

THE DETERMINATION OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTIONS BY SQUARE WAVE VOLTAMMETRY

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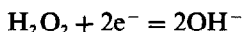
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(Received 29 November 1993. Revised 18 April 1994. Accepted 19 April 1994)

Summary—Hydrogen peroxide in aqueous solutions can be determined directly by square wave voltammetry. The method is applicable to samples with a large range of pH in matrices ranging from distilled de-ionized water to sea-water. Its dynamic range extends from 0.5 to at least 1000 μM and the precision is about $\pm 6\%$ at 2.5 μM and $\pm 2\%$ at 215 μM . In comparison to DC and differential pulse polarography, by using square wave voltammetry the scan time is reduced from minutes to a fraction of a second, the sensitivity is increased by several-fold and the dynamic range has been greatly expanded at both the lower and the upper end by at least an order of magnitude. The low detection limit allows this method to be applied to the determination of H_2O_2 in some samples of rainwater.

INTRODUCTION

Hydrogen peroxide is found in a wide variety of concentrations, ranging from mM to nM , in aqueous solutions in industrial, clinical and natural-water samples.^{1,2} Several methods, such as those based on iodometric titration,³ mass spectrometry,⁴ spectrophotometry,^{2,5} chemiluminescence,⁶ fluorometry,⁷ DC polarography⁸ and differential pulse polarography⁹ have been reported for its determination within different ranges of concentrations. The polarographic methods are based on the irreversible electrochemical reduction of H_2O_2 to the hydroxyl ion:



in a neutral or alkaline solution at a half wave potential of about -1.0 V vs. the saturated calomel electrode (SCE).¹⁰ These electrochemical methods have two main advantages over most of the other methods. They can tolerate large changes in the ionic strength and they require minimal pre-treatment of the samples. Potentially, a compound that can be determined by differential pulse polarography may also be determined by square wave voltammetry (SWV).^{11,12} If the latter analytical approach is feasible, it should be the preferred method since it can be orders of magnitude

more rapid and it may have a lower detection limit, a higher sensitivity and a greater dynamic range. Furthermore, in SWV, an analysis is completed with a single drop of mercury so that the use and eventual disposal of the toxic mercury may be minimized. Thus, this possibility has been explored and the results are reported here.

EXPERIMENTAL

Apparatus

An EG&G/Princeton Applied Research Model 384B-4 polarographic analyzer system, equipped with a Model 303A static mercury dropping electrode (SMDE) in the hanging mercury drop electrode (HMDE) mode, a Model 305 stirrer and a Houston Instrument DMP-40 digital plotter, was used for square wave voltammetry. A platinum wire and a saturated calomel electrode (SCE) connected through a salt bridge were used as the auxiliary electrode and the reference electrode, respectively. The drop-size of the mercury drops was pre-set by the manufacturer as 'small', 'medium' and 'large' drops. While neither the weight nor the volume of the drops were given, the volume-ratio and the area-ratio of these three sizes were listed by the manufacturer as 1:2:4 and 1:1.6:2.5, respectively. The weight of the 'medium' and 'large' drops were

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estimated in this laboratory to be 0.001 and 0.004 g, respectively.

An Orion Model 701A Ionalyzer and a Corning (No. 476570) deep vessel combination electrode were used for monitoring pH.

Reagents

All chemicals used were of the ACS reagent-grade.

A 0.01M stock solution of hydrogen peroxide was standardized iodometrically by using iodate as the primary standard.¹³ Standard solutions at lower concentrations were prepared from dilutions of this standardized solution.

