Analytical Chemistry
ISSN: 0974-7419

Analytical Chemistry: An Indian Journal

Research Article | Vol 21 Iss 3

Refractometric Determination for Hydrogen Peroxide in Aqueous Solution-A Green Alternate to Iodometric Method

Vijendra Kumar*, **Sreelekshmi KR, Shikha KT, Ancy Smitha Alex, Praveen Kumar Solasa**

Indian Space Research Organization, Thiruvananthapuram, Kerala, India

***Corresponding author**: Vijendra Kumar, Indian Space Research Organization, Thiruvananthapuram, Kerala, India, E-Mail: vkvssc@gmail.com

Received: April 06, 2021; **Accepted:** April 20, 2021; **Published:** April 27, 2021

Abstract

Hydrogen peroxide has important applications in space arena such as initiator for the synthesis of Hydroxyl Terminated Polybutadiene (a workhorse propellant binder), and monopropellant or oxidizer component of a bipropellant rocket. As a green monopropellant hydrogen peroxide (70%-98%), offers the advantage of decomposing into steam and oxygen. In order to achieve higher concentration of H_2O_2 for its application as rocket fuel, enrichment from the commercially available 50% solution to as high as 98% by vacuum distillation is essential. During the concentration process, to estimate the concentration of H_2O_2 at various stages of vacuum distillation, a more reliable physical method is desirable besides an established chemical iodometric method of analysis. A fast, reliable and greener physical method based on the refractometric measurements has been evolved. The acquired results were compared with H_2O_2 content evaluated with standard chemical iodometric method. The refractometric method allows the determination of concentration of hydrogen peroxide with relatively faster speed without compromising on accuracy, precision of analytical results and environmental safety.

Keywords:* *Refractometry, hydrogen peroxide, refractive index measurement

Introduction

Hydrogen peroxide, an environmentally friendly oxidizer is an important component of various chemical processes [1]. Hydrogen peroxide (H_2O_2) is also an important high energy material used as mono- and bipropellant for storable liquid rocket propulsion system. Hydrogen peroxide is employed as free radical initiator in the preparation of Hydroxyl Terminated Poly Butadiene (HTPB), a work-horse propellant binder for most of the world's solid propellant systems. Besides, H_2O_2 falls under the category of green propellants as its combustion product is simply water during the combustion process and thus it is a green alternative to currently used hydrazine propellants. H_2O_2 can be considered as best oxidizer for liquid hydrocarbon fuels. However, for H_2O_2 to be considered for propulsion requirements, its concentration needs to be well above 70%. Propellant grades H_2O_2 are available at concentrations ranging from 70%-98%. When propellant grade H_2O_2 is brought in contact with metallic catalytic surfaces, it exothermically decomposes associated with large amount of heat release which is quite enough to fully vaporize all the liquid fuel components even at ambient conditions. The Russian Soyuz launch vehicle in its active service for more than 40 years continued to rely on hydrogen peroxide in its gas generator to drive the main turbine pump and in the reaction control system thrusters used for the descent phase [2]. Other applications of H_2O_2 such as oxidizing agent, bleaching agent as well as germicide are well known in the field of biology, clinical chemistry and environmental science. H_2O_2 is a pale blue liquid, acidic in nature which appears colourless in the dilute solution. Enriched H_2O_2, on storage tends to get diluted due to diverse factors, such as temperature, environmental conditions and its storage arrangement.

Currently concentration of commercially available aqueous solution of H_2O_2 from 50% to as much as 90% has been taken up in our laboratories. Vacuum distillation is adopted to boost the concentration of H_2O_2. During the concentration process assessing hydrogen peroxide concentration at various stages, is essential. Generally, assay of H_2O_2 is estimated by iodometric titration technique. Chemicals means of estimating the concentrations is very tedious and time consuming. Thus, a simple and reliable physical analytical technique, if available, is more desirable so as to get concentration status instantly. In the present report, a more reliable, fast analytical procedure based on refractometric measurements is probed for its applicability to assess the H_2O_2

Citation: Vijendra Kumar, Sreelekshmi KR, Shikha KT, Ancy Smitha Alex, Praveen Kumar Solasa, Refractometric Determination for Hydrogen Peroxide in Aqueous Solution-A Green Alternate to Iodometric Method. Anal Chem Ind J. 2021;21(3):162.

