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Short communication

Rapid determination of hydrogen peroxide in pulp bleaching effluents by headspace gas chromatography

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ABSTRACT

A headspace gas chromatographic (HS-GC) method has been developed for the determination of residual hydrogen peroxide in pulp bleaching effluents. The method is based on the reaction of hydrogen peroxide and permanganate in an acidic medium (0.1 mol/L), in which hydrogen peroxide is quantitatively converted to oxygen within 10 min at 60 °C in a sealed headspace sample vial. The released oxygen is then determined by GC equipped with a thermal conductivity detector. The method is robust, sensitive, and accurate, with reproducibility characterized by a relative standard deviation of <0.5%, a sensitivity whose limit of quantification (LOQ) is 0.96 μmol, and a demonstrated recovery ranging from 98 to 103%. Further, the method is simple, rapid, and automated.

1. Introduction

Due to its minimal environmental impact, hydrogen peroxide (H_2O_2) is an important bleaching agent that is widely used in the totally chlorine-free (TCF) bleaching of virgin and secondary recycled wood pulps. In order to maximize the cost-effectiveness of the process, the bleaching plant must adjust the amount of H_2O_2 used in the mill operation in order to gain the brightness desired in the bleached pulps while minimizing the level of residual H_2O_2 in the bleaching effluents. Clearly, a rapid analytical method for the determination of residual H_2O_2 plays an important role in the process control and optimization.

Traditionally, iodometric titration [1] has been the dominant method used for the determination of hydrogen peroxide in bleaching effluents. However, the method is time-consuming and not particularly sensitive to the samples containing low levels of residual H_2O_2. A batch manometric method based on enzyme catalysis has also been used for hydrogen peroxide determination [2], in which H_2O_2 is enzymatically decomposed to form oxygen that can be measured manometrically. Unfortunately, the enzyme used in this method is not only expensive but also has a limited functional life which also increases the cost of the method. An enzyme-based fluorophotometric method [3] has been reported for the determination of H_2O_2. In addition to the concerns about economics and functional lifetime that limit the previous enzyme-manometric method, the presence of the dissolved lignins and fiber fines in bleaching effluents reduces the effectiveness of this enzyme-fluorophotometric method in practical applications. In 2004, we developed a spectrophotometric method for the determination of residual H_2O_2 in pulp bleaching effluents, in which molybdate was used as a coloring agent [4]. Although the spectral interference of the dissolved lignin (a major interference species) in bleaching effluents can be minimized by a dual-wavelength measurement technique, a large uncertainty was observed in the quantification of lower levels of residual H_2O_2 because of a relatively high UV absorption by the dissolved lignin and the light scattering by fiber suspensions in bleaching effluents. Electrochemical methods, based on a customized membrane-free enzyme electrode, have also been used in the determination of H_2O_2 [5]. However, the response drifting caused by the limited lifetime of enzymatic activity and the poisoning of the electrode surface make the method too unreliable for use in routine test in a mill setting.

In the present work, we report on a headspace gas chromatographic (HS-GC) method designed to rapidly determine the amount of residual H_2O_2 in bleaching effluents. The major efforts in the research were directed at optimization of the reaction conditions for the H_2O_2 conversion and improvement of the detection sensitivity for oxygen in the headspace measurement.

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2. Experimental

2.1. Chemicals and samples

All chemicals used in the experiment were of analytical grade and obtained from commercial sources. A standard hydrogen peroxide solution (35.1 g/L) was prepared by mixing 10 mL of commercial hydrogen peroxide (351 g/L) with 90 mL of distilled water. A potassium permanganate ($KMnO_4$) solution (0.16 mol/L) was prepared by adding 25 g of potassium permanganate to 1 L of distilled water.

A pulp bleaching effluent sample was obtained from a lab-scale hydrogen peroxide bleaching process for wheat straw pulps from a soda-AQ pulping.

2.2. Apparatus and operations

All measurements were carried out using a headspace sampler (DANI HS 86.50, Italy) and gas chromatograph (Agilent HP-7890, Palo Alto, CA, USA) equipped with a thermal conductivity detector (TCD). Headspace sampler operating conditions were as follows: oven temperature = 60 °C; vial pressurization time = 0.2 min; sample-loop fill time = 0.2 min; loop equilibration time = 0.05 min; and loop fill time = 0.2 min. The GC was equipped with a model GS-Q capillary column with an i.d. of 0.53 mm and a length of 30 m from J&W Scientific, Folsom, CA. It was operated at 45 °C with nitrogen as the carrier gas at a flow rate of 3.1 mL/min, with the TCD set at 220 °C.

2.3. Procedure of sample preparation

9 mL of sample solution and 0.5 mL of H_2SO_4 solution (2 mol/L) were added to a headspace sample vial (20 mL), which was sealed by aluminum cap with a rubber septum. Then, 0.5 mL of $KMnO_4$ solution was injected to the sealed vial that was placed in the headspace auto-sampler and allowed to equilibrate at 60 °C for 10 min with shaking. Finally, a headspace sample from the vial was automatically withdrawn and measured by GC.