Procedures

A 5-ml aliquot of the sample was pipetted into a polarographic cell followed by addition of 0.5 ml of a phosphate-citrate solution (a 1M sodium dihydrogen phosphate-1M sodium citrate solution adjusted to pH 7, this solution acts both as an ionic strength adjuster and a pH buffer). The cell was positioned in the SMDE. The sample was purged with argon for 4 min to remove any dissolved oxygen in the sample. The sample was blanketed with a positive pressure of argon to prevent oxygen from re-dissolving into the sample. The sample was analyzed under the following conditions: mode, SWV (square wave voltammetry); scan range, -0.4 to -1.6 V; reference electrode, saturation calomel electrode; frequency, 120 Hz; scan increment, 10 mV; pulse height, 80 mV; drop-size, large. A calibration curve was constructed by internal additions of known volumes of a standardized solution of H₂O₂. (Increments of 0.1 ml of a 0.3, 1, 5 or 10mM standard solution of H₂O₂ were

added to samples with concentration ranges of less than 30 μ M, 30-100 μ M, 100-500 μ M and 500 μ M-1mM, respectively). After each addition of the standard solution of H₂O₂, the sample was purged with argon for 2 min and the voltammogram recorded. The concentration of H₂O₂ in the sample was calculated from this calibration curve.

RESULTS AND DISCUSSION

Optimization of frequency, scan increment and pulse height

The dependence of peak current on frequency, scan increment, and pulse height was determined in a NaCl-KBr-NaHCO₃ solution. The composition of this solution (0.38M in sodium chloride, 1 mM in potassium bromide and 5 mM in sodium bicarbonate adjusted to pH 8) is similar but not identical to that of sea-water which is about 0.5M in sodium chloride, 0.8mM in Br⁻, 2mM in HCO₃⁻, 10mM in K⁺.¹⁴ At a fixed scan increment (10 mV) and pulse height (100 mV), the peak current of H₂O₂ increased approximately linearly with increasing frequency at about 2%/Hz between 20 and 80 Hz [Fig. 1(a)]. Above 80 Hz, the peak current increased more gradually with frequency. A frequency of 120 Hz, the highest frequency that the polarographic analyzer can provide, was chosen as the recommended condition for the method.

The dependence of peak current on scan increment was determined at a frequency of 120 Hz and a pulse height of 100 mV. As predicted by the theory on SWV,^{11,12} the peak current increased systematically with increasing scan

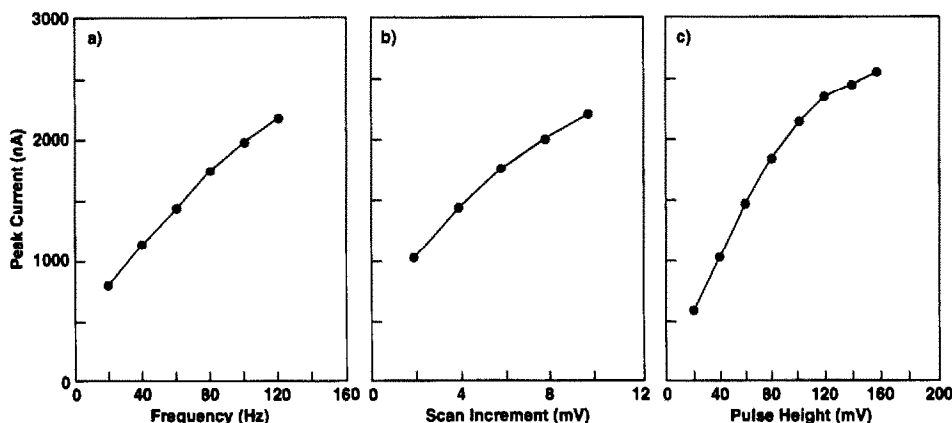


Fig. 1. The effect of (a) frequency (scan increment: 10 mV, pulse height: 100 mV), (b) scan increment (frequency: 120 Hz, pulse height: 100mV) and (c) pulse height (frequency: 120 Hz, scan increment: 10mV) on the peak current of a 95 μ M H₂O₂ solution using a 'medium' drop-size.

increment. The rate of increase was about 14%/mV within the range of values, 2–10 mV, tested [Fig. 1(b)]. A scan increment of 10 mV was selected for the recommended condition. At this scan increment, the peak current was maximized, the time required for the completion of a scan was minimized while the resolution of the current peak was not noticeably compromised. The recommended frequency and scan increment gave an effective scan rate of 1200 mV/sec. This rate is several hundred times faster than the typical scan rate used in differential pulse polarography. As a result, a scan may be completed within a second rather than in several minutes.

