

Kinetic Spectrophotometric Determination of Chromium (VI) by Oxidation of Sodium Pyrogallol-5-sulphonate by Hydrogen Peroxide

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Summary. A new selective, sensitive, and simple kinetic method is developed for the determination of trace amounts of chromium (VI). The method is based on the catalytic effect of Cr(VI) on the reaction of sodium pyrogallol-5-sulphonate (*PS*) with hydrogen peroxide. The reaction is followed spectrophotometrically by tracing the oxidation product at 437 nm within 1 min after addition of H₂O₂. The optimum reaction conditions are *PS* ($1.32 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$), H₂O₂ ($0.32 \text{ mol} \cdot \text{dm}^{-3}$), HClO₄ ($2.6 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) at 25°C. Following this procedure, chromium (VI) can be determined with a linear calibration graph up to $0.25 \text{ ng} \cdot \text{cm}^{-3}$ and a detection limit of $0.024 \text{ ng} \cdot \text{cm}^{-3}$, based on the 3σ criterion. The interference effect of several species was also investigated and it was found that the most common cations and anions do not interfere with the determination. The developed procedure was successfully applied to the determination of Cr(VI) and total Cr in river waters and total Cr in herbal samples.

Keywords. Chromium determination; Kinetic spectrophotometric method; Sodium pyrogallol-5-sulphonate oxidation.

Introduction

The toxicity of chromium depends primarily on its chemical form. Trivalent chromium compounds are much less toxic than those of hexavalent chromium [1, 2]. Due to its high toxicity hexavalent chromium is under environmental scrutiny. Concern about the presence of hexavalent chromium in the environment resulted in the development of numerous analytical methods for the determination of Cr(VI) in different sample matrices.

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Ultrasonic extraction in alkaline solutions was reported to provide good extraction efficiency of Cr(VI) from workplace samples and allowed the retention of Cr(VI) on anion-exchange resin [3]. A field method for the determination of Cr(VI) in environmental and workplace air samples was also reported by applying alkaline ultrasonication and strong anion change solid phase extraction [4]. For speciation of Cr in natural waters, selective *pH* dependent preconcentration of Cr(VI) and Cr(III) was performed on high surface area adsorbents of Al_2O_3 [5] and TiO_2 [6], followed by ETAAS determination of the separated Cr species. Ion chromatographic speciation of Cr in natural waters with diphenylcarbazide spectrophotometric [7, 8] or chemiluminescence [9] detection was also reported and sequential injection wetting film extraction was applied to the spectrophotometric determination of Cr(VI) and Cr(III) [10]. All reported techniques were sensitive enough for the determination of traces of Cr(VI) at $\text{ng} \cdot \text{cm}^{-3}$ levels in natural waters. Atomic absorption spectroscopy [11], voltammetry [12], and high performance liquid chromatography [13] have also been used for determination of chromium (VI) with high sensitivity and selectivity, but suffer from more or less time consuming procedures and/or expensive and complicated instrumentation [7, 8, 10, 12, 13].

Few catalytic kinetic methods (CKM) for Cr(VI) determination at trace levels have also been published using various types of indicator reactions [14–16]. Some of these methods are based on the oxidation reaction of various reagents with H_2O_2 and have been reported to determine nanogram per cubic centimetre amounts of Cr(VI) [17, 18].

This paper describes a highly sensitive kinetic spectrophotometric determination of Cr(VI) based on its catalysis of the sodium pyrogallol-5-sulphonate oxidation by hydrogen peroxide in acidic medium. The proposed method allowed chromium (VI) in the range $0.25\text{--}10.0 \text{ ng} \cdot \text{cm}^{-3}$ to be determined with good accuracy and reproducibility.

