Quantitative Raman determination of hydrogen peroxide using the solvent as internal standard: Online application in the direct synthesis of hydrogen peroxide

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ABSTRACT

H_2O_2 concentrations in aqueous solutions have been determined by means of a 532 nm Raman spectrometer. H_2O_2 is a highly demanded green oxidant agent, and its direct synthesis from H_2 and O_2 is a promising alternative to the traditional production process. Raman spectroscopy is a fast, non-destructive and reliable analytical technique for H_2O_2 quantification, which avoids the drawbacks of traditional iodometric determinations (sample extraction, preparation of the reagents and a long time of analysis). A high pressure view cell has been designed to facilitate the measuring at high pressures, which are often found in a direct synthesis process. A thorough calibration model has been developed, and it has been validated at high pressure (5.0 MPa) and temperature (up to 45 °C). The solvent (water) was used as internal standard to correct multiplicative distortions. The validation of the analytical technique produced reproducible and accurate results compared against classic iodometric titration, allowing the use of a single calibration model for a range of reaction conditions. The feasible use of Raman spectroscopy for real-time quantitative reaction monitoring has been established by analysing the decomposition reaction of H_2O_2 under different conditions.

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1. Introduction

Hydrogen peroxide is a highly polar component with an extremely oxidant behaviour, which decomposes forming hydroxyl radicals with a much higher oxidant potential, only exceeded by fluorine [1]. At ambient conditions (25 °C, 0.1 MPa), hydrogen peroxide is a colourless, unstable liquid which decomposes with light, heat, and in combination with metals, alkalis and organic material, forming water and oxygen. The importance of hydrogen peroxide lies on its industrial applications due to its environmentally friendly character, mainly as bleaching agent in pulp and textile industries and as green oxidant for chemical synthesis [1]. Moreover, it is also used as pollution control agent in environmental applications, as propellant in the aerospacial industry, and as an oxidant in the mining industry [2]. Also, it is used in low concentration (around 3%) for domestic purposes.

Over 95% of the current industrial production of H_2O_2 is carried out via the anthraquinone route (Riedl–Pfleiderer process), which avoids direct contact between H_2 and O_2 and offers con-

tinuous production at moderate temperatures [3]. However, large amounts of by-products are produced and several steps of separation and concentration, and consequently a rather large energy input, are required. Direct synthesis from H_2 and O_2 has become a promising alternative to the anthraquinone route [4]. In this process, the quantitative determination of the hydrogen peroxide produced is usually carried out by volumetric titration, generally with potassium iodide, potassium permanganate or ceric sulphate [5]. However, this technique implies a sample extraction which alters the reaction medium, repeatable preparation of the reagents and a long time of analysis. An analytical method that allows the quantification of H_2O_2 in a greener, faster and non-destructive way would be ideal in order to combine it with the direct synthesis process. Several examples of this are found in the literature using spectroscopic methods, usually intended for online determination. Some authors have been able to determine H_2O_2 indirectly by adding a reagent, namely titanyl sulphate [6] or ammonium molybdate [7], which reacts with the peroxide to form a compound that is then measured by UV/vis spectroscopy. Such indirect method is particularly useful in the presence of spectral interfering compounds. Alternatively, several authors have used infrared (IR) or near-infrared (NIR) spectroscopy, i.e., Woo et al. [8] successfully determined H_2O_2 using a portable infrared spectrometer, and Yam-