The dependence of peak current on pulse height was determined at a frequency of 120 Hz and a scan increment of 10 mV. The peak current increased approximately linearly with increasing pulse height between 20 and 80 mV at a rate of about 4%/mV [Fig. 1(c)]. At higher values, the peak current increased more gradually with increasing pulse height and the current peak broadened as expected in SWB.¹¹ In order to maximize the peak current and minimize the distortion of the peak shape, a pulse height of 80 mV was chosen as the recommended condition.

pH effect

The variations in peak current with pH, between pH 2 and 14, in the NaCl–KBr–NaHCO₃ solution containing 0–457 μ M of added H₂O₂ and using the 'medium' drop-size are shown in Fig. 2. The pH of the solution was adjusted to the desired values by the addition of

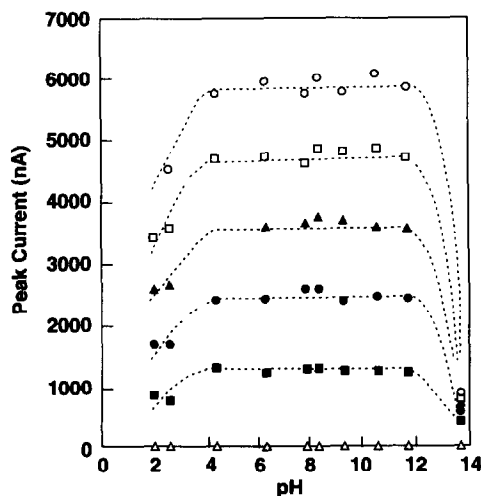


Fig. 2. The effect of pH on peak current at various concentrations of H₂O₂. Δ : 0 μ M; \blacksquare : 95 μ M; \bullet : 188 μ M; \blacktriangle : 280 μ M; \square : 369 μ M; and \circ : 457 μ M.

Table 1. The effect of pH on the relationship between the peak current and the concentration of H₂O₂*

pH	Slope (nA/ μ M)	α †	r^2
2.0	8.6	0.3	0.98
2.6	9.6	0.2	1.00
4.3	12.7	0.1	1.00
6.3	12.9	0.1	1.00
7.8	12.6	0.1	1.00
8.3	13.1	0.1	1.00
9.3	12.8	0.1	1.00
10.5	13.1	0.1	1.00
11.4	12.6	0.1	1.00
11.7	12.7	0.1	1.00

Matrix: NaCl–KBr–NaHCO₃ solution.

Drop-size: medium.

*Result of linear least square fit without an intercept between 0 and 457 μ M of H₂O₂.

†One standard deviation. n (number of data points) = 5 at pH 2.0 and 4.3. N = 6 at all other pH.

r : correlation coefficient.

1M HCl or 1M NaOH. The peak current reached a plateau between pH 4.3 and 11.7 at all concentrations of H₂O₂. At lower and higher pH, the peak current was depressed significantly. Peak current was linearly related to the concentration of H₂O₂ between pH 2 and 11.7 (Table 1). The correlation coefficients, r^2 , ranged between 0.98 and 1.00. Thus, this method is applicable to samples with a wide range of pH even without making any pH adjustment.

Matrix effect

Surface sea-water (salinity = 36.6 psu; pH 8.0), estuarine water (salinity = 23.4 psu; pH 8.0) and rainwater (pH 4.7) were collected from the Sargasso Sea in August 1990 at 32°N, 75°W, from the mouth of the Chesapeake Bay in February 1993 at 37°1.8'N and 76°8.6'W and at Old Dominion University in Norfolk, VA, in March 1992. (The unit 'psu' is the practical salinity unit and is equivalent to about 1 g of salt per kg of sea-water.¹⁵) Upon the addition of known quantities of H₂O₂ to aliquots of each of these samples, to distilled-deionized water and to the NaCl–KBr–NaHCO₃ solution, the voltammograms were recorded. (The residual amount of H₂O₂ that was present initially in the natural water samples was negligible since these samples had been stored in the dark at room temperature for many weeks before they were used in these experiments and the half life of H₂O₂ in natural waters is of the order of only hours to days.^{16,17} We have observed that H₂O₂ in water collected from Chesapeake Bay

Table 2. The relationship between the peak current and the concentration of H_2O_2 in different matrices at two concentration ranges*

