# Headspace Gas Chromatographic Method for the Determination of Hydrogen Peroxide Residues in Bleaching Effluent

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A simple, rapid, accurate, and practical headspace gas chromatographic method is proposed for the determination of hydrogen peroxide residues in bleaching effluent. This method is based on the reaction of hydrogen peroxide with ceric sulfate, under acidic conditions, where hydrogen peroxide is converted to oxygen, which is then measured using headspace gas chromatography (HS-GC) coupled with a thermal conductivity detector (TCD). The results show that a complete conversion of hydrogen peroxide to oxygen can be achieved within 3 min at a temperature of 70 °C and a $H_2SO_4$ concentration of 0.2 M. Under optimized conditions, the method has an excellent measurement precision (relative standard deviation = 0.78%) and good recovery (100.2 ± 2.6%). Meanwhile, the present method does not require the use of organic reagents.

*Keywords: Hydrogen Peroxide; Bleaching effluent; Headspace gas chromatography (HS-GC); Ceric sulfate*

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## INTRODUCTION

Hydrogen peroxide is an important chemical agent that exhibits bleaching, oxidizing, and catalytic capabilities. It has a very important role in many fields, such as industrial chemistry, biochemistry, clinical chemistry, atmospheric chemistry, and analytical chemistry (Kurihara *et al.* 2012). Hydrogen peroxide bleaching of pulp is a fairly well known technology (Brogdon and Hart 2012; Heimburger 2012). Hydrogen peroxide is relatively safe to use in pulp bleaching and has a minimal environmental impact. As a more environmentally compatible bleaching agent, hydrogen peroxide has long been used for the bleaching of chemical, mechanical, and deinked pulps. It is an integral part of totally chlorine-free (TCF) bleaching sequences for chemical pulps. An important parameter in peroxide bleaching of pulp is the amount of residual peroxide in the spent bleaching effluent. Very low peroxide residues in the bleaching effluent can result in pulp brightness reversion, and excessive residual peroxide increases the chemical costs of the bleaching (Chai *et al.* 2004). Hence, a simple, rapid, and accurate analytical method for measuring hydrogen peroxide residues in bleaching effluent is needed.

A number of analytical methods have been reported for the quantification of hydrogen peroxide concentrations, such as by titration (Kieber and Helz 1986; Klassen *et al.* 1994; Reichert *et al.* 1939; Schumb *et al.* 1955), spectrophotometric analysis (Chai *et al.* 2004; Sellers 1980; Sunil and Narayana, 2008; Zhang *et al.* 2013), chemiluminescent analysis (Hu *et al.* 2007; Lu *et al.* 2009), fluorometric analysis (Hwang and Dasgupta

1986; Luo *et al.* 2009), and electrochemical analysis (Frew *et al.* 1986; Sato *et al.* 2008). Most of the widely used analytical methods are titration-based, and these are very popular, especially in the pulp and paper industry; however, titrimetric methods are prone to interference by extraneous substances and can result in significant experimental error. This has led us to look for a novel method suitable for the determination of hydrogen peroxide residues in spent bleaching effluent.

In this paper, a headspace gas chromatographic (HS-GC) method for the determination of hydrogen peroxide residues in bleaching effluent is proposed. The optimized conditions (*i.e.*, dosage of ceric sulfate, temperature, time, and sulfuric acid concentration) were studied to ensure the complete reaction of hydrogen peroxide with ceric sulfate. The precision and accuracy of the proposed method for quantifying hydrogen peroxide resides were also evaluated. The present method was successfully applied to the determination of hydrogen peroxide residues in bleaching effluent.

## EXPERIMENTAL

### Chemicals and Samples

All reagents used in these experiments were from commercial sources. The ceric sulfate solution was prepared by dissolving 4.0 g of ceric sulfate in 100 mL of 0.2 mol/L $H_2SO_4$. A standard solution of hydrogen peroxide was prepared by the suitable dilution of 30% hydrogen peroxide. The sample was obtained from hydrogen peroxide bleaching of CTMP hardwood pulp experiment.

### Apparatus and Operations

All measurements were implemented using an HSS 80.65 Automatic Headspace Sampler (DANI, Italy) and Model HP-7890 capillary gas chromatograph (Agilent, USA). GC conditions were as follows: capillary column with an I.D. = 0.53 mm and a length of 30 m (model GS-Q, J&W Scientific, Folsom, CA, USA) at 50 °C; and nitrogen carrier gas (high purity) at a flow rate of 3.2 mL/min. A thermal conductivity detector (TCD) (Agilent Technologies, USA) was employed. The detector temperature was 250 °C. Headspace sampler operating conditions were as follows: oven temperature of 70 °C; vial pressurization time of 0.2 min; sample-loop fill time of 0.2 min; loop equilibration time of 0.05 min; loop fill time of 0.2 min; and vial equilibration time of 3 min.