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aguchi et al. [9] reported a method suitable for measuring aqueous samples of H_2O_2 as well as for continuous monitoring of a reaction system where H_2O_2 is being either formed or decomposed. These optical methods, albeit faster and more environmentally friendly than volumetric titrations, still have not given conclusive results in high pressure processes. Since direct synthesis of H_2O_2 is more efficiently carried out under high pressure [10], a method suitable for online direct determination at the reaction pressure would be desirable. Raman spectroscopy has proved to be a very effective analytical method with a wide range of applications [11], including reaction monitoring [12], even at high pressure [13]. It has been used to accurately measure hydrogen peroxide concentrations in aqueous solutions [14–16]; however, no reports are found in the literature of H_2O_2 Raman measurement under high pressure. In this work, we successfully carried out the measurement of hydrogen peroxide solutions flowing through a high-pressure cell using a portable Raman spectrometer in order to apply it as monitoring system, and we were able to confirm the possibility of using the solvent which is normally used in the direct synthesis reaction as internal standard for H_2O_2 Raman determination. Aarnoutse and Westerhuis [17] have confirmed that it is possible to use the solvent, particularly 1-methyl-2-pyrrolidinone, as internal standard for Raman monitoring of a liquid-phase Heck reaction. Water was utilised in this work since it is a green and common solvent in the direct synthesis of H_2O_2 [4]. As for inert gases, nitrogen and carbon dioxide were employed when the system was pressurised, both of which are also commonly found in direct synthesis reactions. Due to the extreme importance of side reactions in the overall direct synthesis process, the decomposition reaction of the peroxide has also been studied in the literature [18]. In this work, we have chosen said decomposition reaction to be monitored online and therefore validate the setup and the calibration model.

2. Experimental

2.1. Materials

H_2O_2 (33 wt/v%, reagent grade, Panreac Química S.A.U.) was used to prepare a set of 18 standard solutions (from 0.06 to 8.62 wt/v%) for quantitative calibration models. A second set of 17 samples was prepared for validation. Distilled water (Millipore quality) was used as solvent. Spectra were collected immediately after sample preparation to minimise possible errors due to decomposition of the hydrogen peroxide. In order to determine the concentration of the samples, KI (PRS-Codex, Panreac Química S.A.U.), H_2SO_4 (PA-ISO, Panreac Química S.A.U.) and $Na_2S_2O_3 \cdot 5H_2O$ (PA-ACS, Panreac Química S.A.U.) were used for conventional iodometric titration. Industrial grade nitrogen and carbon dioxide were

purchased from Carburos Metálicos (Spain) and used without further modification. A commercial 5 wt% Pd/C (Sigma, Spain) was used for the H_2O_2 decomposition reactions.

2.2. Instrumentation and data processing

All the spectra were obtained with a portable Raman spectrometer BWTEK i-Raman (BWS415) equipped with a 40 mW diode laser emitting at 532 nm with a focal distance in air of 10 mm and an effective focal distance of _ca._ 13.5 mm through the quartz window. The laser system includes a CCD array detector with a thermoelectric cooling (TE-cooling) system which decreases the dark noise allowing a better resolution. The spectral range of the detector is 530–700 nm (0–4000 cm^{-1} Raman shift) and the best resolution is 5 cm^{-1}.

The equipment was connected to a computer for data collection. Each spectrum was collected using a total acquisition time of 60 s (4 accumulations of 15 s). A total of 134 spectra were collected. Of these, 36 spectra were obtained at atmospheric pressure and room temperature and were used to build the calibration model; while 34 spectra from independent sample solutions were obtained under different pressures and temperatures and used as validation sets in order to check the accuracy of the quantification. The remaining 64 spectra were obtained during the decomposition reactions. Data processing of the spectra, including dark noise substraction, baseline correction and integration, was accomplished using a commercial software package.

2.3. Experimental procedure

Samples were taken from the bottom of a reaction vessel [10] through a 1 μm filter and pumped using a Jasco 2080 HPLC pump through a specifically designed high-pressure SS316 view cell of 3 mL of volume. The cell has a window cap supporting a UV grade quartz window of 20 mm diameter and 10 mm thickness (see Fig. 1). The cell, sealed with one Viton O-ring (id. × od. × thickness, 17.463 mm × 20.638 mm × 3.175 mm) and one Teflon ring (id. × od. × thickness, 11 mm × 20 mm × 2.5 mm), was hydrotested up to 25.0 MPa at room temperature. In order to avoid interference of possible gas bubbles that could be carried in the liquid flow, the high pressure cell was placed upside down and the inlet was lower than the outlet, so that the bubbles would gather on the top. The inlet was 1/16 in od. stainless steel tube located just 1 mm above the quartz window to increase the response time of the on-line measurement. In order to minimise background noise, the high pressure cell along with the Raman probe were isolated in an airtight compartment.
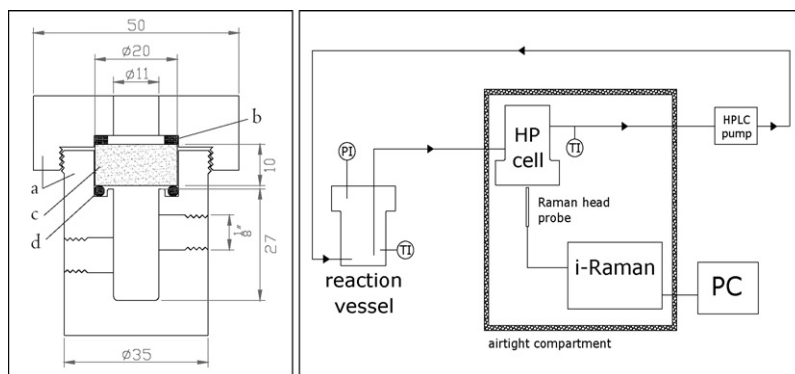