Matrix	0-25 μM			25-1000 μM		
	Slope ($nA/\mu M$)	σ †	r^2	Slope ($nA/\mu M$)	σ †	r^2
Drop-size: medium						
DDW	10.3	0.5	0.98	17.5	0.3	1.00
Rain	10.7	0.5	0.99	17.3	0.3	1.00
NaCl	9.5	0.6	0.97	No data		
Estuarine water	8.9	0.5	0.97	No data		
Sea-water	8.1	0.5	0.97	16.3	0.2	1.00
Drop-size: large						
DDW	23.7	0.3	1.00	27.1	0.2	1.00
Rain	23.6	0.3	1.00	27.0	0.2	1.00
NaCl	21.4	0.5	1.00	No data		
Estuarine water	20.3	0.4	1.00	No data		
Sea-water	17.9	0.5	0.99	26.2	0.2	1.00

*Result of linear least square fit without an intercept.

†One standard deviation. n (number of data points) = 5 at 0-25 μM .
 $n = 7$ at 25-1000 μM .

r : correlation coefficient.

DDW: distilled-deionized water.

NaCl: NaCl-KBr-NaHCO₃ solution.

decreased from 0.43 μM to less than 0.02 μM after one day of storage.) The relationship between peak current and the concentration of added H_2O_2 in these solutions are tabulated in Table 2. In all cases, the peak current increased linearly with concentration with correlation coefficients, r^2 , exceeding 0.97. Thus, this method is applicable to samples with a wide variety of compositions and ionic strengths. However, the slope of the linear relationship decreased with increasing ionic strength. In solutions with similar ionic strengths, such as distilled-deionized water and rainwater, and the estuarine water and the NaCl-KBr-NaHCO₃ solution, the slopes were similar.

The effect of sample matrix on the slope of the linear relationship between peak current and concentration was also concentration dependent. At higher concentrations, the matrix effect was smaller. For highest precision, a calibration line should be constructed for each sample by internal additions.

Sensitivity, dynamic range and precision

The sensitivity of the method is given by the slope of the linear regression line relating the peak current to the concentration of H_2O_2 . It is pH-dependent (Table 1). With a 'medium' drop-size, the slope increased with increasing pH between pH 2 and 4.3 from 8.6 to 12.7 $nA/\mu M$. Thus, while the method is still valid at these lower pH values, the sensitivity of the method is

reduced. Between pH 4.3 and 11.7, the sensitivity was independent of pH as the slope remained approximately constant, varying randomly between 12.6 and 13.1 $nA/\mu M$. At pH 13.7, in a 0.5M NaOH solution, the linear relationship broke down. In the recommended procedure, the maximum sensitivity is assured by maintaining the pH of the sample at about pH 7 by adding the phosphate-citrate solution, which acts both as a pH buffer and an ionic strength adjuster, to the sample.

The sensitivity of the method is also dependent on the size of the hanging mercury drop. At concentrations below 25 μM , it decreased by a factor of slightly larger than two, from 23.7 to 10.3 $nA/\mu M$ in distilled-deionized water and from 17.9 to 8.1 $nA/\mu M$ in sea-water, as the drop-size was reduced from 'large' to 'medium' (Table 2) as pre-set by the manufacturer of the polarographic analyzer system. In order to maximize the sensitivity, the 'large' drop-size is recommended. Boto and Williams⁹ reported that the sensitivity of the differential pulse polarographic determination of H_2O_2 was about 4 $nA/\mu M$ at concentrations between 5 and 20 μM . Under the recommended procedure reported here, the sensitivity of the square wave voltammetric method will be about four to six times and two to three times that of the polarographic method when the 'large' and the 'medium' drop-sizes are used, respectively.