Results

Catalytic Action of Chromium (VI)

The absorption spectra of *PS* recorded in perchloric acid solution (Fig. 1, curve 1), *PS*-perchloric acid-Cr(VI) ($c_{\text{Cr(VI)}} \geq 1 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$) and *PS*-perchloric acid-Cr(VI) ($c_{\text{Cr(VI)}} \leq 5 \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$) (curves 2 and 3, respectively), *PS*-perchloric

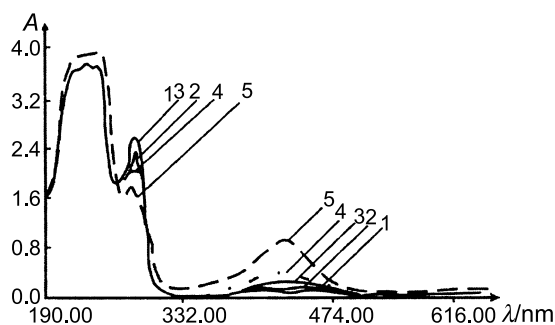


Fig. 1. Absorption spectra: spectrum 1, *PS* in HClO_4 ; spectra 2 and 3, *PS*- HClO_4 -Cr(VI); spectrum 4, *PS*- HClO_4 - H_2O_2 ; spectrum 5, *PS*- HClO_4 - H_2O_2 -Cr(VI) mixture 1 h after mixing

acid-hydrogen peroxide (curve 4), and *PS*-perchloric acid-hydrogen peroxide-Cr(VI) ($c = 1 \cdot 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$) (curve 5) 1 h after mixing (the absorbation maxima is constant 1 h after mixing).

The oxidation of *PS* with dichromate at the higher concentrations of $1 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ lead to the formation of a yellow oxidation product at 437 nm. The reaction is catalyzed by traces of As(III) and is used for its kinetic-catalytic determination [20]. However, the aim of this paper is to study the catalytic effect of Cr(VI) on the oxidation of *PS* by the hydrogen peroxide reaction. For further work chromium (VI) concentration of $10^{-7} \text{ mol} \cdot \text{dm}^{-3}$ was selected. No characteristic absorption maxima are seen in the visible part of the spectrum of a *PS*-perchloric acid-Cr(VI) solution mixture (curve 3) under the given optimum conditions for chromium (VI).

However, the oxidation of *PS* by a higher concentration of hydrogen peroxide ($c_{\text{H}_2\text{O}_2}/c_{\text{Cr(VI)}} \approx 10^5$) in the presence of perchloric acid is characterised by a slight maximum at 437 nm which significantly increases in the presence of chromium (VI). Therefore it can be concluded that chromium (VI) acts as catalyst in the *PS*-hydrogen peroxide reaction.

Effects of Reaction Variables

The influence of temperature, perchloric acid, *PS*, and hydrogen peroxide concentrations was studied for both, the catalytic and non-catalytic, reactions in order to establish optimum conditions for determination of chromium (VI).

The influence of temperature on the reaction rate was studied in the range 22–34°C. The absorbance-time curves at different temperatures showed that the absorbance increases linearly during the first 10 min, and does not change after 35 min. The slopes of these curves become steeper when the temperature increases. However, although higher sensitivity could be obtained at higher reaction temperature, it was troublesome to control the temperature precisely at the elevated temperature, hence a reaction temperature of 25°C was chosen.

Keeping all other experimental parameters constant, the perchloric acid dependence of the system was studied in the range $2.2 \cdot 10^{-3}$ – $6 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ (Fig. 2).

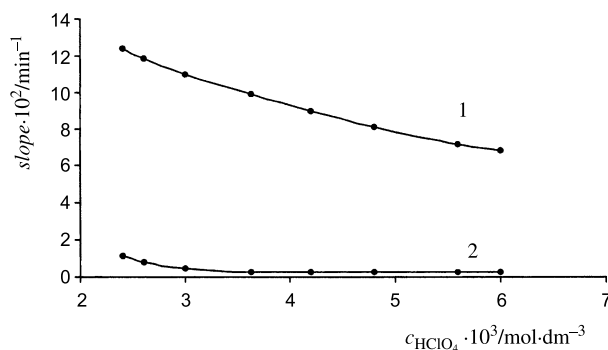


Fig. 2. Dependence of the reaction rate on the HClO_4 concentration; initial concentrations: *PS*, $8.8 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$; H_2O_2 , $0.16 \text{ mol} \cdot \text{dm}^{-3}$; Cr(VI), $0.1 \mu\text{g} \cdot \text{cm}^{-3}$, curve 1, catalytic reaction; curve 2, non-catalytic reaction