Fig. 1. Left: Design of high pressure cell. The inlet tube (1/16 in od.) was put near the quartz view window, 1 mm approximate distance (a: 316SS view cell body and window cap; b: Teflon ring; c: quartz window; d: Viton O-ring). Right: Layout of the experimental system. The high-pressure cell, laser and CCD sensor were introduced in an airtight compartment.
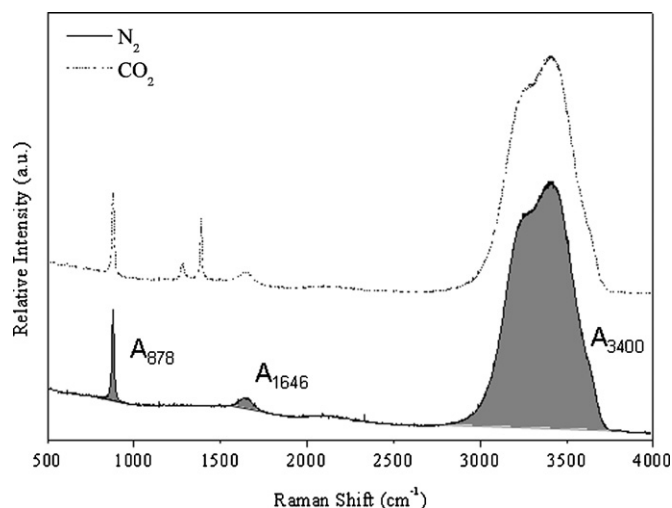
Fig. 2. Raman spectra of 2.5 wt/v% H_2O_2 in water and N_2/CO_2.

The H_2O_2 decomposition reactions were carried out under pressure (5.0 MPa). In all cases, the initial mixture consisted of 100 mL of an aqueous solution approximately 3.5 wt/v% H_2O_2 without any promoters so that the decomposition effect could be clearly followed without any interference. A first iodometric titration was carried out to confirm the initial concentration, and then the Pd/C catalyst (25 mg) was added to the mixture. Reaction time was 120 min since the catalyst was added. The system was pressurised with carbon dioxide. Raman spectra were taken automatically every 10 min, and 3 samples (1 mL) were extracted for titration at different times (30, 60 and 90 min) to confirm the results obtained.

3. Results and discussion

3.1. Spectral features

The Raman spectrum of a 3 wt/v% H_2O_2 solution in water is shown in Fig. 2, where the peroxide band at 878 cm^{-1} (stretching of the O–O bond) can be clearly observed without any interference. The assignment of the remaining bands [19,20] is listed in Table 1. Note that CO_2 produces a stronger Raman signal (at 1280 and 1388 cm^{-1}) than N_2 (at 2330 cm^{-1}), although it does not interfere with the peroxide signal. Since the laser power of the Raman equipment may suffer occasional variations, resulting in a change of the intensity of the bands, all the spectra must be normalised against an internal standard. By relating the band of interest to the area of at least one of the solvent bands – preferably a clearly defined, non-overlapping and intense one –, all multiplicative distortions are corrected. The areas used in the calculations are also shown in Fig. 2.