content in the solution at various stages of concentration process. The method based on refractive index (RI) is not only instantaneous but also reliable and green. By definition, vacuum has a RI of 1, and the RI of a solution or pure fluid is calculated by equation (1).

$$\text{Refractive index}\left(\text{RI}\right)=\frac{\text{speed of light in a vacuum}}{\text{speed of light through the substance}} \qquad (1)$$

It is generally noted that in binary solutions RI is directly related to solute content or concentration. Often it has been reported that concentration of solutes can be deduced from RI of the solution. Most beneficial aspect of RI based analytical methods can be applied to instances where specific chemical analytical method is not existing. It is inferred that substantial difference for RI between pure water (1.333) and a concentrated H_2O_2 solution (1.408) would be particularly helpful for adopting RI based assay determination in the case of H_2O_2 solutions. Present day sophisticated digital refractometers help to measure RI with great accuracy and reproducibility. Feasibility of determining RI within an accuracy of ± 0.0001 enables to quantify very small changes in the H_2O_2. Therefore, the property appears appealing to differentiate the concentration of hydrogen peroxide. As the refractivity of a solution can easily be determined to within 0.0001, the percentage of hydrogen peroxide could be known to within 0.14 which is sufficient for most purposes [3]. Refractometry serves several benefits such as simplicity in the measurement, fast, and reasonably accurate quantification.

Presently, numerous experimental procedures have been developed for measuring hydrogen peroxide assay. They include chemiluminescent biosensing, [4-5] spectrophotometry, [6] luorophotometry, [7] fluorescence-based imaging-fiber electrode chemical sensors [8] and amperometric sensor [9]. The above-mentioned methods help to measure H_2O_2 quite precisely. But the method based on RI seems to be the easiest and very fast. Some key physiochemical properties of water and hydrogen peroxide are displayed in Table 1.

TABLE 1**. Key physiochemical properties of water and hydrogen peroxide.**

Physiochemical Property	**H_2O**	**Concentrated H_2O_2**
Boiling Point (^oC)	100	150.2
Vapour Pressure (25^oC) (kPa)	2.3	0.2
Viscosity (mPa.s) (20^oC)	1.002	1.249
Heat of Vaporization ($J.g^{-1}.K^{-1}$ at 25^oC)	2443	1519
Heat of Vaporization ($J.g^{-1}.K^{-1}$ at boiling point)	2258	1387
Density (g/mL at 25^oC)	0.998	1.45
Refractive Index (nD, 20^oC)	1.333	1.4084

For the present work, calibration curve was constructed between H_2O_2 concentration in the solution and the corresponding RI determined using a very sensitive refractometer. To accomplish the above task, solutions with different H_2O_2 concentration were prepared and the concentrations of H_2O_2 in such solutions were accurately determined adopting the standard chemical iodometric analytical method. Using the calibration curve, concentration of H_2O_2 for any given solution can be directly elucidated from the RI value for that solution.

Experimental

Chemicals and Materials

Hydrogen peroxide (about 90%) was prepared in Propellant Fuel Complex, Vikram Sarabhai Space Centre, Trivandrum, Kerala, adopting vacuum distillation of commercially available 50% solution. Solutions of H_2O_2 at various concentrations were prepared with HPLC grade water (Make: CDH, New Delhi). The lowest concentration made was 5 %.

Apparatus

The digital J-Series (Model J357, Rudolph, USA) bench-top automatic refractometer equipped with scratch proof artificial sapphire prism was employed for the measurement of refractive index of the solutions. The refractometer operates on total internal reflection mode. It is ensured that temperature gradient across the specimen totally negated and operating temperature could be controlled within ± 0.01^oC accuracy. The instrument very accurately determines the critical angle and from which RI is calculated and displayed. The salient feature of the instrument is that RI values obtained are literally unaffected by the turbidity of the solution. The precision obtained with the instrument is ± 0.00004. Instrument used for the measurement of refractive index of aqueous solutions of H_2O_2 is shown in FIG.1.