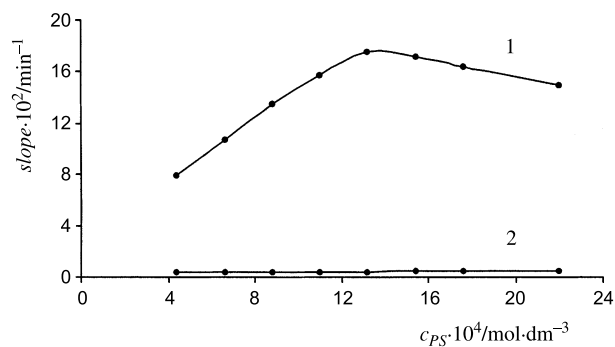


Fig. 3. Dependence of the reaction rate on the *PS* concentration; initial concentrations: H_2O_2 , $0.32 \text{ mol} \cdot \text{dm}^{-3}$; HClO_4 , $2.6 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, Cr(VI) , $0.1 \mu\text{g} \cdot \text{cm}^{-3}$; curve 1, catalytic reaction; curve 2, non-catalytic reaction

It can be seen that the greatest difference between the reaction rates occurs at $2.6 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$. For further work a perchloric acid concentration of $2.6 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ was selected. The logarithmic plot ($\log(\text{slope} \cdot 10^2) - \log c_{\text{HClO}_4}$) shows that the reaction rate is inversely proportional to the perchloric acid concentration (non-catalytic reaction is -0.8 and catalytic reaction is -0.4 order with respect to the HClO_4 concentration, respectively).

The dependence of the reaction rate on H_2O_2 concentration shows that with increasing hydrogen peroxide concentration the difference between the rates of the catalytic and non-catalytic reaction increases. Both reactions are first order with respect to the H_2O_2 concentration. For further work a H_2O_2 concentration of $0.32 \text{ mol} \cdot \text{dm}^{-3}$ was selected.

The dependence of the reaction rate on the concentration of *PS* is shown in Fig. 3. It shows that the non-catalytic reaction is first order with respect to the *PS* concentration, whereas the catalytic reaction is first order with respect to *PS* concentration up to $1.32 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ and inversely proportional for higher concentrations. For further work a *PS* concentration of $1.32 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ was selected.

The absorbance-time curves for solutions containing different amounts of chromium (VI) were recorded against a similar solution containing no chromium. The initial slopes indicate a first order reaction with respect to chromium (VI).

On the basis of the kinetic investigation, the following equation is suggested for the chromium (VI) catalyzed oxidation of *PS* by hydrogen peroxide in acidic medium.

$$\frac{dx}{dt} = k_1 \cdot [\text{HClO}_4]^{-0.4} \cdot [\text{H}_2\text{O}_2] \cdot [\text{PS}] \cdot [\text{Cr(VI)}], \quad \text{for } [\text{PS}] < 1.32 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \quad (1)$$

The kinetic equation for the non-catalytic reaction under the same conditions may be written as follows (Eq. (2)) where k_1 and k_0 are the relative rate constants for the catalytic and non-catalytic reactions. On the basis of these equations the rate constants for the catalytic and non-catalytic reactions were calculated.

$$\frac{dx}{dt} = k_0 \cdot [\text{HClO}_4]^{-0.8} \cdot [\text{H}_2\text{O}_2] \cdot [\text{PS}] \quad (2)$$

Table 1. Linear concentration range, accuracy, and precision of the kinetic methods for the determination of chromium (VI)

Method	Concentration range of Cr(VI)/ng · cm ⁻³	Relative standard deviation ^a /%	<i>t'</i> _{exp}
Tangent	0.25–15.00	<0.9 ^b	0.98 ^c
Fixed-time	0.25–15.00	<1.18 ^b	1.82 ^c
Fixed-absorbance	2.00–15.00	<1.25 ^b	3.05 ^c

^a n = 5, ^b for the concentration range mentioned, ^c *t* = 2.77

A linear relationship between the logarithm of the relative rate constant and the reciprocal of the absolute temperature was found for the catalytic as well as the non-catalytic reaction. The activation energies were found to be 25.2 kJ · mol⁻¹ for the catalytic reaction and 45.6 kJ · mol⁻¹ for the non-catalytic reaction.

