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Detection of H_2O_2 in food samples by FTIR

Ülfet Şansal, Güler Somer *

Department of Chemistry, Gazi University, 06500 Ankara, Turkey

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Abstract

A simple and rapid method to detect hydrogen peroxide was developed. The FTIR peak of hydrogen peroxide was used for this purpose. A peak was observed at 669.18 cm^{-1} on NaCl window and another at 418.48 cm^{-1} on KBr window. In a reaction mixture of ascorbic acid, riboflavine and citrate buffer in a total of 0.1 M concentration,10^{-4}M hydrogen peroxide could be detected which was formed after a visible light illumination of this solution. This method enabled the detection of hydrogen peroxide in aqueous solution. Since no reactant has to be added, the composition would not change after the measurement. This method can also be applied to food samples having similar composition with the above given solution.

Keywords: Hydrogen peroxide; Infrared spectroscopy; Detection; Fruit juice

1. Introduction

The detection and determination of H_2O_2 during chemical reactions is a difficult procedure, because of the complicated structure of the reaction medium. Carbon paste electrodes containing horseradish root tissue (Wang & Lin, 1989) or pineapple tissue (Lin & Than, 1990) have been used to measure H_2O_2. Horseradish peroxidase was found to adsorb strongly on a graphite electrode surface with retained catalytic activity. It was possible to detect O.2 μM of H_2O_2 using amperometric bio sensors (Wang & Lin, 1989). Hydrogen peroxide is also determined spectrophotometrically by the formation of indamine dye with the catalyst of water soluble iron porphirine (Nakano & Takahashi, 1990). In plants 0.1–0.2 milimole hydrogen peroxide is determined using nitrocellulos paper on which KI and starch was absorbed (Schopher, 1994). In a solution of hydrogen peroxide using electrocatalysis and flow injection techniques 0.4 μM–1 mM hydrogen peroxide could be detected amperometrically (Gao, Ivaska, Lui, & Pin, 1992).

Using a peroxioxalate chemiluminescence reaction 50 picomoles/200 μL peroxide could be assayed photographically (Nakashima, Kawaguchi, Givens, & Akiyama, 1990). The pasteurized cream is analyzed for its hydrogen peroxide content, for this purpose it is complexed with $TiCl_4$ and the absorbance is measured at 415 nm, 10 μg H_2O_2/g could be detected (Black & Cunnington, 1985). It was possible to determine 20 ppm of hydrogen peroxide in foods using KI and ammonium molybdate (Matsushita, 1977). In most of these determination and detection methods the sample contains only hydrogen peroxide and therefore no interference studies are needed. But of course this is not a natural situation if a reaction is under investigation. Besides this in many cases depending to the method some reagents have to be added, which may disturb the chemical composition.

In photochemical oxidation and reduction reactions it is known that (Somer & Green, 1973; Somer & Temizer, 1984; Şahbaz & Somer, 1993, Şansal & Somer, 1997) hydrogen peroxide is formed. We have followed its formation by differential pulse polarographic technique (Somer & Temizer, 1984; Şahbaz & Somer, 1993, 1997) using the polarographic wave of oxygen. Although it was quantitatively determined its formation had to be proven by a detection technique which is very specific for hydrogen peroxide. This paper describes a simple nondestructive method for the assay of hydrogen peroxide in an aqueous solution of ascorbic acid, citrate buffer, using infra red spectroscopic technique.

2. Experimental

2.1. Reagents

Reagents such as ascorbic acid, citric acid, potassium hydroxide, riboflavine and hydrogen peroxide were of

* Corresponding author. Tel.: +90-312-212-2900; fax: +90-312-212-2279; e-mail: gsomer@quark.fef.gazi.edu.tr

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analytical reagent grade. Triple distilled water was used for the preparation of the standard solutions and at all other stages of analysis. The analytical concentrations of citrate buffers were approximately 0.2 M. Hydrogen peroxide was standardized by titration with potassium permanganate The dissolved oxygen was removed from the solutions by bubbling high purity argon gas.

2.2. IR measurements

A Mattson 1000 FTIR instrument was used for IR measurements. The IR spectrum of pure, de aerated (using argon) solution of hydrogen peroxide is taken using KBr, NaCl and polystyrene windows in the 400–700 cm^{-1} range. Further the IR spectrum of the solution containing ascorbic acid, buffer and riboflavine after de aeration is taken. The same solution is illuminated with visible light for 20 min and once more the IR spectrum is taken and the formation of hydrogen peroxide peak was observed.

