₂O₂...Cr^{V(IV)}...SA}. The presence of a maximum in pH and concentration dependencies could be reliable evidence for the formation of such a ternary complex.

It is worth noting that the initial reaction rate in the presence of chromium(VI) was greater than that in the presence of the same concentration of chromium(III). Chromium(III) was introduced in the reaction system in the form of its characteristic configuration, that is kinetically inert aquacomplexes (dark green CrCl₂(H₂O)₄Cl·2H₂O and violet Cr (H₂O)₆ Cl₃)²⁰. The replacement of water ligands in these complexes proceeds very slowly²⁰. That is why the formation of the catalytically active complex is slowed down.

The greater reaction rate in the presence of chromium(VI) could be explained by its reduction to chromium(IV) or chromium(V); thus the formation of the above-mentioned complex occurs without difficulties.

The definitive confirmation of the proposed mechanism needs some additional investigations, which are beyond the scope of the present work.

Study of interferences

The results of a study of the effect of 29 foreign ions on chromium(III) and chromium(VI) catalyzed reactions showed the same influences. The tolerated limits for the ions assayed are given in Table 1, where the tolerance level was defined as the concentration of foreign ion that produced a change in the absorbance of the catalyzed reaction of less than 5%. As can be seen, most ions were tolerated at high concentrations. The interferences of Cu²⁺ and Co²⁺ can be avoided by adding potassium cyanide.

Application

The results of our study showed that the reaction of oxidation of SA by hydrogen peroxide, catalyzed by chromium(III) or chromium(VI), can be applied for the determination of total chromium content.

The usefulness of the proposed method was tested by determining the chromium concentration in samples of circulating industrial water from a glass factory (Pleven, Bulgaria) and in tap water. The chromium concentration in the industrial water was previously determined by AAS to be 405 ng mL⁻¹.

Table 1. Effect of foreign ions on the determination of chromium (50 ng mL⁻¹).

Foreign ion	Tolerated ratio [ion] : [Cr(III)]	Tolerated ratio [ion] : [Cr(VI)]
K ⁺ , Na ⁺ , NH ₄ ⁺ , BO ₃ ³⁻ , PO ₄ ³⁻ , CH ₃ COO ⁻	>1000	>1000
Ca ²⁺ , Ba ²⁺ , Mg ²⁺ , Zn ²⁺ , Hg ²⁺ , Al ³⁺ , Mn ²⁺ , SO ₄ ²⁻ , Cl ⁻ , F ⁻	100	100
Cd ²⁺ , citrate, CN ⁻	45	50
Ni ²⁺ , Ag ⁺ , SCN ⁻	23	25
Fe ²⁺ , Fe ³⁺ , Pb ²⁺ , Mo ^{VI} , EDTA	18	20
Co ²⁺	5	5
Cu ²⁺	0.2	0.2

The chromium concentration was determined by applying the calibration curve and standard addition methods. Recovery tests (Table 2) were satisfactory (about 96.0%–103.8%) with relative standard deviations of 2.3%–4.1%.

Table 2. Recovery test for chromium determination in water samples.

Sample	Chromium concentration, ng mL ⁻¹		Relative standard deviation, %	Recovery, %
	Added	(mean ± standard deviation) (n = 5)		
Tap water 1	-	11.4 ± 0.4	3.5	-
	5.0	16.3 ± 0.6	3.7	98.0
	10.0	21.7 ± 0.6	2.8	103.0
Tap water 2	-	16.2 ± 0.4	2.5	-
	5.0	21.1 ± 0.5	2.4	98.0
	10.0	25.8 ± 0.6	2.3	96.0
Industrial water	-	394.7 ± 11.2	2.8	-
	50.00	446.6 ± 18.4	4.1	103.8
	100.00	492.8 ± 15.5	3.1	98.1

Conclusion

The catalytic effect of chromium(III) and chromium(VI) on the oxidation of SA by hydrogen peroxide was studied. A new catalytic kinetic spectrophotometric method for the determination of chromium was developed. The results suggest that during the reaction chromium(VI) is reduced and chromium(III) is oxidized to an intermediate oxidation state and the catalytic action of chromium is due to the formation of a ternary complex between oxidant, catalyst and substrate. The proposed method was successfully applied to chromium determination in tap and industrial waters with recovery of 96.0% –103.8%.

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