

NOTE

Estimation of H₂O₂ Content in Free Radical Bromination and Oxidation Reactions by the H₂O₂-HBr System Generated Effluent Samples by Iodometry Method

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(Received: 15 March 2012;

Accepted: 30 January 2013)

AJC-12768

A simple accurate and precise green analytical iodometric titration method was optimized for the estimation of hydrogen peroxide (H₂O₂) content in free radical bromination and oxidation reactions by using hydrogen peroxide (H₂O₂) and hydrogen bromide (HBr) system generated effluent samples. These process generated effluents are containing good amount of H₂O₂ and HBr reagents. Hydrogen peroxide will react rapidly with other compounds found air and if released to soil, will be broken down by reacting with other compounds. Hence the estimation of H₂O₂ is very crucial and important towards the protection of the environment. In view of this we have applied iodometry for this system. During straightforward analysis with KMnO₄ titration method was not helpful to estimate the H₂O₂ content in this system and USP general chapters thiosulphate standardization by iodometry method was also attempted, which is not helping to estimate the H₂O₂ in the system again. The same iodometry titration method was attempted in presence of sulphuric acid medium which is encouraging accurate estimation of H₂O₂ content in bromination and oxidation reactions by using H₂O₂ and HBr process generated effluents.

Key Words: Iodometry titration, Bromination, Oxidation, E-factor, Green chemistry, Green analytical method.

Hydrogen peroxide reacts rapidly with other compounds found air and if released to soil, will be broken down by reacting with other compounds. Hence the estimation of H₂O₂ is very crucial and important towards the protection of the environment¹. Hydrogen peroxide is a quite reactive substance in the presence of other substances, elements, radiation, materials or cells. Both biotic and a biotic degradation processes are important routes in the removal of hydrogen peroxide in the environment. Hydrogen peroxide decomposes into water and oxygen at rates which depend on contact with catalytic materials. This reaction is highly exothermic and takes place in the presence of small amounts of catalyst even in aqueous solution². In view of this hydrogen peroxide content is very important in process generated effluent samples. This paper deals with the determination of H₂O₂ in free radical bromination and oxidation by using H₂O₂-HBr system³ given effluent samples. In order to estimate the H₂O₂ in our samples attempted by KMnO₄ titration method⁴, this is not helping to identifying the end point due to evolving the bromine gas during titration and also attempted iodometry basic condition sodium bicarbonate media⁵ which is also not helping to the estimation of H₂O₂. The same iodometry titration method was attempted in presence of sulphuric acid medium which is encouraging accurate

estimation of H₂O₂ content in bromination and oxidation reactions process generated effluents. By this method H₂O₂ contents in the range of 2-8 % levels in our samples and also established detection level 0.001 % (10 ppm). Spiking experiments also performed in the range from 0.001 to 10 % level in sample matrix. This help us to optimize the reaction by addition of sufficient amount of H₂O₂ in the reaction medium and also helps to reduce H₂O₂ concentration in effluents. Indirectly to decrease the e-factor values in the above chemical reactions to encourage the green chemistry concepts⁶. The method was validated in limited parameters and it is showing satisfactory results⁷. The optimized method was simple precise and accurate green analytical method⁸ for the estimation of H₂O₂ in our effluent samples.

Halogenations and oxidations reactions by using H₂O₂ and HBr reagents in the process generated effluent sample taken from process research department of custom pharmaceutical services of Dr. Reddy's Laboratories Limited, Hyderabad, India. Analytical reagent grade Sodium thiosulphate pentahydrate, potassium iodide, hydrogen peroxide 50 % v/v and sulphuric acid 98 % v/v were purchased from Merck, Germany. High pure water was prepared by using Millipore Milli Q plus purification system.

Preparation and standardization of 0.1 N sodium thiosulphate pentahydrate solution: Preparation standardization of 0.1 N sodium thiosulphate solution followed as per USP general chapters.