3. Results and discussion

3.1. Effects of reaction conditions on H_2O_2 conversion

The present method is based on measuring the oxygen that is quantitatively generated by the reaction of potassium permanganate and hydrogen peroxide in an acidic medium [6]; i.e.

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{2+} + 5O_2 + 8H_2O \quad (1)$$

The effects of the reaction conditions, i.e., the dosages of potassium permanganate and sulfuric acid and the reaction temperature and time, on the completion of the conversion are discussed below.

3.1.1. Dosage of potassium permanganate

Fig. 1 shows that for a sample of 103.4 μmol of H_2O_2, a quantitative conversion can be achieved by adding 50 μmol of $KMnO_4$ under the given reaction conditions. It can be seen that $KMnO_4$ in a 1.21-fold stoichiometric excess drives the reaction to completion under these conditions. In the subsequent studies, 80 μmol (that is, about 2-fold stoichiometric excess) of $KMnO_4$ was used to insure sufficient reactant to oxidize the peroxide, even if some of it was consumed by the other substances in the samples. Comparing the reaction with H_2O_2, the side reactions with organic substances in the sample are usually slow and could produce some organic acids or even CO_2 (rather than O_2), which would not interfere with the measurement.

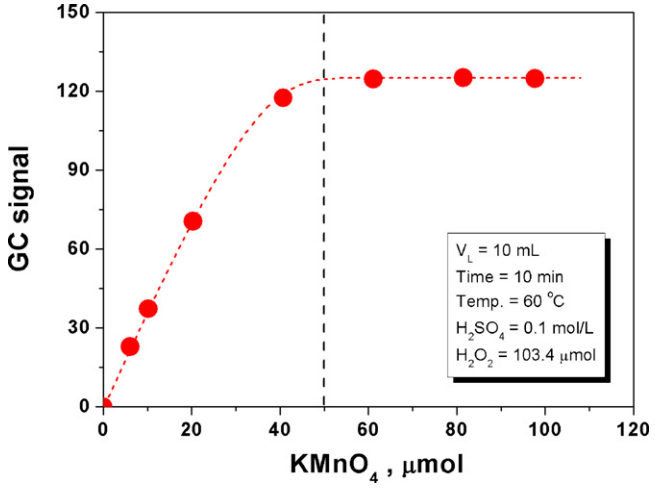

Fig. 1. Effect of $KMnO_4$ dosage on the conversion of hydrogen peroxide.

3.1.2. Concentration of sulfuric acid

Fig. 2 shows the effect of sulfuric acid concentration on the conversion reaction. It can be seen that to insure a complete reaction at the given conditions, the amount of sulfuric acid added should be greater than 0.04 mol/L. Therefore, 0.1 mol/L of sulfuric acid was used in subsequent studies.

3.1.3. Reaction temperature and time

In general, a higher temperature accelerates chemical reactions. In this work, a mild reaction temperature (60 °C) was selected in order to minimize reaction between $KMnO_4$ and the other coexisting species in bleaching effluents. As shown in Fig. 3, it takes about 5 min to reach a complete conversion of H_2O_2 to oxygen. Thus, 10 min was selected as the reaction time in the rest of the study.

3.2. Confirmation of the completion of the conversion

In order to prove that the H_2O_2 is completely converted to oxygen under the above conditions, a set of samples with the different molar amounts of H_2O_2 was analyzed by the present method. The amount of oxygen (99.6 μmol) in the headspace (air) of the sample vial for a H_2O_2-free solution (blank) can be calculated by Eq. (2).

$$C_0 = \frac{n_g}{V_g} = \frac{P_0 \cdot \varphi}{RT_0} \quad (2)$$

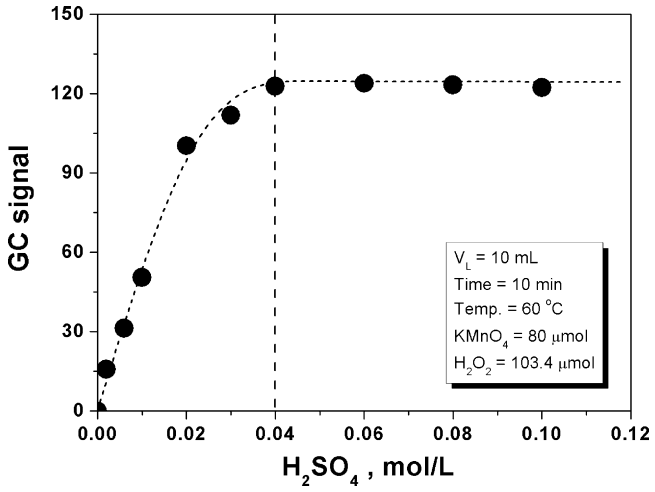

Fig. 2. Effect of H_2SO_4 concentration on the conversion of hydrogen peroxide.

