Full Paper

Application of H-Point Standard Addition Method and Multivariate Calibration Methods to the Simultaneous Kinetic-Potentiometric Determination of Hydrogen Peroxide and Peracetic Acid

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Abstract- The H-point standard addition method (HPSAM), partial least squares (PLS) and principal component regression (PCR) were used, during the present study, for the simple, accurate and simultaneous determination of two oxidants of hydrogen peroxide (H₂O₂) and peracetic acid (PAA) using the kinetic data from novel potentiometric method. The methods are based on the difference observed in reaction rate of iodide ion with PAA and H₂O₂ in the presence of Mo(VI) in acidic media. Therefore, the reaction rate of iodide ion with PAA and H₂O₂ was monitored by an iodide ion-selective electrode (IISE). Results have demonstrated that the simultaneous determination of H₂O₂ and PAA can be done in the concentration ranges of 0.5-14.0 and 0.05-2.0 µg mL⁻¹, respectively. The total relative standard error for applying the PLS and PCR methods to 8 synthetic samples in the concentration ranges of 2.0-11.0 µg mL⁻¹ for H₂O₂ and 0.3-1.9 µg mL⁻¹ for PAA, were 2.70 and 3.24, respectively. The effects of certain foreign ions, upon the reaction rate, were determined for assessing the selectivity of the
method. The proposed methods (HPSAM, PLS and PCR) were evaluated, using a set of synthetic sample mixtures, and applied for the simultaneous determination of $\text{H}_2\text{O}_2$ and PAA in water samples.

**Keywords** - Simultaneous determination, Kinetic-potentiometric, Hydrogen peroxide, Peracetic acid, Multivariate calibration methods

### 1. INTRODUCTION

Hydrogen peroxide ($\text{H}_2\text{O}_2$) and peracetic acid (PAA) are well-known in industry for the disinfection and bleaching purposes due to their ecologically beneficial properties [1]. PAA is primarily used in clean equipment, milking parlors, stalls, barns and the veterinary facilities. PAA is also used as an effective killer of microbial biofilms at low concentrations [2]. The high biocidal power, resulting from the mixture of PAA and $\text{H}_2\text{O}_2$, makes the highly effective products for killing microorganisms, viruses, bacteria and fungi [3].

PAA is synthesized by the reaction of acetic acid and hydrogen peroxide, which is allowed to continue for up to 10 days in order to achieve high product-yield according to the following equation:

\[
\text{CH}_3\cdot\text{C} - \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\cdot\text{C} - \text{O} - \text{OH} + \text{H}_2\text{O} \tag{1}
\]

Although a potent biocide, PAA is unique because it does not produce toxic byproducts while its decomposition products (acetic acid, water, and oxygen) are innocuous, environmentally acceptable and can easily be dissolved in water.

Simultaneous analysis of PAA and $\text{H}_2\text{O}_2$ is difficult because of the similarities of their behaviors. Different methods have been reported for determination of PAA and $\text{H}_2\text{O}_2$ individually [4-13]. Several methods have been also reported for simultaneous determination of PAA and $\text{H}_2\text{O}_2$ using different techniques [14-18]. Recently, simultaneous determination of PAA and $\text{H}_2\text{O}_2$, based on their spectral kinetics, has been stated with the help of multiple linear regression (MLR) analysis [3] and reversible reagent-less biosensor [19]. However, to the best of our knowledge, there is not any report for the simultaneous determination of PAA and $\text{H}_2\text{O}_2$ by electroanalytical techniques using chemometric methods.

During recent years, electroanalytical techniques are well known as excellent and cheap procedures for the determination of trace chemical species. Chemometrics methods are increasingly used in electroanalytical chemistry for extraction of more information from experimental data as in other areas of analytical chemistry [20-25]. In the field of potentiometry, several methods have been reported based on the flow injection system and
titration using partial least squares (PLS), artificial neural network (ANN) and Kalman filter as modeling methods [26-32]. We are reported the first application of PLS and principal component regression (PCR) multivariate calibration methods and HPSAM to the simultaneous kinetic-potentiometric determination of binary mixtures of hydrazine and its derivatives [33,34] and binary mixture of levodopa and carbidopa drugs [35]. Recently, we also reported the application of PLS and PCR methods for the simultaneous determination of ternary mixtures of Fe(III), Al(III) and Zr(IV) [36].