Calibration

The tangent method was used to calculate the rate of the catalyzed reaction, which was plotted as a function of the chromium (VI) concentration. The fixed-time and the fixed absorbance (variable time) methods were also used. For the fixed-time method, measurements were made after 5 min. For the fixed-absorbance method, the inverse of the time necessary to obtain an absorbance of 0.200 was plotted against the chromium concentration. In all cases, the calibration graph is linear in the concentration range indicated in Table 1. The accuracy and precision of the three methods applied for 3.0 ng · cm⁻³ Cr are included in Table 1, from which it is concluded that the fixed-absorbance method has a positive systematic error (*t'*_{exp} > *t*) whereas the tangent method is more precise. Therefore the tangent method is recommended.

The least squares' equation for the calibration graph is given in Eq. (3) with *r* = 0.985, where *c*_{Cr(VI)} is the chromium concentration expressed in ng · cm⁻³.

$$\text{slope} \cdot 10^2 = 0.0055 \cdot c_{\text{Cr(VI)}} + 0.0042 \quad (3)$$

It was established that the detection limit was 2.4 · 10⁻² ng · cm⁻³ Cr(VI) and the determination limit was 8.0 · 10⁻² ng · cm⁻³ Cr(VI) [21].

Interferences Studies

The interference of several foreign ions was investigated by 2σ (σ-standard deviation) criteria [22, 23] on the determination for a constant chromium (VI) concentration of 10.0 ng · cm⁻³. In Table 2 tolerance levels of anions and cations usually found in real samples are presented.

Many of the cations and anions do not interfere at a ratio of foreign ion to Cr(VI) of 1000:1 and 100:1, respectively. Positive interference was observed for Cu²⁺ and Fe³⁺, because they also act as catalysts of the oxidation reaction [24]. To avoid interference of Fe³⁺ and Cu²⁺, they were masked by addition of fluoride and S₂O₃²⁻ ions, respectively.

Table 2. Tolerance levels of interferents in the kinetic determination of $10 \text{ ng} \cdot \text{cm}^{-3}$ chromium (VI)

Ion added ^a	Tolerance level, $c_{\text{ion}}/c_{\text{Cr(VI)}}$
Ca(II), Sr(II), Mg(II), Ba(II), $\text{S}_2\text{O}_3^{2-}$, Sn(II), Se(IV)	1000 ^b
VO_3^- , S^{2-} , Br^- , CN^- , F^-	500
Cd(II), Ni(II), Al(III), AsO_3^{3-} , WO_4^{2-} , SO_4^{2-} , PO_4^{3-} , SCN^- , $\text{C}_2\text{O}_4^{2-}$, acetate, citrate, tartarate	100
Zn(II), Pb(II), Hg(II), Co(II), MoO_4^{2-}	10
Cu(II), Fe(III) (catalyzed)	5

^a Cations added as chlorides or nitrates, anions as sodium or potassium salts, ^b maximum concentration studied

Applications

The technique described in Experimental was applied to the determination of chromium (VI) and total chromium in river waters and total chromium in herbal samples. The results obtained by interpolation of a calibration graph and by the

Table 3. Determination of chromium in waters

Water sample	Cr(VI) found/ $\text{ng} \cdot \text{cm}^{-3}$		Total Cr found/ $\text{ng} \cdot \text{cm}^{-3}$		
	Kinetic method		Kinetic method		Atomic absorption method ^c
	I ^a	II ^b	I ^a	II ^b	
Nishava river (selected at Piro)	9.25 ± 0.21	9.23 ± 0.28	32.89 ± 0.38	31.21 ± 0.60	30.2 ± 0.8
Nishava river (selected at B. Palanca)	8.92 ± 0.20	9.00 ± 0.23	22.42 ± 0.36	22.04 ± 0.52	20.3 ± 0.7
Nishava river (selected at Nis)	8.88 ± 0.21	8.90 ± 0.32	20.63 ± 0.42	19.52 ± 0.50	20.0 ± 0.8