Table 1
Raman band assignments.

Raman shift (cm^{-1})	Assignment
878	OO stretch
1646	OH bend
1280	CO stretch
1388	CO stretch
2330	NN stretch
ca. 3400	OH stretch

Table 2
Calibration results in water at room temperature and pressure (C, wt/v% H_2O_2; and A_{xxx}, area of the band at xxx cm^{-1}).

# meas.	R^2	SEC (wt/v%)	%RSEC	Equation
36	0.9991	0.130	2.95%	$C = 149.7590 \pm 1.0705 \times \frac{A_{878}}{A_{878}+A_{1646}+A_{3400}}$

3.2. Calibration

The calibration curve was built using concentrations ranging from 0.06 to 8.62 wt/v% at room pressure and temperature (25 °C). The data were adjusted by linear regression. The standard error of calibration (SEC) and the relative standard error of calibration (%RSEC) are related to the predictive capacity of the model, and have been calculated according to the following equations [21]:

$$SEC = \sqrt{\frac{\sum_{i=1}^{n}(C_{RAMAN_i} - C_{REF_i})^2}{n}} \qquad (1)$$

$$\%RSEC = \sqrt{\frac{\sum_{i=1}^{n}(C_{RAMAN_i} - C_{REF_i})^2}{\sum_{i=1}^{n} C_{REF_i}^2}} \times 100 \qquad (2)$$

where n is the number of samples included in the calibration set, C_{RAMAN} is the concentration of H_2O_2 obtained from the Raman spectrum, and C_{REF} is the concentration of H_2O_2 obtained by the reference method, i.e., iodometry.

A total of 18 concentrations were used for the calibration, and each one was measured twice (2 spectra and 2 titrations per concentration). Table 2 shows a summary of the calibration results obtained. In order to use the solvent (water) as internal standard, both its bands, at 1646 and 3400 cm^{-1}, were included in the calibration equation (see Fig. 2). The values of SEC and %RSEC obtained are quite low, being the SEC 0.130 wt/v% and the %RSEC 2.95%, which agrees with previous results for H_2O_2 Raman calibrations [16].

Although a linear regression was used in this work, the data show a slight deviation best fitted by a second order polynomial regression, in which case the values of SEC and %RSEC drop considerably (0.049 wt/v% and 1.10%, respectively).

3.3. Validation

To study the suitability of the calibration models, several validation sets were prepared. The first validation was carried out at room temperature and pressure, i.e., under the same conditions as the calibration. The second set was carried out under pressure (5.0 MPa) using either nitrogen or carbon dioxide as inert gases. A last validation set was carried out to study the influence of temperature on the calibration model (increasing the temperature up to 45 °C and ensuring that the temperature in the measuring cell was the same as in the reaction vessel). The standard error of prediction (SEP) and the relative standard error of prediction (%RSEP) were calculated according to Eqs. (1) and (2), and their values are shown in Table 3. Fig. 3 shows two scattering plots representing the correlation or parity between the Raman and reference values (both for validation and calibration). In all cases, the Raman prediction matches the reference value correctly with values of SEP lower than 0.156 wt/v% and %RSEP lower than 3.06%, thus validating the

Table 3
Validation results for different pressures and inert gases.