The present study reports, for the first time, the application of HPSAM, PCR and PLS as chemometric methods for the simultaneous determination of PAA and H$_2$O$_2$ using potentiometric technique. The methods were based on the difference observed in the reaction rate of iodide ion with PAA and H$_2$O$_2$ in the presence of Mo(VI). Therefore, the rate of iodide-ion reaction with these oxidants was monitored by an iodide ion-selective electrode (IISE).

2. EXPERIMENTAL

2.1. Apparatus and Software

A solid-state iodide ion-selective electrode (Metrohm, Model 6.0502.160) was used in conjunction with a double junction Ag/AgCl reference electrode (Metrohm, Model 6.0726.100) with the outer compartment filled by a saturated solution of KCl. The Metrohm Model 780 potentiometer was connected to a computer for recording the kinetic potentiometric data. All of the measurements were carried out at 25±0.2 °C in a double-walled reaction cell with continuous magnetic stirring. Both the stirring speed and the electrode distance were kept constant throughout the experiment. The electrode was kept in 1×10$^{-3}$ M KI solution when not in use. For pH measurements, a Metrohm Model 780 pH meter with a combination glass electrode was used. PLS and PCR analyses was performed using a MATLAB 7.0 software.

2.2. Materials and reagents

All of the chemicals were of analytical grade and prepared with double distilled water. Stock solutions of H$_2$O$_2$ (30% w/v) and PAA (39% w/v) were used for the preparation of corresponding experimental solutions my making dilutions in double distilled water. The peroxide concentration was determined by redox titration with potassium permanganate. These solutions were prepared daily and kept in dark at 4 °C in an amber-colored bottle. A stock solution of potassium iodide (1 mg mL$^{-1}$) was prepared by dissolving 1.677 g KI in 100 mL water. While, the stock solution of 0.1 M ammonium heptamolybdate (abbreviated as Mo(VI)) was prepared by dissolving 1.76 g Mo(VI) in 100 mL water. A solution of pH 1.0
was prepared by mixing 0.2 M KCl and 0.2 M HCl solutions. All of the chemicals were obtained from Merck.

2.3. Procedure

Twenty five milliliters of double distilled water, 2.0 mL of acidic solution of pH 1.0, 1.0 mL of KI (1×10^{-3} M) and 1.0 mL of ammonium heptamolybdate (1×10^{-3} M) were added into the thermostatic (25 °C) reaction cell. One milliliter of the standard or sample solution of PAA, H_2O_2 or a mixture of both of them was injected quickly into the cell and the data were recorded 30 seconds after the potential stabilization. The changes of potential versus time were recorded after the interval of every one second. Synthetic sample containing different concentration ratios of PAA and H_2O_2 were prepared and simultaneous determination was conducted by recording the changes of potential for each solution from 30 to 300 seconds. After each run, the cell was emptied and washed twice with double distilled water.

Using the standard analyte solutions, we could construct a calibration graph of (10^{AE/S}-1) versus concentration (fixed-time method) \[33,37\] for each of the analytes, where \(\Delta E\) is the potential variation in a selected time interval \(\Delta t\) (usually 270 seconds) and \(S\) is the slope of the IISE response, which is determined periodically by the successive additions of micro-amounts of 100 µL (1.0×10^{-2}-1.0 M) KCl standard solutions in 25 mL of water mixed with 2.0 mL buffer solution. Standard solutions of PAA and H_2O_2 can simultaneously be determined in the concentration ranges of 0.1-2.0 and 0.5-14.0 µg mL^{-1}, respectively.

The simultaneous determination of PAA and H_2O_2 standard solutions was performed via HPSAM by measuring the potential changes (\(\Delta E\)) at 150 and 200 seconds after the initiation of reaction for each sample solution. Then HPSAM plots of (10^{AE/S}-1) versus the added H_2O_2 concentration were constructed for the mixtures of PAA and H_2O_2. Simultaneous determination of PAA and H_2O_2 was performed with the help of PLS and PCR methods by recording the potential of each solution from 30 to 300 seconds. Then, by using MATLAB software, the concentrations of PAA and H_2O_2 were obtained for PLS and PCR.