^a Standard addition, ^b direct calibration, ^c at 357.9 nm

Table 4. Determination of total chromium in herbal samples

Herbal sample ^a	Cr found/ppb		
	Kinetic method		Atomic absorption method ^d
	I ^b	II ^c	
cabbage	13.54 ± 0.12	13.90 ± 0.20	13.0 ± 0.9
lettuce	17.05 ± 0.52	17.18 ± 0.32	16.9 ± 0.5
spinach	23.32 ± 0.48	23.03 ± 0.40	23.8 ± 0.3

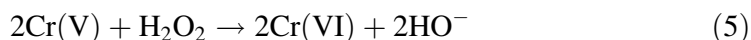
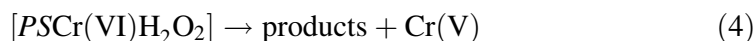
^a Herbal samples were digested in HNO_3 and then Cr(III) was oxidized to Cr(VI) (it was only possible to determine total chromium), ^b standard addition, ^c direct calibration, ^d at 357.9 nm

method of standard additions are given in Tables 3 and 4, respectively. The results obtained by the proposed method were compared with those obtained by atomic absorption spectrometry (AAS). The values for river waters and herbal samples are in good agreement with those obtained by the AAS method. These results show that, the proposed method is applicable to determination of chromium in waters and in other samples.

Discussion

The mechanism of the catalytic reaction applied has not been completely elucidated. Figure 4 shows the absorption spectra of the oxidation product in the presence of Cr(VI) (curve 1) and Cr(III) (curve 2). It can be seen that chromium (VI) strongly catalyzed the oxidation of *PS* by hydrogen peroxide in acidic media. The aquacomplexes of Cr(III) are reported to be kinetically very inert. The catalytic action of Cr(III) on the formation of the complex with *PS* is probably related to the prior decomposition of the aquacomplexes [25].

The dependence of the reaction rate on the H_2O_2 or *PS* concentration indicates that the reaction proceeds under prior formation of a peroxocomplex $[\text{Cr(VI)}-\text{H}_2\text{O}_2]$ [26] followed by the formation of an intermediate complex of the catalyst-reductant-oxidant type [27] and the catalyst (reactions 4 and 5).



It can be assumed that the second reaction proceeds much faster than the first one. The reduced chromium (V) is oxidized to chromium (VI) by hydrogen peroxide and than the chromium (VI) formed to reacts with *PS* again [28, 26]. Probably for this reason, a large excess of hydrogen peroxide with respect to the reagent is needed. The oxidation product was not identified. However, *PS* could be oxidized by a one-electron mechanism to produce a resonance-stabilised product [29, 23, 24], a quinoid species seems probable.

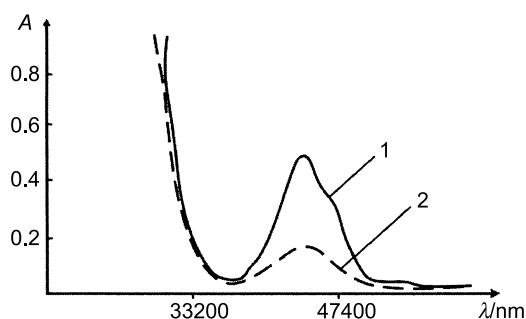


Fig. 4. Absorption spectra of the *PS*- HClO_4 - H_2O_2 mixture in the presence of (1) Cr(VI) ($0.1 \mu\text{g} \cdot \text{cm}^{-3}$) and (2) Cr(III) ($1.0 \mu\text{g} \cdot \text{cm}^{-3}$) 5 min after mixing

Experimental

Reagents and Apparatus

All chemicals were of analytical reagent grade from Merck unless indicated otherwise. Solutions were made up in deionised water. Hydrogen peroxide solution ($3.2 \text{ mol} \cdot \text{dm}^{-3}$) was prepared by appropriate dilution of the Merck pro analysi reagent and was standardised against potassium permanganate solution. Sodium pyrogallol-5-sulphonate (*PS*) was synthesized by dissolving pyrogallol in sulphuric acid (96%) [19]. The $8.8 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ solution of the reagent was used. Chromium (VI) stock solution ($1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) was prepared by dissolving 0.2942 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in deionised water and dilution to 1 dm^3 . Chromium (VI) working solution was prepared by appropriate dilution of the stock solution. The perchloric acid solution ($0.026 \text{ mol} \cdot \text{dm}^{-3}$) was prepared from the 70% reagent.