Preparation of sample solution: Weighed 1 g of test sample and transferred into 100 mL volumetric flask and made up to mark with water.

Preparation of standard solutions: A stock solution prepared 20 % v/v and further diluted 0.001, 0.01 0.1, 1, 5 and 10 % v/v solutions for linearity and method sensitivity.

Preparation of spiked solutions: Spiked sample solutions were prepared 10 % v/v, 5 % v/v, 1 %v/v, 0.1 % v/v of H₂O₂ added in the samples.

Dilute the sample solution in the level of 0.3 % v/v approximately into 250 mL into iodine flask added 90 mL water, mixed thoroughly and added 0.75 g of potassium iodide, 3-5 mL of concentrated sulphuric acid. Kept in dark place for 10-15 min to liberate the free iodine. Then the solution becomes yellowish it indicates the free iodine was produced by the reaction with H₂O₂. After this solution titrated against 0.1 N standardized thiosulphate solution by addition of starch solution. The observed endpoint is blue to colour discharge of the sample solution.

Precision: A standard solution of 5 % v/v H₂O₂ is used for this study and five times performed titration in the same level. The % RSD calculated for the H₂O₂ content.

Linearity: The above standard linearity solutions were used for this study and estimates H₂O₂ in each level of solution and plotted the graph concentrations on x-axis and peroxide content on y-axis.

Accuracy and limit of detection: The above spikes solutions are estimated peroxide content and calculated % Recovery against standard solution and also checked detection limit by this method.

The % RSD of peroxide content (% w/w) was found to be less than 2 % and the corresponding results are given in Table-1. Correlation co-efficient value was observed in the linearity parameter 0.9982 and the respective results are shown in Table-2, linearity graph also shown in Fig. 1. % Recovery values are in the range of 79.1 to 90.9 % and the obtained recovery values are presented in Table-3. This method is able to detect 0.001 % v/v level of peroxide in the above samples. Based on the results, the method is linear, precise and accurate for the estimation of peroxide content in the described effluent samples.

TABLE-1
PRECISION TEST RESULTS

S. No.	Trial	H ₂ O ₂ content
1.	Trail -1	4.95
2.	Trail -2	4.91
3.	Trail -3	4.98
4.	Trail -4	4.85
5.	Trail -5	4.75
6.	Trail -6	4.94
	Mean	4.90
	%RSD	1.72

TABLE-2
LINEARITY TEST RESULTS

S. No.	Conc. of H ₂ O ₂ Sol'n used (% v/v)	Obtained conc. of H ₂ O ₂ (% v/v)
1.	0.00985	0.00801
2.	0.0985	0.0885
3.	0.985	0.899
4.	4.925	4.341
5.	9.85	9.855
Correlation Co efficient (r)		Slope
0.9982		-0.101

Conclusion

The current iodometry method is good for quantitative determination of peroxide content in effluent samples which are generated from Bromination and oxidation reactions by using H₂O₂ and HBr. The method was partially validated showing satisfactory data for the limited method validation parameters tested.

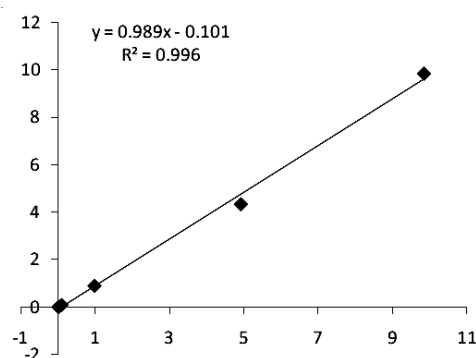


Fig. 1. Linearity graph

TABLE-3
ACCURACY TEST RESULTS

S. No.	Amount of H ₂ O ₂ added (%v/v)	Obtained (% v/v)	% of recovery
1.	0.00985	0.00785	79.7
2.	0.0985	0.0801	81.3
3.	0.985	0.811	82.3
4.	4.925	4.183	84.9
5.	9.85	8.952	90.9

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