3. RESULTS AND DISCUSSION

The concept of the present study for the simultaneous analysis of PAA and H_2O_2 was based on the difference in their oxidizing power. Preliminary studies have shown that the difference of reaction rates of PAA and H_2O_2 was suitable when I^- was used as reducing reagent and IISE for monitoring difference. It is well-known that the oxidation rate of I^- is much higher in the presence of PAA as compared to H_2O_2 \[3,17,19,38\]. Therefore, such phenomenon could be used to monitor different kinetic behaviors during simultaneous analysis of PAA and H_2O_2. In order to carry out the simultaneous kinetic potentiometric determination of PAA and H_2O_2 by HPSAM, PCR and PLS; a series of experiments were
conducted to establish the optimum system to achieve maximum sensitivity.

Upon the addition of oxidant (PAA and H$_2$O$_2$) into the I$^-$ solution in the presence of Mo(VI) as a catalyst, the oxidation reaction of iodide, in the presence of PAA and H$_2$O$_2$, takes place as follows:

\[\text{CH}_3\text{COOOH} + 2 \text{I}^- + 2 \text{H}^+ \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O} + \text{I}_2 \quad (2)\]
\[\text{H}_2\text{O}_2 + 2 \text{I}^- + 2 \text{H}^+ \rightarrow 2 \text{H}_2\text{O} + \text{I}_2 \quad (3)\]

However, in order to find the most appropriate difference of kinetic behavior between the two components, optimization of the conditions is required. Therefore, all experimental parameters, affecting the reaction rate of I$^-$ in the presence of PAA and H$_2$O$_2$ (response-time, I$^-$ and Mo(VI) concentration and pH, etc.), were carefully optimized.

3.1. Study of the electrode characteristics

The characteristics of the IISE were studied while present in the acetate buffer. Typical calibration graphs of IISE showed a linear response in the presence of 5×10$^{-5}$-1×10$^{-1}$ M iodide. The slope was found to be 57.3 mV/decade and remained almost constant up to 0.5 mV, in this system, over an application period of 7 months.

3.2. Effect of pH

The acidity of the solution has an influence over the potential response of IISE and the reaction rates of PAA and H$_2$O$_2$. The effect of pH was examined on the reaction rate of PAA and H$_2$O$_2$ in the presence of I$^-$ over the pH range of 1.0-6.0. Maximum differences in kinetic behavior and the exhibition of larger values of potential change ($\Delta E$) between PAA and H$_2$O$_2$ were seen at pH 1.0, which was selected as the optimum pH for both analytes.

The change of the amount of potential ($\Delta E$) was investigated for the reaction of certain amount iodide ions with PAA and H$_2$O$_2$ in different acidic solutions of HNO$_3$-H$_3$BO$_3$, citrate-HCl and KCl-HCl. In the KCl-HCl solution (pH 1.0), both $\Delta E_{\text{PAA}}$ and $\Delta E_{\text{H}_2\text{O}_2}$ had larger potential values. According to obtained results, the mixture of 0.1 M KCl-0.1 M HCl (pH 1.0) was chosen as the ground acidic solution.

3.3. Effect of iodide concentration

The iodide ion easily oxidized to I$_2$ by the powerful oxidizing agents. The I$^-$ concentration must be in excess in order to start the pseudo-first-order reaction. The effect of 1.0×10$^{-5}$–1.0×10$^{-1}$ M I$^-$ concentration was investigated on the linear range of calibration graph and the H$_2$O$_2$ and PAA reaction rate. When the I$^-$ concentration is low, a gentle slope is realized in the calibration graph while, higher concentration produces a steeper slope. Our results have shown that the I$^-$ concentration has a great effect on the linear range and the change of
potential value. Since, maximum differences in kinetic behavior of H₂O₂ and PAA were observed in the presence of 1.0×10⁻³ M I⁻ and both species showed larger values of potential change (ΔE) at this concentration. Therefore, the I⁻ concentration of 1.0×10⁻³ M was selected as the optimum concentration for further studies.