### HS-GC Measurement

A 2.0-mL sample of the bleaching effluent was added to a headspace test vial, which was sealed with a septum. A 1.0-mL ceric sulfate solution (0.1 M) was injected into the sealed vial by a micro-syringe. The vial was then immediately put in the headspace sampler for the GC measurement.

## RESULTS AND DISCUSSION

### Effects of Reaction Conditions on the Conversion of Hydrogen Peroxide

Hu *et al.* (2012) developed a method involving the reaction of potassium permanganate and hydrogen peroxide in an acidic medium. The basis of this method is the oxidation of hydrogen peroxide by ceric sulfate under acidic conditions and the quantitative generation of oxygen, as described by (Reichert *et al.* 1939) in Eq. 1:

$$2Ce(SO_4)_2 + H_2O_2 \rightarrow Ce_2(SO_4)_3 + H_2SO_4 + O_2\uparrow \quad (1)$$

The reaction conditions to achieve complete peroxide conversion to oxygen by Eq. (1) are discussed below. The variables studied were as follows: dosage of ceric sulfate, reaction temperature, reaction time, and concentration of sulfuric acid. The concentration of hydrogen peroxide used in the optimization was 2.0g/L.

*Effect of ceric sulfate dosage*

For the complete conversion of hydrogen peroxide to oxygen, an excess amount of ceric sulfate is necessary. Figure 1 shows the effect of ceric sulfate dosage on the conversion reaction. It can be seen that a molar ratio of ceric sulfate to hydrogen peroxide of 2.2 was sufficient to achieve the complete conversion of hydrogen peroxide at the specified conditions.

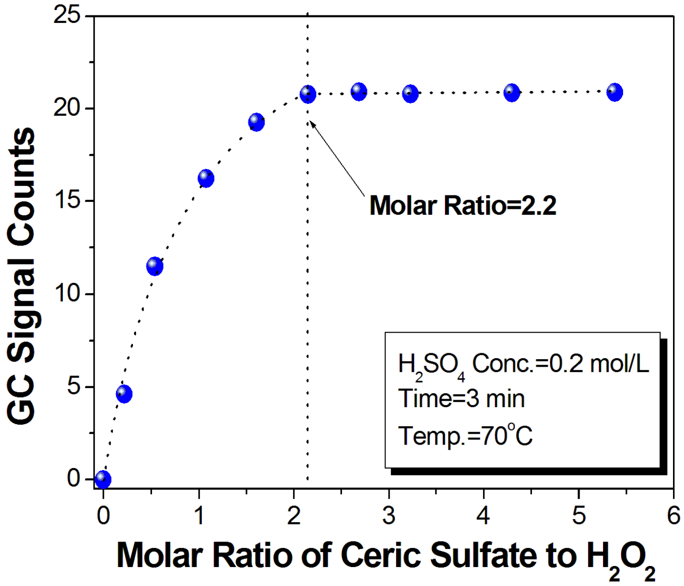

**Fig. 1.** Effect of ceric sulfate dosage

*Effects of reaction temperature*

The temperature in the HS-GC plays an important role: a higher temperature can accelerate the chemical kinetics of Eq. 1 and increase the removal rate of oxygen to the headspace. However, it was noticed that higher temperatures will lead to higher water vapor pressures, which may affect the separation performance of the GC column. In this study 70 °C was selected as the reaction temperature.

*Effects of reaction time*

Figure 2 presents the equilibration time effect on the conversion reaction. To ensure a complete reaction at the given conditions, a minimum reaction time of 3 min was required for complete conversion.

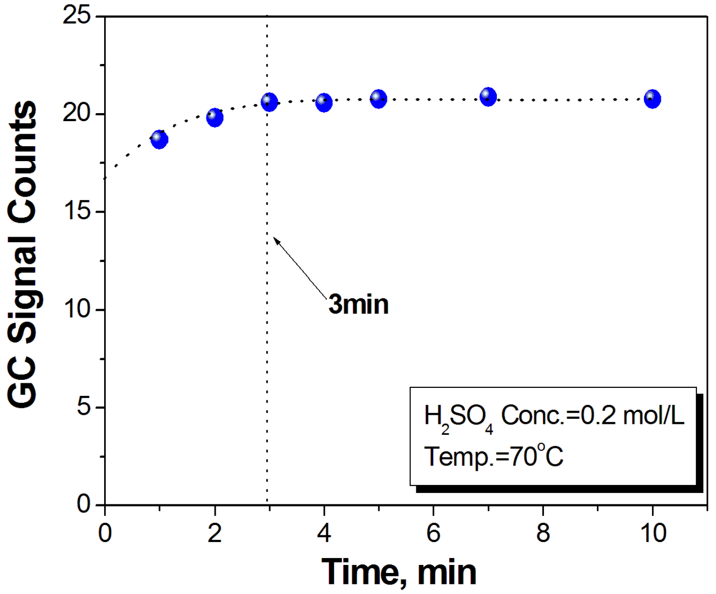

**Fig. 2.** Effects of reaction time

*Effect of sulfuric acid concentration*

The reaction of ceric sulfate and hydrogen peroxide was conducted under acidic conditions. The effect of sulfuric acid concentration on the hydrogen peroxide conversion is shown in Fig. 3. It was found that to ensure complete conversion of peroxide by Eq. 1 at the given conditions, the concentration of sulfuric acid should not be less than 0.2 M. Therefore, a sulfuric acid concentration of 0.2 M was chosen for the rest of the experiments.