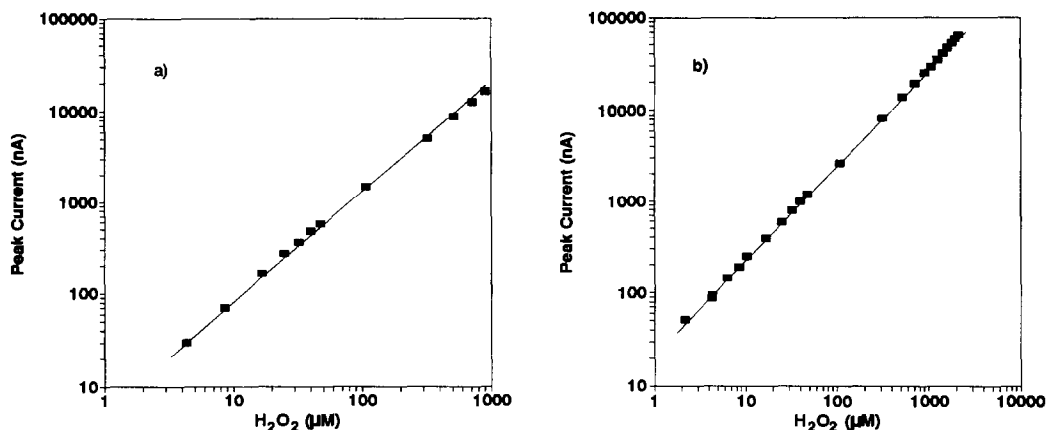


Fig. 3. The relationship between peak current and the concentration of H₂O₂ using different drop-sizes. (a) 'Medium' drop-size, 0–1000 μM . (b) 'Large' drop-size, 0–2200 μM .

The relationship between the concentration of H₂O₂, between 0 and 1000 μM with a 'medium' drop-size and between 0 and 2200 μM with a 'large' drop-size, and the associated peak current are shown in Fig. 3. As a first approximation, on a log–log scale, peak current is linearly related to concentration. However, in a linear plot, over these ranges of concentrations where the lowest and the highest concentration differed by more than an order of magnitude, a slight concave curvature was evident and the curvature was more pronounced when the 'medium' drop-size was used. Thus, the slopes of the linear relationships between 0 and 25 μM were significantly lower than those between 25 and 1000 μM (Table 2). The difference was especially pronounced in solutions with higher ionic strength and/or when the 'medium' drop-size was used such that the slope increased by 70% from 10.3 to 17.5 nA/ μM in distilled-deionized water and by 100% from 8.1 to 16.3 nA/ μM in sea-water. When the 'large' drop-size was used, the slope increased only by 14% from 23.7 to 27.1 nA/ μM in distilled-deionized water and by 46% from 17.9 to 26.2 nA/ μM in sea-water. The uncertainty in the slope was also slightly larger when the 'medium' drop-size was used. Thus, using the 'large' drop-size is recommended since the curvature in the relationship between peak current and concentration and the associated uncertainty in the calibration curve may then be minimized. None the less, within smaller ranges of concentrations, a highly correlated linear relationship between peak current and concentration was found regardless of the drop-size that was used. The linear correlation coefficient, r^2 , exceeded 0.97 in every case, at concentrations below 25 μM

and between 25 and 1000 μM (Table 2). In internal additions, the calibration curve will be kept within a linear range if the final concentration of H₂O₂, including the amount added to the sample, does not exceed the concentration in the sample by more than a factor of three to four. Furthermore, the upper end of the dynamic range of this method should reach at least 1000 μM .

Known amounts of H₂O₂ were added to a sample of aged rainwater which had been stored for one year and to distilled-deionized water, and the concentration of H₂O₂ in these solutions were measured repeatedly (Table 3). The solutions prepared from the sample of rainwater were analyzed with the 'medium' drop-size while those prepared in distilled-deionized water were analyzed using the 'large' drop-size. With the 'medium' drop-size, the precision ranged from $\pm 19\%$ at 2.7 μM to $\pm 8\%$ at 5.4 μM . With the 'large' drop-size, higher precision was achieved. It ranged from $\pm 6\%$ at 2.5 μM to $\pm 2\%$ at 215 μM . The amount of added H₂O₂ recovered ranged from 90 to 104%. If the detection limit of this method is taken as three times the standard deviation of the blank,¹⁸ it can be estimated to be about $\pm 0.5 \mu\text{M}$ when the 'large' drop-size is used. Thus, H₂O₂ may be measured by square wave voltammetry between 0.5 and at least 1000 μM . This dynamic range is much larger than that of 5–20 μM of differential pulse polarography.⁹

