Research Article

Development of a Spectrophotometric Method for Determination of Hydrogen Peroxide using Response Surface Methodology

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Abstract

A spectrophotometric method was introduced for determination of hydrogen peroxide in different samples. The method is based on the hydroxylation of phenol. The reaction takes place in the presence of Fe^{2+} in the sulfuric acid medium. Factors influencing the reaction were explored by response surface methodology. Inoptimal conditions, a wide linear range for calibration was obtained as 2.0×10^{-7}-3.0×10^{-4}mol L^{-1} and its detection limit was 9.5×10^{-8}mol L^{-1}. The product of the reaction possesses two bands with maxima located at 245 and 300 nm. The method was successfully applied for determination of hydrogen peroxide in water and rainwater samples.

Keywords: Spectrophotometric; Hydrogen peroxide; Response surface methodology; Rain water

Introduction

Hydrogen peroxide (H_2O_2) is one of the reactive oxygen species found in seawater as a product formed photo chemically from dissolved organic matter (DOM) [1]. Hydrogen peroxideis a key species in the reactions of the troposphere, being involved in important reactions such as the catalyzed and uncatalyzed aqueous phase oxidation of Sulphur dioxide (SO_2) and the ultraviolet enhanced aqueous phase oxidation of organic species [2].

Hydrogen peroxide is widely used in the fields of foods, pharmaceuticals, dental products, textiles, environmental protection and it is also involved in advanced oxidation processes and various biochemical processes [3-6].

Determination of hydrogen peroxide is usually based on the production of colored peroxy compounds or on its oxidizing and reducing properties [7]. Based on this property, numerous methods have been developed for the determination of hydrogen peroxide. These methods can be classified into spectrophotometric [2,5,8-11], spectrofluorimetric [12-14] and electrochemical methods [15-22]. However, chromatographic methods have also been applied for determination of hydrogen peroxide [23-25].

Exploration of the literatures reveals that hydrogen peroxide has been found rather ubiquitously in a wide range of concentrations in natural waters. In ground water, the concentrations as low as 50 nmol L^{-1} [26] has been reported. In the surface oceans, concentration of hydrogen peroxide varies from about 10 to several hundred nmol L^{-1} [27,28]. In lakes, estuaries and rivers, higher concentrations up to several µmol L^{-1} have been reported [29,30]. In rain water, the highest concentrations ranging from several µmol L^{-1} to tens of µmol L^{-1} [30-33] have been obtained. Therefore, in addition to the need for a rapid, simple and sensitive method for determination of hydrogen peroxide, it is necessary to develop a method with a wide dynamic linear range.

Hydrogen peroxide involves in Fenton reaction, which is very important in both laboratories and industries [5,34,35]. In the present work, the reaction of hydrogen peroxide with phenol in acidic solution and in the presence of Fe^{2+} provides a method for the spectrophotometric determination of hydrogen peroxide in aqueous solution.

Experimental

Apparatus

Recording of the absorption spectra in the spectral range of 200–400 nm was performed by an Agilent 8453 UV-Vis spectrophotometer equipped with diode array detector in 1 cm path length quartz cells. Design and analysis of the experiments were carried out by the MINITAB (Minitab Inc. Release 16.0) statistical package.

Sample collection

Rainwater was collected in three container located in different area of Razi University during a rainy night. Volumes equivalent to 10 mL of each container were taken and mixed and homogenized well. Three 100 mL tap water samples were collected in different times in a day without adding any preservative. After mixing the water samples of each type and homogenizing, an appropriate volume was taken for the analysis. The selected water samples were filtered through a Whatman No. 41 filter paper.

Reagents and solutions

All of the chemicals and reagents used in this work were of analytical reagent grade. Iron chloride ($FeCl_2$), H_2O_2 (35%, w/w), phenol and sulfuric acid were purchased from Merck (Darmstadt, Germany).Deionized water was used in all experiments.

A stock 0.01molL^{-1} standard solution of hydrogen peroxide was prepared in deionized water. Working solutions were prepared by diluting the standard stock solution to appropriate volumes with deionized water whenever required. Stock 300.0 mgL^{-1} standard

Table 1: Experiments based on the central composite design with three factors (responses at 245 nm and 300 nm).