3. Results and discussion

3.1. IR detection of hydrogen peroxide

For the detection of hydrogen peroxide the transmittances in 400–700 cm^{-1} range were measured using different types of windows. In 500–400 cm^{-1} range the IR spectrum was taken on KBr window, the hydrogen peroxide peak appeared at 418.48 cm^{-1}. The transmittance measurements in 700–600 cm^{-1} range were made on NaCl window and by the addition of hydrogen peroxide a peak at 669.19 cm^{-1} was observed. However, it was not possible to observe a peak on polystyrene window in the 600–400 cm^{-1} range. Using KBr and NaCl windows 10^{-4} M hydrogen peroxide could be detected easily. Thus it was decided to detect the hydrogen peroxide formed during a photochemical reaction using the IR technique.

3.2. IR detection of H_2O_2 in the reaction mixture

The aim of this work was to detect hydrogen peroxide formed during the photoreaction. The reaction mixture contained 5×10^{-4} M ascorbic acid, 1.6×10^{-5} M riboflavine and 0.1 M citrate buffer. It was suspected that hydrogen peroxide was formed during the visible light illumination. Its formation during the reaction had been followed by differential pulse polarography using the polarographic wave of oxygen in various solutions (Somer & Temizer, 1984; Şahbaz & Somer, 1993, Şansal & Somer, 1997) and it was quantitatively determined. Since the formation of hydrogen peroxide had to be proven by another technique which would be very specific for it, the IR method was chosen for this purpose. The above mentioned solution is de aerated for about one hour using argon gas. One drop of it is taken onto

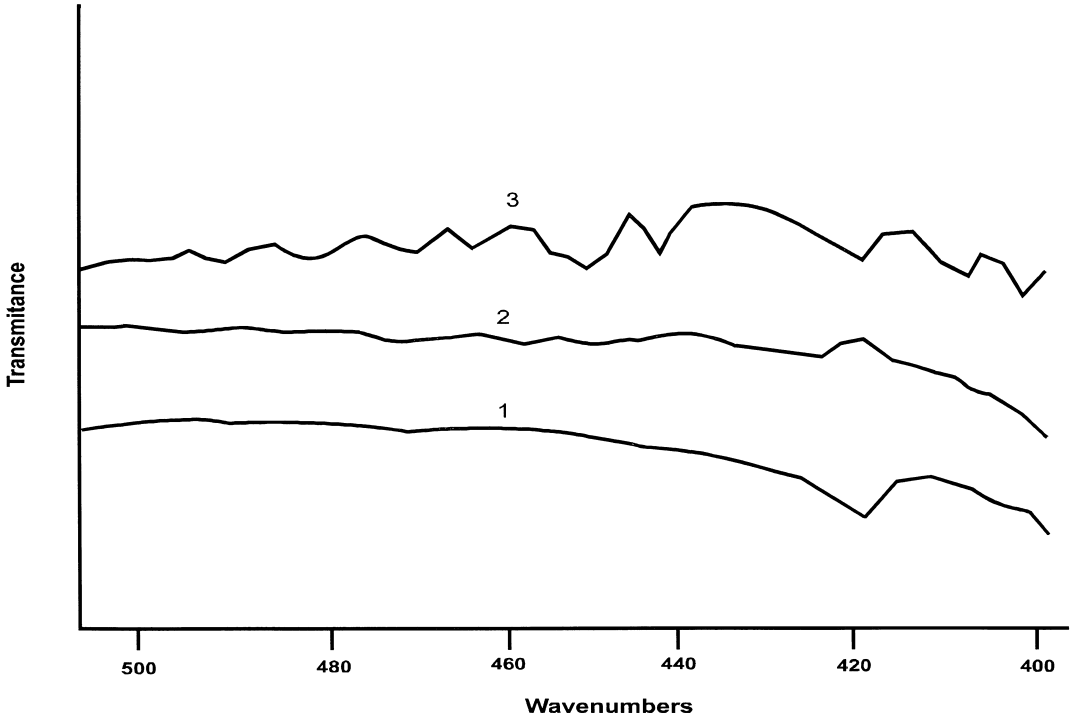

Fig. 1. Detection of H_2O_2 formed during a photochemical reaction (KBr window) (500–400 cm^{-1}). 1. FTIR spectrum of 10^{-4} M H_2O_2. 2. FTIR spectrum of ascorbic acid, citrate buffer medium; 3. FTIR spectrum of ascorbic acid, citrate buffer medium after 20 min irradiation.