3.4. Effect of Mo(VI) concentration

Ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄.4H₂O (abbreviated as Mo(VI))] act as a catalyst [39,40]. The effect of Mo(VI) concentration on the reaction rates of H₂O₂ and PAA, over a concentration range of 1×10⁻⁵-1×10⁻¹, was studied. The results have shown that the increase of Mo(IV) concentration, up to 1×10⁻³ M, causes an increase in the potential change, which remained nearly constant at higher concentrations. Therefore, 1×10⁻³ M Mo(VI) was selected as the optimum concentration for further studies.

3.5. Effect of surfactants

In some of the simultaneous kinetic determinations, use of the surfactants gives a better data of kinetic difference since, micellar media have long been known to alter the reaction rates [41,42]. Thus, the effect of surfactants on the reaction rate of I⁻ with H₂O₂ and PAA was evaluated during the present study. According to the obtained results, cationic surfactant (cetyl trimethyl ammonium bromide, CTAB) decreased the rate of H₂O₂ and PAA reaction while, anionic (sodium dodecyl sulfate, SDS) and non-ionic (Triton X-100, TX-100) surfactants showed no effect on the reaction rate of both analytes. Therefore, the reaction was preferably carried out without the presence of surfactants.

3.6. Effect of surfactants

The potential-time behavior of the I⁻ reaction with H₂O₂, PAA and the mixture of both of them, at the optimized conditions, is shown in Fig. 1. Fig. 2 shows typical reaction curves for the I⁻ reaction with H₂O₂ and PAA at different concentrations.
Fig. 1. Potential-time curves for the reaction of $\Gamma^-$ with 1.8 µg mL$^{-1}$ PAA (a), 4.0 µg mL$^{-1}$ H$_2$O$_2$ (b) a mixture of both of them (c)

As shown in Figs. 1 and 2, the reaction of PAA is faster than that of H$_2$O$_2$ and was almost completed in 100 seconds after its initiation while H$_2$O$_2$ reaction was very slow and took relatively longer time. This difference of reaction rates allowed us to apply the HPSAM, PLS and PCR methods for simultaneous determination of H$_2$O$_2$ and PAA.

Table 1 shows the characteristics of calibration graphs for H$_2$O$_2$ and PAA determination under optimum conditions.

Fig. 2. Typical potential-time curves for the reaction of $\Gamma^-$ with different concentrations (µg mL$^{-1}$) of PAA (a) and H$_2$O$_2$ (b)
3.7. Requirements for HPSAM application

We have been reported the basis of HPSAM application for the treatment of kinetic data under conditions when one component has completed the reaction while the other has not [33].

![Plot of potential changes](image)

**Fig. 3.** Plot of potential changes ($10^{\Delta E/S-1}$) for the reaction of $\Gamma^-$ with 1.8 µg ml$^{-1}$ PAA (a), 4.0 µg ml$^{-1}$ H$_2$O$_2$ (b) and a mixture of both of them (c)

Considering a binary mixture of H$_2$O$_2$-PAA, as an example, we can assume that the amount of ($10^{\Delta E/S-1}$) of the produced during H$_2$O$_2$-KI reaction was $P_i$ and $R_i$ at times $t_1$ and $t_2$, respectively. While those of the PAA-KI reaction, under the same conditions, was $P$ and $R'$, respectively (Fig. 3). Both of them are equal in this case. The following equations demonstrate the relation between them:

For H$_2$O$_2$: \[ R_i = P_i + m_it_i \quad (t_1 \leq t_i \leq t_2; \quad i=0,1,...,n) \] (4)
For PAA: \[ R' = P + mt_j \quad (m=0) \] (5)

where, subscripts \( i \) and \( j \) denote different solutions for the \( n \) additions of \( \text{H}_2\text{O}_2 \) concentration, prepared to apply the HPSAM, and the time comprising the \( t_1\)-\( t_2 \) range, respectively. Thus, the overall amounts of \( (10^{\Delta E/S} - 1) \) (or \( R \)) of the \( \text{H}_2\text{O}_2\)-PAA mixture are:

At \( t_1 \): \[ Rt_1 = P_0 + P_i \] (6)
At \( t_2 \): \[ Rt_2 = R' + R_i \] (7)