Experiment no.	x_1 (mol L^{-1})	x_2 (mol L^{-1})	x_3 (mg L^{-1})	Response 245 nm	Response 300 nm
1	0.25	5.00×10^{-5}	50.0	0.006	-0.021
2	0.15	0.00	100.0	-1.551	-1.232
3	0.00	2.75×10^{-4}	100.0	0.772	0.236
4	0.25	5.00×10^{-5}	150.0	0.164	0.092
5	0.15	2.75×10^{-4}	100.0	0.806	0.466
6	0.05	5.00×10^{-4}	50.0	1.045	0.638
7	0.25	5.00×10^{-4}	50.0	0.918	0.567
8	0.25	5.00×10^{-4}	150.0	1.009	0.610
9	0.15	2.75×10^{-4}	100.0	0.913	0.537
10	0.05	5.00×10^{-5}	150.0	0.272	0.141
11	0.32	2.75×10^{-4}	100.0	0.665	0.358
12	0.15	2.75×10^{-4}	100.0	0.722	0.407
13	0.05	5.00×10^{-5}	50.0	0.151	0.081
14	0.15	2.75×10^{-4}	100.0	0.951	0.561
15	0.15	2.75×10^{-4}	100.0	0.820	0.476
16	0.15	6.50×10^{-4}	100.0	1.078	0.637
17	0.15	2.75×10^{-4}	100.0	0.753	0.430
18	0.05	5.00×10^{-4}	150.0	1.237	0.719
19	0.15	2.75×10^{-4}	184.0	0.818	0.486
20	0.15	2.75×10^{-4}	16.0	0.821	0.488

Table 2: ANOVA table for the factors and different interaction terms.

Term	Coefficient	Standard error	t^a	p^b
Constant	0.472	0.085	5.544	0.000
x_1	-0.009	0.056	-0.162	0.874
x_2	0.394	0.056	6.973	0.000
x_3	0.022	0.056	0.382	0.710
$x_1×x_1$	-0.020	0.055	-0.363	0.724
$x_2×x_2$	-0.230	0.055	-4.183	0.002
$x_3×x_3$	0.047	0.055	0.859	0.411
$x_1×x_2$	-0.004	0.074	-0.050	0.961
$x_1×x_3$	0.002	0.074	0.025	0.981
$x_2×x_3$	-0.006	0.074	-0.084	0.935
Regression				
F	7.55			
p	0.002			
R^2%	87.17			

a. Statistical t value.
b. Probability value.

solutions of phenol and 5.00×10^{-3}molL^{-1} FeCl$_2$ were prepared in deionized water.

Results and Discussion

Response surface methodology

By using design of experiment (DOE) based on statistical principles, researchers can extract, from a minimum number of experiments, a maximum of useful information about the system under study [36]. Among this information is the interaction between the factors. For this purpose, all factors are changed from one experiment to the next, simultaneously. The reason of performing this type of experiment is that variables can influence each other and the optimal value for one of them may be dependent on the values of the others [36]. Interaction means that the effect of a factor on the response depends on its level or on the level of the other factor(s). In response surface methodology (RSM), surface illustration of the variation of the response with the change in the level of factors is used to decide about how the levels of factors influence the response. In central composite design (CCD), as a response surface methodology, the central point for each factor in the coded form is zero and the design is symmetrical around it [37]. Factors and their considered center points in the current experiments are concentration of sulfuric acid (x_1), Fe^{2+}(x_2) and phenol (x_3) are 0.15 mol L^{-1}, 2.75×10^{-4}mol L^{-1} and 100.0 mg L^{-1}, respectively. For a system with three factors (n = 3), CCD consists of 20 experiments. Values of the factors in these 20 experiments and obtained responses are shown in Table 1. Concentration of hydrogen peroxide in these experiments is 1.00×10^{-4}mol L^{-1}.