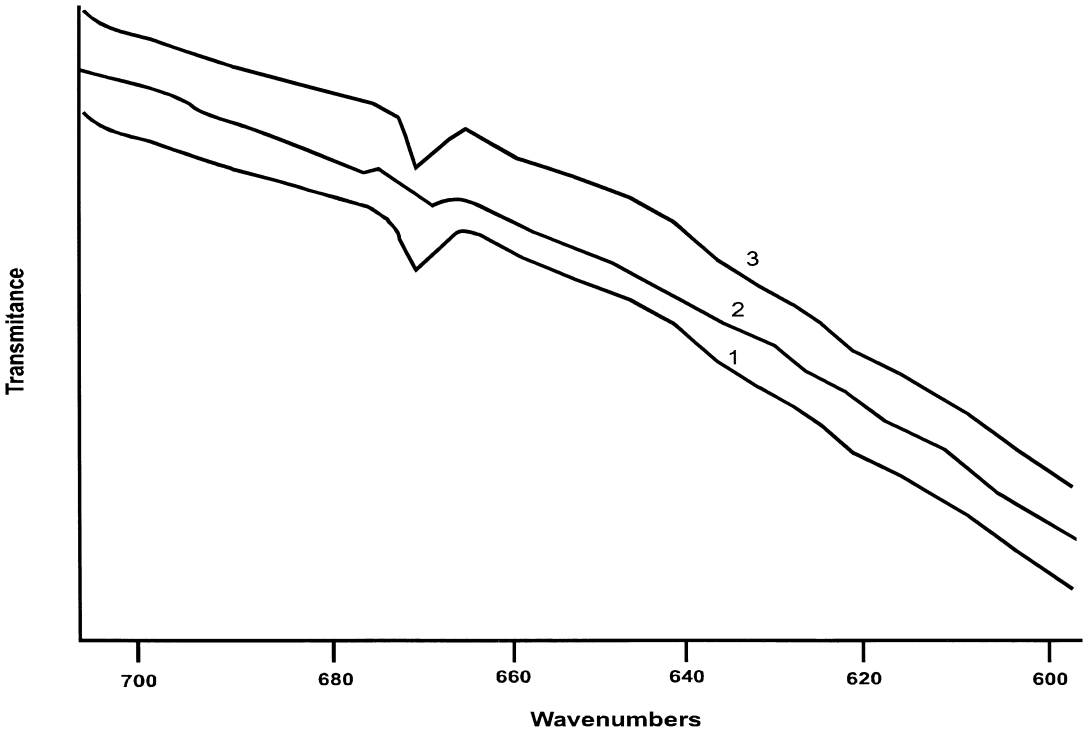

Fig. 2. Detection of H_2O_2 formed during a photochemical reaction (NaCl window) (700–600 cm^{-1}). 1. FTIR spectrum of 10^{-4} M H_2O_2; 2. FTIR spectrum of ascorbic acid, citrate buffer medium; 3. FTIR spectrum of ascorbic acid, citrate buffer medium after 20 min irradiation.

KBr window and the IR spectrum is taken in 500–400 cm^{-1} range in a very short time. No peak is observed for hydrogen peroxide at the expected place, at 418.18 cm^{-1}. The solution in the cell is then illuminated for 20 min while it was stirred with argon gas during that time. From the same solution is taken and the IR spectrum is taken on the KBr window. This time a peak at 418.18 cm^{-1} appeared which increased by the addition of hydrogen peroxide. The results are given in Fig. 1.

The same experiment is repeated with the solution in the same composition using NaCl window. After illumination with visible light a peak at 667.26 cm^{-1} was observed, although there was no peak before illumination (Fig. 2). This peak must belong to hydrogen peroxide according to our former studies. It increased with the addition of hydrogen peroxide. Thus it was possible to detect hydrogen peroxide in a complex solution containing organic and inorganic substances in fairly high concentrations. This method is very specific for hydrogen peroxide and it enables to work in aqueous solutions. According to our former studies (Şansal & Somer, 1997) we know that in this reaction mixture about 10^{-4} M hydrogen peroxide was formed. So it is possible to detect hydrogen peroxide in aqueous solution using IR which is very specific for it and this method can be applied to fruit juices or some foodstuff with the resembling composition.

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