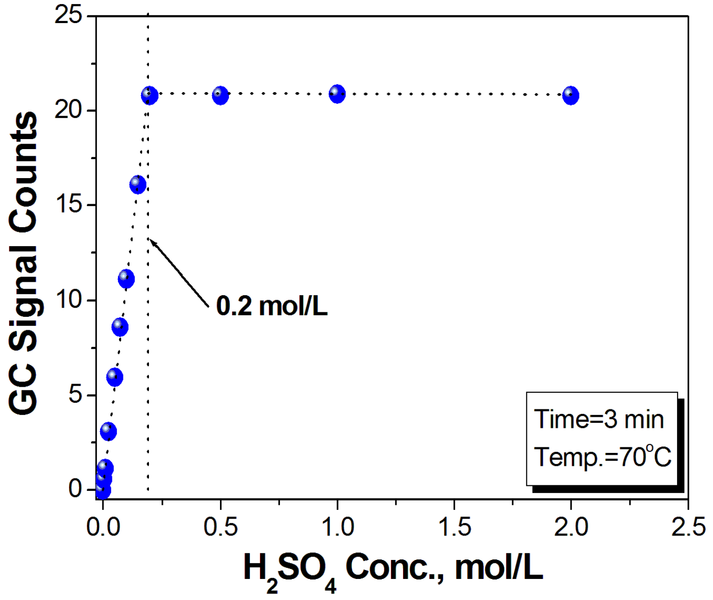

**Fig. 3.** Effect of sulfuric acid concentration

### Interference

The present method is based on measuring the oxygen released from the reaction given in Eq. 1. Therefore, the oxygen in ambient air involved in the headspace sample vial can affect the accuracy of measurements. In this work, a blank test run (*i.e.*, the sample added to a solution without ceric sulfate) was conducted under the same headspace GC conditions. Thus, the effect of oxygen in ambient air can be easily accounted for using a blank sample.

In bleaching effluent, there are many inorganic and organic species present, such as dissolved lignin, carbohydrates, and volatile organic compounds. When these species react with ceric sulfate, oxygen is not generated. Therefore, interference from other species can be eliminated in this method.

### Method Calibration, Precision, and Evaluation

In the present method, a calibration curve was created by adding different volumes (0 to 2 mL) of a standardized hydrogen peroxide solution (0.025 M) in a set of headspace sample vials; the contents of the vials were reacted using the optimized conditions previously discussed. Using the data from the GC measurement on these samples, a standard calibration curve was obtained that follows Eq. 2,

$$C = 27.10(\pm 0.052)A - 1.004(\pm 3.32) \qquad (R^2 = 0.998,\ n = 9) \qquad (2)$$

where $A$ and $C$ represent the GC signal count of oxygen and its absolute amount (in μg) in the headspace sample vial, respectively.

The limits of detection and the limits of quantification in the present method were 6.6 and 19.7 μg, respectively. They were calculated as three and ten times the standard deviation of ten measurements of the blank, respectively, divided by the slope in Eq. (2) (Gustavo González and Ángeles Herrador 2007).

The precision of this method is expressed by the relative standard deviation (RSD) of the replicated data. The results showed that the RSD in six measurements was less than 0.78%, indicating the good precision of the developed method. The random errors are associated with the uncertainties in both the sampling and the HS-GC measurement. To validate this method, the accuracy of the method was established by the percent recoveries of spiked amounts of hydrogen peroxide to a bleaching effluent sample. The samples were then measured by this method. The recovery values ranged from 97.5% to 102.8% (Table 1).

**Table 1.** Method validation*

| Sample No. | Hydrogen Peroxide, μg | | Recovery, % |
|---|---|---|---|
| | Added | Measured | |
| 1 | 238 | 232 | 97.5 |
| 2 | 435 | 446 | 102.8 |
| 3 | 880 | 885 | 100.6 |
| 4 | 1252 | 1269 | 101.4 |
| 5 | 1615 | 1603 | 99.3 |

* The amount of $H_2O_2$ in 2 mL of the original bleaching effluent was 1500 μg.

The good hydrogen peroxide recoveries indicated that this method is suitable for the determination of hydrogen peroxide in bleaching effluent.

## CONCLUSIONS

1. A simple, rapid, accurate, and practical headspace gas chromatographic method was successfully demonstrated for the determination of hydrogen peroxide residues in bleaching effluent.
2. Excellent measurement precision (RSD < 0.78%) and accuracy (recovery = 100.2 ± 2.6%) are the hallmarks of this method.
3. The method is useful for the determination of hydrogen peroxide in pulp bleaching effluents with satisfactory results.

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