The responses are the changes of absorbances at the specified
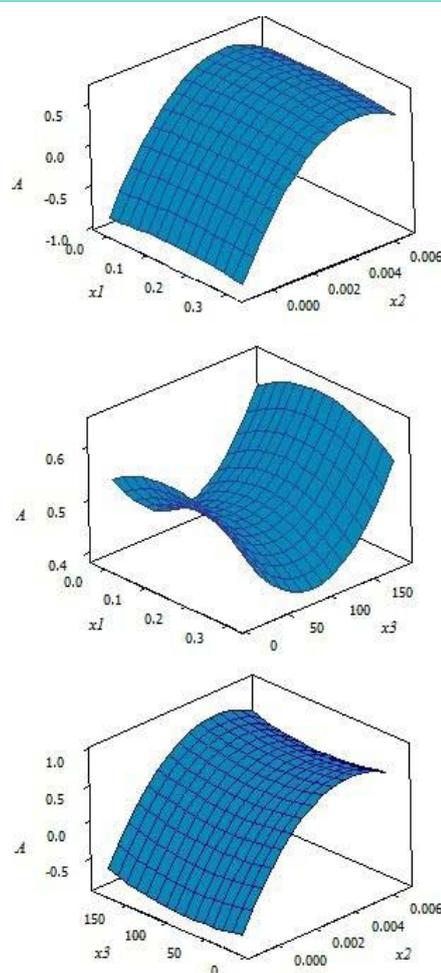
Figure 1: Variation of the response with (a) x_1 and x_2, (b) x_1 and x_3 and (c) x_2 and x_3.

wavelengths after addition of hydrogen peroxide to the mixture of the reagents at optimal values. In experiments 1 and 2, negative values can be seen. In these cases, after addition of hydrogen peroxide, absorbances decrease. In experiment 2, this decrease is very large. This can be due to the absence of Fe^{2+}.

Analysis of variance (ANOVA) of the experiments in Table 1, considering responses at 300 nm, has been collected in Table 2. Relatively high values of errors of the coefficients refer to the selection of a narrow range of the factors in the designed experiments. In fact, the main purpose was to optimize the factors not to find the significant factors.

Statistical parameters of the model (F, p and R^2%) with the terms in the Table 2 indicate that the model is reliable and can be utilized for prediction purposes. Very small value of the p value of the model reveals that the variation in response is mainly due to the change in the level of factors not noise and isn't by chance. As the value of R^2% shows, the regression explains 87.17% of the variations in the response with change in factor levels. Exploring the p values of the square terms shows that the overall effect of the linear terms is statistically significant at the 95% confidencelevel ($p< 0.05$). Among them, concentration of Fe^{2+}(x_2) is the most significant term with $p=0.000$. The most significance square term is $x_2 \times x_2$. The interaction terms are not significant at the 95% confidence level.

In order to gain insight about the effect of each factor and also analyze the variation of the response surfaces, the three dimensional (3D) graphs for the response were plotted based on the nonlinear polynomial model as shown in Figure 1. These figures show the relationship between two factors and response at the center of the other factor. As can be seen from Figure 1a and Figure 1c, with change in the level of x_2 (concentration of Fe^{2+}), curvature occurs in the response surface. This confirms the significance of the term $x_2 \times x_2$ which was also concluded from p values. Response surfaces in Figure 1a and Figure 1c show that in relatively high concentrations of Fe^{2+} the response is higher. The lowest influence on the response can be seen for x_1 (concentration of sulfuric acid).

Spectral behavior

Spectrum of the reagent mixture (phenol, Fe^{2+} and sulfuric acid) and spectrum of the mixture in the presence of two concentrations of hydrogen peroxide have been shown in Figure 2. As can be seen, the reagent mixture has a main intense peak located at about 275 nm with a broad shoulder. The peak at 275 nm can be related to phenol and the shoulder to Fe^{2+} in the sulfuric acid medium. In the presence of hydrogen peroxide, the absorbance in the whole range (220-400 nm) increases (see Figure 2). The increase in absorbance results in the evolution of two new bands at 245 and 300 nm which are attributed to the product. The intense band at about 275 nm belongs to phenol. Therefore, this band can't be used for the analysis.