FIG.1**. Rudolph J357 automatic refractometer with Peltier temperature control.**

Procedure

Solutions of varying concentrations H_2O_2 (5%-90%) using HPLC grade water. The refractometer was calibrated using water standard provided by the manufacturer. A drop of the solution is placed between the prism plates which are thermostated at 30°C. For each concentration RI measurement is repeated for five times and the average is recorded. For each solution, H_2O_2 content is determined adopting iodometric chemical analytical technique. Basic calibration plot is constructed between these two values.

Results and Discussion

The correlation between the refractive index and concentration depends on the solvent and the solute, temperature and wavelength. Use of monochromatic light and built in precise thermostat takes care of wavelength and temperature related ambiguities. H_2O_2 water system is a very simple binary system for which RI connection to concentration can be unambiguously brought out.

RI of H_2O_2 solutions at various concentrations are tabulated against the corresponding concentration of H_2O_2 as determined by iodometric technique in TABLE.2.

TABLE 2. **Refractometric data acquired with respect to aqueous solutions of H_2O_2.**

Actual concentration of H_2O_2 in water (w/w, %)	Refractive index value at 30°C (nD)
90.19	1.39681
79.72	1.38799
69.74	1.37998
59.92	1.37236
50.27	1.36519
39.58	1.35756
24.88	1.34757
9.03	1.33741
5.06	1.33497
0	1.33192

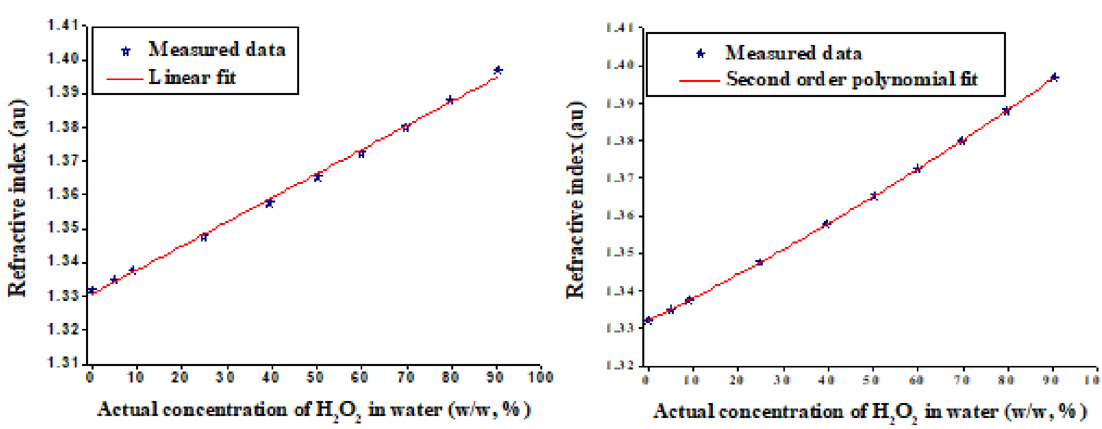

FIG.2. **Linear fit (left) and second order polynomial fit calibration plots for H_2O_2, water system.**

The second order fit equation is given as:

RI = 1.4315 × 10-6[H_2O_2]2 + 5.8923 × 10-4 [H_2O_2] + 1.3320 (2)

The validity of the above approach was applied to a set of solutions for which concentrations were deduced from RI values and compared with the values obtained with iodometric method. The calculated and experimentally evaluated values are tabulated in Table 3.

TABLE 3. **Comparison between concentration deduced from RI value and that determined using Iodometric chemical. analysis.**

RI of the solution at 30°C (nD)	Concentration deduced from RI value (%)	Concentration determined from iodometric analysis (%)
1.4003	89.66	89.69
1.3958	84.32	84.34
1.3918	79.41	79.47
1.3877	74.38	74.45
1.38	64.55	64.61
1.3749	57.92	57.97
1.3731	55.47	55.52
1.3654	44.99	44.99
1.3584	35.05	34.96
1.3573	33.5	33.44
1.3433	12.08	12.05
1.3390	4.98	5.00

Surprisingly, very narrow difference between the concentration determined with standard chemical analytical method and the values deduced from RI values applying the second order fit equation validates the approach adopted in the present report.