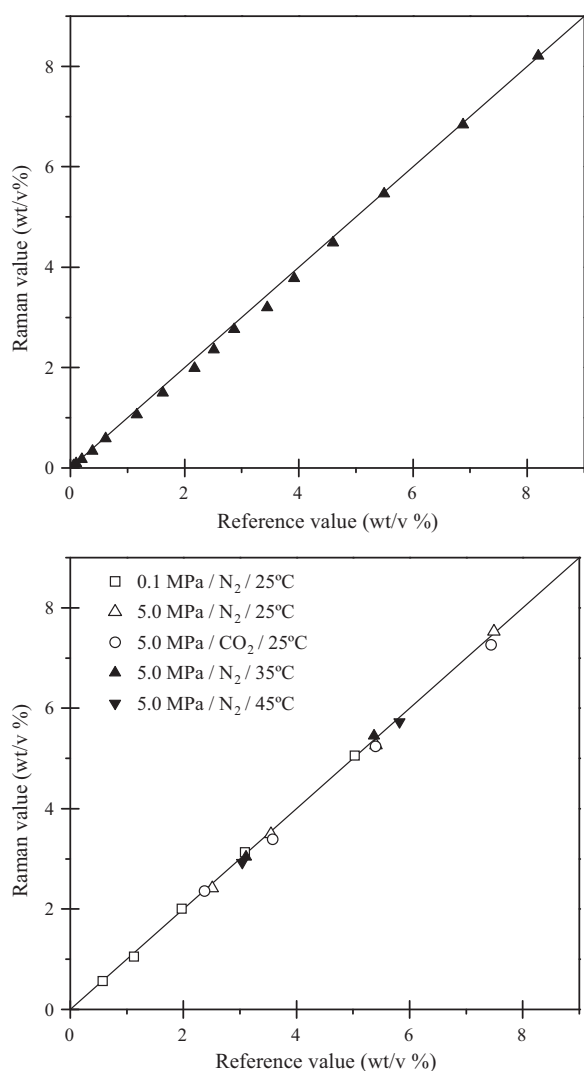|	# meas.	SEP (wt/v%)	%RSEP
0.1 MPa, 25 °C	10	0.042	1.48%
5.0 MPa, N_2, 25 °C	8	0.092	1.81%
5.0 MPa, CO_2, 25 °C	8	0.156	3.06%
5.0 MPa, N_2, 35 °C	4	0.074	1.69%
5.0 MPa, N_2, 45 °C	4	0.103	2.22%

Fig. 3. Parity plot of data vs. fit (top: calibration, bottom: validation at different pressures and temperatures).

Fig. 4. H_2O_2 decomposition over different Pd/C catalysts (■ 1 wt% Pd/C, ● 3 wt% Pd/C, ▲ 5 wt% Pd/C).

calibration model. No deviation in the measurement was observed in the validations at an increased pressure (5.0 MPa), which could indicate that the pressure effect onto the H_2O_2 molecule is not strong enough to modify the stretching movement of the O–O bond substantially. The influence of temperature was also studied, and the calibration model (obtained at 25 °C) was valid at temperatures up to 45 °C. However, to obtain more accurate results, we recommend insulating the measuring cell and keeping its temperature at the calibration temperature. The volume of the cell has been optimised to minimise the volume of sample and the residence time in the cell (this is related to the stabilisation time). Since the volume flowing through the cell is negligible in respect to the reaction volume, the temperature in the reaction vessel is not affected (see Section 3.4).

3.4. Online application: real time monitoring of hydrogen peroxide decomposition

The non-intrusive and non-destructive nature of this analytical technique makes it an attractive option for online monitoring of reactions involved in the direct synthesis of hydrogen peroxide. The fact that the Raman probe needs not be immersed in the reaction medium to obtain accurate measurements helps avoid
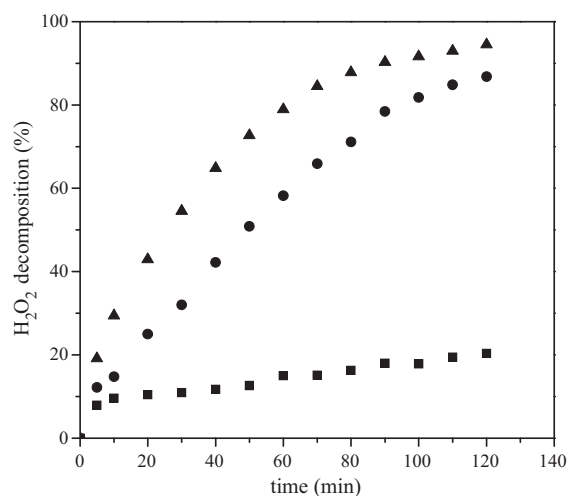
interferences from the other phases present in the liquid (i.e., suspended catalyst and gas bubbles). Additionally, this setup allows working at high pressure without any special Raman requirements.