To select the appropriate times, the following principles were followed. At the two selected times, \( t_1 \) and \( t_2 \), the amount of \( R \) of the \( \text{H}_2\text{O}_2 \) must be linear with the concentrations, while the amount of \( R \) of the PAA must remain constant, even if the \( \text{H}_2\text{O}_2 \) concentrations are varying. The amount of \( R \) of the \( \text{H}_2\text{O}_2\)-PAA mixture should be equal to the sum of individual \( R_s \) of the two compounds. In addition, the slope difference of the two straight lines, obtained at \( t_1 \) and \( t_2 \), must be as large as possible to achieve the good accuracy [43-45]. Then, known concentrations of \( \text{H}_2\text{O}_2 \) were successively added to the mixture so as to measure the resulting potential changes at the two time intervals, as expressed below:

\[ R_{t1} = (10^{\Delta E(t1)/S} - 1)t_1 = P_0 + P + M_{t1}C_i \] (8)
\[ R_{t2} = (10^{\Delta E(t2)/S} - 1)t_2 = R_0 + R' + M_{t2}C_i \] (9)

where \( \Delta E(t_1) \) and \( \Delta E(t_2) \) are the potential changes, measured at \( t_1 \) and \( t_2 \), respectively. \( P_0 \) and \( R_0 \) are the amounts of \( R \) of the \( \text{H}_2\text{O}_2 \) in a sample at the time intervals of 150 and 200 seconds, respectively. \( P \) and \( R' \) are the amounts of \( R \) of the PAA at \( t_1 \) and \( t_2 \), respectively. \( M_{t1} \) and \( M_{t2} \) are the slopes of the standard addition calibration lines at \( t_1 \) and \( t_2 \), respectively. \( C_i \) is the added \( \text{H}_2\text{O}_2 \) concentration. The two obtained straight lines intersect at the so-called H-point (\(-C_H, R_H\); Fig. 4), since \( R_{t1} = R_{t2}, C_i = -C_H, H(-C_H, R_H) = (-C_{H2O2}, R_{PAAd}) \) from Eqs. (4) and (5) is as follows:

\[ P_0 + P + M_{t1}(-C_H) = R_0 + R' + M_{t2}(-C_H) \] (10)
\[-C_H = [(R' - P) + (R_0 - P_0)]/(M_{t1} - M_{t2}) \] (11)

As species PAA is assumed not to evolve over the considered range of time,

\[ R' = P \]

and

\[ C_H = (R_0 - P_0)/(M_{t1} - M_{t2}) \] (12)
Which is equivalent to the existing $C_{H_2O_2}(=P_0/M_{t1}=R_0/M_{t2})$. Combining this with Eq. (8) yields $R_H = P$. The overall equation for the absorbance at H-point is simply represented as:

$$R' = P = R_H = R_{PAA}$$

(13)

The intersection of the straight lines (Eqs. 8 and 9) directly yields the unknown $H_2O_2$ concentration ($C_{H_2O_2}$) and the $R$ of PAA species ($R_{PAA}$) corresponds to $t_1$ and $t_2$ in the original samples, as the two times were chosen in such a way that the later species had the same $R$ at both times. This analytical signal enabled the calculation of the PAA concentration from a calibration curve.

![Fig. 4. Plot of HPSAM for the simultaneous determination of a mixture of $H_2O_2 (2.0 \mu g mL^{-1})$ and PAA (1.3 $\mu g mL^{-1}$)](image)

Since, $H_2O_2$ is selected as the analyte, it is possible to select several pairs of time intervals that present the same $R$ for PAA. Some of the selected pairs of time were 145-290, 150-185, 150-200, 170-220, 200-240 seconds. However, the time pair, which gives the greatest slope increment, lower error and shortest analysis time, was selected. For this reason, the time pair of 150-200 seconds was employed.

A summary of the obtained results for various analyte concentrations is given in Table 2. The concentration was calculated directly by solving a system of equations of the two straight lines. The results have shown that both the accuracy and precision of the method were satisfactory.