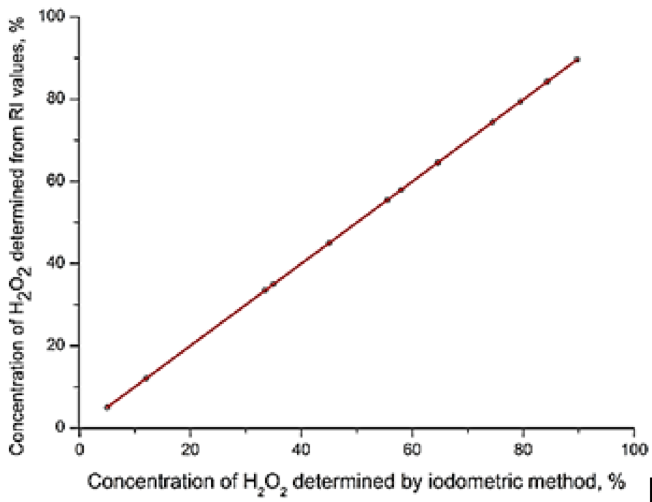

FIG.3. **Concentration of H_2O_2 determined by Iodometric and Refractometric methods.**

The precision with which concentration can be obtained from RI values is demonstrated in the following table 4. To arrive at the table RI for each was determined for five times and there from concentrations were calculated using the 2nd order fit. The precision with which the values are determined is evident from the table.

TABLE 4. **Repeatability test results for determination of H_2O_2 by refractometric method.**

Sl. No.	Concentrations acquired from refractometric method from five trials (%)					Difference between maximum and minimum value	Average	Standard Deviation
	1	2	3	4	5			
1	79.41	79.40	79.37	79.39	79.35	0.06	79.38	0.02

2	55.43	55.40	55.38	55.40	55.39	0.05	55.40	0.02
3	35.04	35.05	35.06	35.04	35.05	0.02	35.05	0.01
4	12.05	12.04	12.05	12.06	12.06	0.02	12.05	0.01
5	5.06	5.07	5.06	5.06	5.06	0.01	5.06	0.00

CONCLUSION

Refractometric measurements offer a rapid and accurate method of determining the composition of aqueous solutions of hydrogen peroxide. It appears that the RI method can be successfully applied for a binary system comprising of H_2O_2 and water. Against the expected lines the fit between RI and concentration belongs to second order. Astonishingly close values between chemical and RI methods encourage the adoption of the RI method for instant checking the concentration of H_2O_2 solution in water.

CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

ACKNOWLEDGEMENT

The authors are thankful to all staff members of Analytical Division, Vikram Sarabhai Space Centre, Thiruvananthapuram, Kerala, India who have assisted in this work.

REFERENCES

1. Li Y, Buckin V. Ultrasonic real-time monitoring of the process of decomposition of hydrogen peroxide in aqueous solutions. Anal. Methods. 2016; 8(24):4828-34.
2. Pasini A, Torre L, Romeo L et al. Testing and characterization of a hydrogen peroxide monopropellant thruster. J. Propuls. 2008; 24(3):507-15.
3. Giguère PA. The refractive indices of hydrogen peroxide and its aqueous solutions. Can. J. Res. 1943; 21(8):156-62.
4. Rubtsova MY, Kovba GV, Egorov AM. Chemiluminescent biosensors based on porous supports with immobilized peroxidase. Biosens. Bioelectron.1998; 13(1):75-85.
5. Janasek D, Spohn U, Beckmann D. Novel chemiluminometric H2O2 sensors for the selective flow injection analysis. Sensor Actuat B-Chem. 1998; 51(1-3):107-13.
6. Clapp PA, Evans DF. Spectrophotometric determination of hydrogen peroxide with leuco Patent Blue Violet .Anal. Chim. Acta. 1991; 243:217-20.
7. Donahue WF. Interference in fluorometric hydrogen peroxide determination using scopoletin–horseradish peroxidase. Environ. Toxicol. Chem.1998 ; 17(5):783-7.
8. Khan SS, Jin ES, Sojic N et.al. A fluorescence-based imaging-fiber electrode chemical sensor for hydrogen peroxide. Anal. Chim. Acta.2000; 404(2):213-21.
9. Westbroek P, Temmerman E, Kiekens P. Measurement and control of hydrogen peroxide concentration in alkaline solution by means of amperometric sensor system. Anal. Chim. Acta. 1999; 385(1-3):423-8.