All stock solutions were stored in polyethylene containers. Working solutions of chromium, hydrogen peroxide, and *PS* were prepared immediately before use.

All polyethylene containers and glassware used were cleaned in aqueous HCl (1:1) and then thoroughly with deionised water.

A Perkin-Elmer Lambda 15 spectrophotometer, connected to a thermocirculating bath was used for the absorbance measurements. The *pH* was measured by means of a Radiometer PHM 29 *pH* meter and a combined glass-calomel electrode GX 2311 C. The solutions were thermostated at $25 \pm 0.1^\circ\text{C}$ before the beginning of the reaction.

Treatment of River Water Samples for Determination of Chromium (VI)

The sample (1 dm^3) of freshly collected water was filtered through a $0.45 \mu\text{m}$ Millipore filter and perchloric acid was added to the filtrate. 1 cm^3 of the sample was used for the kinetic procedure. Selected amounts of the reagents were transferred to a 10 cm^3 standard flask in the order *PS*, perchloric acid, sample, catalyst, and F^- ($1 \mu\text{g} \cdot \text{cm}^{-3}$) and $\text{S}_2\text{O}_3^{2-}$ ($1 \mu\text{g} \cdot \text{cm}^{-3}$) (masking agents for Fe^{3+} and Cu^{2+}). The absorbance at 437 nm was measured every 30 s over a period of 5–8 min after the addition of H_2O_2 .

Treatment of River Water Samples for Determination of Total Chromium

The sample (1 dm^3) of freshly collected water was filtered through a $0.45 \mu\text{m}$ Millipore filter and perchloric acid was added to the filtrate. The chromium (III) is oxidized to chromium (VI) by perchloric acid. After this treatment 1 cm^3 of the sample was used for the kinetic procedure. Selected amounts of the reagents were transferred to a 10 cm^3 standard flask in the order *PS*, perchloric acid, sample, catalyst, and F^- ($1 \mu\text{g} \cdot \text{cm}^{-3}$) and $\text{S}_2\text{O}_3^{2-}$ ($1 \mu\text{g} \cdot \text{cm}^{-3}$) (masking agent for Fe^{3+} and Cu^{2+}). The absorbance at 437 nm was measured every 30 s over a period of 5–8 min after the addition of H_2O_2 .

Treatment of Cabbage, Lettuce, and Spinach Samples for Determination of Total Chromium

1 g of each herbal sample was digested with 5 cm^3 of 16 M HNO_3 in a covered beaker to near dryness. If necessary, another 5 cm^3 portion of 16 M HNO_3 was added as often until the sample solutions became clear. 1 cm^3 of 0.12 M HCl was then added to ensure complete digestion. After cooling to room temperature, the digested solutions were diluted to 100 cm^3 with deionized water for Cr analysis [11]. The concentration of this acid, after dilution with deionized water as indicated in the procedure, did not modify the working *pH*. After this treatment 2 cm^3 were used for the recommended procedure. Into a series of 10 cm^3 standard flasks pipette aliquots of the sample, *PS*, perchloric acid, catalyst, F^- and

$\text{S}_2\text{O}_3^{2-}$ solutions were transferred. The absorbance at 437 nm was measured every 30 s over a period of 5–8 min after the addition of H_2O_2 .

Determination of Chromium

Into a 10 cm^3 standard flask with a glass stopper, a suitable aliquot of chromium (VI) solution was transferred. Then, 1 cm^3 of perchloric acid solution and 1.5 cm^3 of PS solution were added, and the solution was diluted to 9 cm^3 with water. The solution was kept at $25 \pm 0.1^\circ\text{C}$ in the thermostated bath. After the temperature of the solution had reached 25°C (about 5 min), 1 cm^3 of hydrogen peroxide solution was added to initiate the reaction. The spectrophotometer cell was rinsed well and filled with the solution. The absorbance at 437 nm was measured every 30 s over a period of 5–8 min after the addition of hydrogen peroxide. The method of tangents was used and the reaction rate (dA/dt) was calculated from the slope of the initial linear part of the absorbance-time graph. The measurements were made at $25 \pm 0.1^\circ\text{C}$.

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