Hydrogen peroxide in rainwater

The detection limit of this method, 0.5 μM , is low enough so that it may be applicable to the determination of H₂O₂ in rainwater since the concentration in rainwater usually lies between

Table 3. Precision and recovery in the determination of H_2O_2

Matrix	$[\text{H}_2\text{O}_2]$ added (μM)	$[\text{H}_2\text{O}_2]$ found (μM)	Average $[\text{H}_2\text{O}_2]$ (μM)	σ^* (μM)	RSD† (%)	Recovery (%)
Drop-size: medium						
ARW	3.0	2.2, 2.4, 3.4 2.3, 3.0	2.7	0.5	19	90
ARW	5.9	5.9, 5.0, 4.9 5.8, 5.6	5.4	0.5	8	92
Drop-size: large						
DDW	2.4	2.4, 2.6, 2.7 2.4, 2.4	2.5	0.1	6	104
DDW	4.5	4.3, 3.9, 4.1 3.9, 3.9, 4.0	4.1	0.3	7	91
DDW	235	4.8, 4.2, 4.2 210, 217, 218 217, 214	215	3	2	92
Rain	—	18.4, 17.8	18.1	0.4	2	—
Rain	—	3.7, 2.8, 3.0	3.2	0.5	16	—
Rain	—	7.5, 8.3, 7.2	7.7	0.6	8	—

ARW: aged rainwater.

DDW: distilled-deionized water.

* One standard deviation.

† Relative standard deviation

several μM to several tens of μM .^{17,19,20} The concentrations of H_2O_2 in three samples of rainwater collected between July 1992 and February 1993 were measured with the proposed method. The measurements were made immediately after the collection of the samples. The concentrations of H_2O_2 in these samples were 18.1 ± 0.4 , 3.2 ± 0.5 and $7.7 \pm 0.6 \mu\text{M}$ (Table 3). This range of concentrations is within the range of reported concentrations of H_2O_2 in rainwater.^{17,19,20} The voltammograms of the sample containing $3.2 \mu\text{M}$ of H_2O_2 and this sample upon the addition of 5.3 and $10.6 \mu\text{M}$ of H_2O_2 are shown in Fig. 4. The current peak in the sample without any added H_2O_2 at about -1.05 V was still well defined with a peak height of 22

nA. In applying this method to the determination of H_2O_2 in rain, it should be noted that organic hydroperoxides may be present occasionally in this type of samples.²¹ Although it has been shown that the polarographic method can distinguish between organic hydroperoxides and hydrogen peroxide,^{8,22} this possible interference has yet to be specifically evaluated and definitively ruled out in square wave voltammetry.

CONCLUSIONS

Square wave voltammetry can be used for the rapid direct determination of H_2O_2 in aqueous solutions. It can tolerate large changes in the composition of the sample. In comparison to DC and differential pulse polarography, the scan time can be shortened from minutes to a fraction of a second while the sensitivity is increased several-fold. The dynamic range of the method extends from 0.5 to at least $1000 \mu\text{M}$.

Acknowledgements—This work was supported in part by the National Science Foundation under grant Nos OCE-8910956 and OCE-9301298 to G. Wong. It also constitutes part of the doctoral dissertation research of Ling-Su Zhang.

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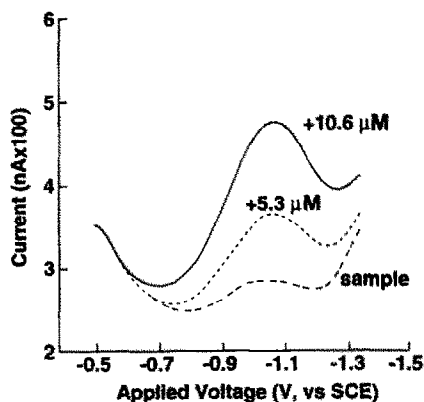


Fig. 4. The voltammogram of a sample of rainwater before and upon the addition of 5.3 or $10.6 \mu\text{M}$ H_2O_2 . The concentration of H_2O_2 in the sample was $3.2 \mu\text{M}$.

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