In the case of monitoring reactions outside of the reactor vessel, sampling should be representative of the reaction medium but not cause significant alterations in the amount of the reaction mixture plus catalyst. The monitoring system in this case has a volume of 4 mL accounting the sample lines. Coupled to a reaction vessel with 100 mL liquid phase, this represents a 4% of the volume of the liquid phase in which the reaction is carried out. The analysis time required to determine the conversion of the reaction also needs to be considered, and it should be quite small compared to the reaction rate, in order to capture the modifications occurred in the reaction itself. The reaction rate values found for the H_2O_2 direct synthesis are generally low (between 10^{-3} and 10^{-5} mol $H_2O_2/g_{cat}/s$) [22,23], making the time necessary to obtain the spectra negligible in respect of the time in which the reaction produces a significant change. In this work, the sample flow extracted by the HPLC pump was kept at 10 mL/min, and since each measurement takes 60 s, the cell volume is renewed over 2 times with every spectrum acquired. This ensures that the analysed sample is representative of the liquid phase inside the reactor.

To illustrate the possibilities of this quantification system, several H_2O_2 decomposition reactions were carried out under CO_2 pressure (5.0 MPa) using a Pd/C catalyst, which we have previously used to study the direct synthesis reaction and is also known to be active for the decomposition reaction [10]. The experimental setup presented in this work allowed us to quantify the concentration of H_2O_2 in the reaction mixture online every 10 min, without decompression or disturbances. Three verification titrations were carried out in each case (at 30, 60 and 90 min) extracting 1 mL samples from the system, and the results were in all cases within the standard error of the calibration. Fig. 4 shows the evolution of the decomposition with time for different Pd loadings on the catalyst, while Fig. 5 represents the influence of reaction temperature on the decomposition. As expected, both factors clearly have a strong influence on the decomposition reaction and these effects, along with others, will be further studied and presented in a future research. However, for the purpose of this work, we will focus on the fact that the reaction was successfully monitored with the Raman equipment, being this achievement a great step forward in the field of direct synthesis of hydrogen peroxide.
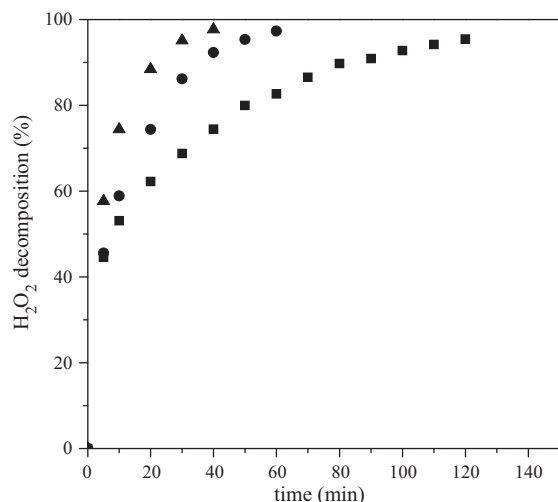
Fig. 5. H_2O_2 decomposition over a 5 wt% Pd/C catalysts at different temperatures (■ 23 °C, ● 30 °C, ▲ 40 °C).

4. Conclusions

This work presents the measurement of H_2O_2 solutions flowing through a high-pressure cell by means of a Raman spectrometer. The solvent of choice was water, which is commonly found in the direct synthesis of H_2O_2, and has been successfully used as internal standard to quantify the concentration of peroxide when its three Raman bands were considered (SEC 0.130 wt/v%, %RSEC 2.95%). The calibration obtained was validated at atmospheric pressure and also under high pressure (5.0 MPa) using both nitrogen and carbon dioxide, although the results were slightly better for nitrogen (%RSEP 1.81% vs 3.06%). It was also validated for higher temperatures (up to 45 °C) without significant deviations. This determination method is a promising alternative for online monitoring of H_2O_2 in a direct synthesis reaction, since it is non intrusive and no sample volume needs to be extracted. In order to further validate the calibration model and to exemplify the possibilities of the system for online measurement, the decomposition reaction of H_2O_2 has been successfully monitored under different reaction conditions. As the measurement can be made at the reaction pressure, it does not cause any disturbances in the system. Future work includes coupling this measuring system to a H_2O_2 direct synthesis semi-batch reactor.

Acknowledgements

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