The mechanism of the reaction between phenol and hydrogen peroxide in the presence of Fe^{2+} in sulfuric acid medium can be written as [5,34,35]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \qquad (1)$$

$${}^{\bullet}OH + C_6H_5OH \rightarrow C_6H_4(OH)_2 \qquad (2)$$

As stated by Zazo et al. [38], the main products of the oxidation of
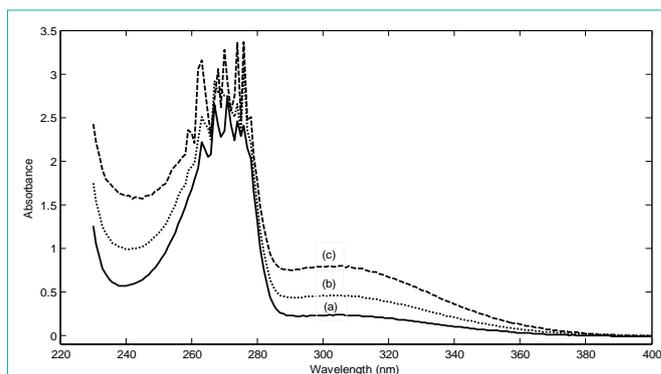
Figure 2: (a) Spectra of reagent mixture (phenol = 180 mg L^{-1}, Fe^{2+} = 5.0×10^{-4} mol L^{-1} and sulfuric acid = 0.05 mol L^{-1}), (b) reagent mixture in the presence of hydrogen peroxide with concentration of 4.0×10^{-5} mol L^{-1} and (c) reagent mixture in the presence of hydrogen peroxide with concentration of 1.0×10^{-4} mol L^{-1}.

Table 3: Statistical results of the calibration of hydrogen peroxide by the proposed method.

Parameters	Characteristic	
	Calibration curve1	Calibration curve 2
RSD% λ_{max} (nm)	245	300
Molar absorptivity (L mol^{-1} cm^{-1})	4.6×10^3	2.6×10^3
Linear range (µmolL^{-1})	0.20-300.00	0.20-300.00
Intercept of calibration curve	0.060	0.042
Slope of calibration curve	4477.9	2594.1
Standard error of intercept	0.020	0.015
t statistics of intercept	3.07	2.72
Standard error of slope	168.5	137.7
Standard error of regression	0.045	0.037
t statistics of slope	26.57	18.84
R^2	0.9916	0.9807
Detection limit (µmol L^{-1})[a]	0.095	0.170

a. Calculated as DL = y_B + 3s_B, where y_B is the signal of the blank (intercept of the calibration curve) and s_B is the standard deviation of the blank.

phenol by Fenton's reagents (hydrogen peroxide and Fe^{2+}) are catechol, hydroquinone and p-benzoquinone. The first two compounds have two hydroxyl groups in the benzene ring. Under the experimental conditionsof the work by Zazo et al. [38], close to 90% of phenol is converted in about 30 min, giving rise to dihydroxybenzenes upon hydroxylation of the aromaticring and catechol is the main primary oxidation product. This indicates that hydroxylation takes place predominantly in the ortho position.

Calibration

The calibration graphs for the determination of hydrogen

Table 4: Results of the analysis of the real samples by the proposed method. The results are for five determinations.

Real sample	Added concentration	Predicted concentration	RSD%	Percent recovery
Tap water	0.0	9.7	4.3	98.6
	50.0	59.0	4.2	
Rain water	0.0	42.0	3.5	106
	50.0	95.0	3.1	

Table 5: Reported results for determination of hydrogen peroxide.