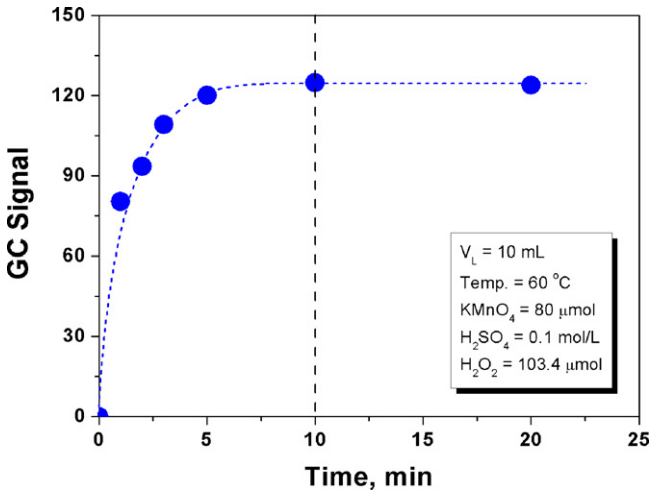

Fig. 3. Effect of the reaction time on the conversion.

Table 1
Comparison of the amounts of hydrogen peroxide added and the oxygen generated in the present method.[a]

H_2O_2 added (μmol)	O_2 generated (μmol)	Difference, %
10.3	10.7	3.88
20.7	19.7	−4.83
41.4	43.0	3.86
62.0	59.2	−4.52
82.7	82.1	−0.73

[a] Reaction conditions: in a 10 mL of solution containing 0.1 mol/L of H_2SO_4 and 80 μmol of $KMnO_4$ for 10 min at 60 °C.

where φ, P_0, R, T_0, n_g and V_g represent the volume fraction of oxygen (21%), standard atmospheric pressure (101.325 kPa), the universal gas constant (8.314 J/mol/K), room temperature (298.15 K), amount of oxygen in vial (mol), and volume of gas phase in the headspace of the vial (0.0116 L), respectively. Thus, the net amount of the oxygen generated by the hydrogen peroxide in an effluent sample can be calculated by subtracting the blank value from the sample value.

As seen in Table 1, the differences between the molar amounts of hydrogen peroxide added and the oxygen generated are within 5%. Therefore, we conclude that the conversion reaction in this method is complete under the given conditions.

3.3. Method calibration, precision, and validation

The method calibration was performed by adding different amounts (1–100 μmol) of the standard hydrogen peroxide solution into a set of headspace sample vials that were then tested by the present method to generate a standard calibration curve; i.e.,

$$A = 0.51(\pm 0.07) + 1.26(\pm 0.006)C \quad (n = 7,\ r^2 = 0.999) \tag{3}$$

where A and C represent, respectively, the GC signal response for oxygen and the hydrogen peroxide content added (in μmol) in the headspace sample vial.

The limit of quantitation (LOQ) of the present method is 0.96 μmol, which was calculated by the following equation [7].

$$\mathrm{LOQ} = \frac{a + 10 \times |\Delta a|}{s} \tag{4}$$

where a, Δa and s represent the intercept, uncertainty of the intercept, and the slope in Eq. (3), respectively.

Table 2
Method validation.[a]

Sample no.	Amount of H_2O_2, μmol		Recovery (%)
	Added	Measured	
1	3.30	3.26	98.8
2	16.5	16.9	102
3	33.0	33.7	102
4	49.5	48.8	98.6
5	66.0	67.8	103

[a] The amount of H_2O_2 in 9 mL of the original bleaching effluent was 29.2 μmol.

The hydrogen peroxide content (C_{HP}) in the bleaching effluent sample can be calculated by

$$C_{HP}\ (\mathrm{mg/L}) = \frac{A - 0.51}{1.26V_0} \times 34 \tag{5}$$

where V_0 is the volume (in mL) of pulp bleaching effluents added in the headspace sample vial, and 34 is the molecular weight (in g/mol) of hydrogen peroxide.

The reproducibility of results obtained by the present method was investigated by the quintuplicate determination of hydrogen peroxide content in a bleaching effluent sample. The results show that the relative standard deviation (RSD) was less than 0.5%.

To verify the present method, we prepared a set of spiked sample solutions by adding different amounts (1.0–100 μmol) of hydrogen peroxide to a set of headspace sample vials, each of which contained 9 mL of bleaching effluent, 0.5 mL of H_2SO_4 (2 mol/L) and 0.5 mL of $KMnO_4$ (0.16 mol/L). The samples were then measured by the present HS-GC method. The original bleaching effluent was served as the reference blank. The net contributions from the added hydrogen peroxide in these spiked samples were calculated by Eq. (5). As shown in Table 2, the recoveries achieved in the present method are in the range of 98–103%, which is appropriate for many purposes.

4. Conclusions

A HS-GC technique for the determination of hydrogen peroxide in pulp bleaching effluents, based on the determination of the oxygen generated from the oxidation of residual hydrogen peroxide by $KMnO_4$, has been developed. The method is simple, rapid, accurate, and automated.

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