Reagents	Dynamic linear range ($\mu molL^{-1}$)	Limit of detection ($\mu molL^{-1}$)	Remarks	Ref.
Metal nanoparticle loaded carbon nanotube modified screen printed carbon electrode	100.0-1000.0	20	Amperometry	[19]
Rhodium nanoparticle-modified screen-printed graphite electrodes	5-600	2	Electrochemical	[20]
MWCNT-cysteamine-Nafion modified gold electrode	0.1-70.0	-	Electrochemical	[21]
An ionic liquid-Fe_3O_4 nanoparticles-graphite composite electrode	1–25	0.5	electrochemical	[18]
l-anilinonaphthalene-8-sulfonic acid	l-50	0.3	spectrophotometric	[39]
Eriochrome black T	0.2–10.0	-------------	Spectrophotometric	[40]
2,9-dimethyl-l,l0-phenanthroline (DMP)	1.0-120.0	_____	spectrophotometric	[41]
titanium(IV)in presence of H_2SO_4	4.0 -60.0	1.0	spectrophotometric	[42]
1,l0-Phenanthroline	2.94 – 74.0	--------------------	Spectrophotometric	[43]
4,7-diphenyl-1,l0-phenanthroline	0.882- 2.94	--------------------	Spectrophotometric	[43]
Ceric ion in acid solution	----------------	2.94	Spectrofluorimetric	[7]
Amodifed p-hydroxyphenylacetic acid (PHPA)	1.47- 1.47×10^3	0.29	Spectrophotometric	[2]
	0.5–58.75	0.4	Amperometric	[44]
Leuco Crystal Violet		0.02	Spectrophotometric	[45]
Osmium(VIII) and m-carboxyphenylfluorone (MCPF)	0.588–11.94	------------	Spectrophotometric	[46]
Phenol,Fe_2+,H_2SO_4	0.20-300.00	0.0946 (245nm)	This method	
		0.17 (300nm)		

peroxide were obtained under the optimal reaction conditions. Calibration curves were obtained by adding different concentrations of hydrogen peroxide to the solution containing Fe^{2+}, phenol and sulfuric acid in optimal values. Absorbances at 245 nm and 300nm were used to obtain calibration curves. Statistical parameters of the calibration curves have been collected in Table 3.

Clearly, sensitivities of the calibration curves are different in different wavelengths. This is due to the different absorptivity of the product in different wavelengths.

As can be inferred from data in Table 3, linear range of the two calibrations is wide (more than three orders of magnitude). Therefore, they can be employed to determine hydrogen peroxide in different samples with a wide range of concentrations. The high value of correlation coefficient of the regression equations which are close to unity validates the linearity of the calibration curves. Moreover, sensitivity of the method can be realized from the calculated detection limits and the lower limit of the calibration curves especially for the calibration at 245 nm.

Application of the method

In order to examine the suitability of the recommended method for determination of hydrogen peroxide in real samples, it was applied to tap and rain water samples. The results of the analyses have been collected in Table 4. The data in Table 4 show that the method is accurate and precise.

Comparison with the reported results

In Table 5, the results of the published spectrophotometric and spectrofluorimetric methods for determination of hydrogen peroxide have been collected. The criteriaused for comparison are limit of detection and dynamic linear range. As can beinferred from the dynamic linear ranges in the second column of Table 5, the proposed

Table 6: Effect of interfering ions on the determination of hydrogen peroxide (100.00 μmol L^{-1}).

Foreign species	Tolerance limit	
	245 nm	300 nm
SO_4^{2-}	24	40
NO_3^-	60	10
NO_2^-	14	14
Cl^-	30	30
Mg^{2+}	16	24
Acetic acid	30	30
Formaldehyde	30	30
Formic acid	10	8
Glucose	16	28

method have the widest dynamic linear range. Moreover, the lowest limit of the linear range of the proposed method is lower compared with the methods collected in Table 5. In terms of limit of detection, in both wavelengths; a comparable or even lower detection limits have been obtained.

Effect of foreign ions

The interference of foreign ions commonly present in water samples was studied by adding known amounts of the foreign ions to a solution containing hydrogen peroxide with a concentration of 1.00×10^{-4} mol L^{-1}. The tolerance limit of a potentially interfering ion was taken as its maximum amount causing an error of $\geq \pm 5\%$ during the determination of hydrogen peroxide in water samples. The tolerance limits for the ions studied are given in Table 6. As can be inferred from data in Table 6, in most cases the interference from the studied species is low.

Conclusions

This paper proposes a simple spectrophotometric method for fast determination of H_2O_2 in water samples. Applying the method to real samples resulted in satisfactory precision and accuracy. The relatively low detection limit proved that the proposed method in question was sensitive. The proposed method has a wide dynamic linear range which is one of the advantages of the method over the reported ones for determination of hydrogen peroxide different samples.

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