### 3.8. Multivariate calibration

The theories and applications of chemometrics methods such as PCR and PLS, to the analysis of multi-component mixtures, have been discussed by several workers [46-50]. PCR and PLS modeling are powerful multivariate statistical tools, which are successfully applied
to the quantitative analysis of spectrochemical and electrochemical data [51-54]. The first step in the simultaneous determination of the species by PCR and PLS methodologies involves the construction of calibration matrix for the binary mixture of H$_2$O$_2$ and PAA. For constructing the calibration set, factorial design was applied to five levels in order to extract a great deal of quantitative information, using only a few experimental trials. In this research, a synthetic set of 33 solutions, including different concentrations of H$_2$O$_2$ and PAA, was prepared. A collection of 25 solutions was selected as the calibration set and the other 8 solutions were used as the prediction set (Table 3). Their composition was randomly designed to obtain more information from the calibration procedure. Changes in the solution potential were recorded during a time period of 150 seconds.

Table 2. Results of five replicate experiments for analysis of H$_2$O$_2$ and PAA mixtures using HPSAM

<table>
<thead>
<tr>
<th>$R$-C equation</th>
<th>r</th>
<th>Spiked (µg mL$^{-1}$)</th>
<th>Found (µg mL$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PAA</td>
<td>H$_2$O$_2$</td>
</tr>
<tr>
<td>$R_{200} = 0.0449 CI + 0.6325$</td>
<td>0.9987</td>
<td>0.9</td>
<td>3.0</td>
</tr>
<tr>
<td>$R_{150} = 0.0297 CI + 0.5898$</td>
<td>0.9966</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{200} = 0.0448 CI + 0.6328$</td>
<td>0.9987</td>
<td>0.9</td>
<td>3.0</td>
</tr>
<tr>
<td>$R_{150} = 0.0301 CI + 0.5874$</td>
<td>0.9988</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{200} = 0.0442 CI + 0.6341$</td>
<td>0.9950</td>
<td>0.9</td>
<td>3.0</td>
</tr>
<tr>
<td>$R_{150} = 0.0295 CI + 0.5917$</td>
<td>0.9942</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{200} = 0.0385 CI + 0.6147$</td>
<td>0.9984</td>
<td>0.9</td>
<td>3.0</td>
</tr>
<tr>
<td>$R_{150} = 0.0255 CI + 0.5755$</td>
<td>0.9962</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{200} = 0.0374 CI + 0.6177$</td>
<td>0.9975</td>
<td>0.9</td>
<td>3.0</td>
</tr>
<tr>
<td>$R_{150} = 0.0247 CI + 0.5785$</td>
<td>0.9930</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Mean | 0.92 | 2.97 |
| SD   | 0.02 | 0.11 |
| RSD (%) | 2.20 | 3.70 |

To select the number of factors in the PCR and PLS algorithm, as a cross-validation method, leaving out one sample method was employed [55]. The prediction error was calculated for each species of the prediction set. This error was expressed as the prediction residual error sum of squares (PRESS):
\[
\text{PRESS} = \sum_{i=1}^{m} \left( \hat{C}_i - C_i \right)^2
\]  

(14)

Where \( m \) is the total number of calibration sample, \( \hat{C}_i \) represents the estimated concentration while \( C_i \) is the reference concentration for the \( i \)th sample left out of the calibration during the cross validation. Fig. 5 shows a plot of PRESS against the number of factors for a mixture of components. To find out minimum factors, we also used the F-statistics to carry out the significant determination [51]. The optimal number of factors, for the two components, was obtained as 3 for both PCR and PLS.

![Fig. 5. Plot of PRESS against the numbers of factors for PLS (■) and PCR (▲)](image)

For evaluating the predictive ability of a multivariate calibration model, the root mean square error of prediction (RMSEP), relative standard error of prediction (RSEP) and squares of correlation coefficient \((R^2)\), which is an indication of the quality fit of all the date to a straight line, can be used as follows [42,51,55]:

\[
\text{RMSEP} = \left( \frac{\sum_{i=1}^{N} \left( \hat{C}_i - C_i \right)^2}{n} \right)^{\frac{1}{2}}
\]  

(15)

\[
\text{RSEP}(\%) = \left( \frac{\sum_{i=1}^{N} \left( \hat{C}_i - C_i \right)^2}{\sum_{i=1}^{N} (C_i)^2} \right)^{\frac{1}{2}} \times 100
\]  

(16)

\[
R^2 = \frac{\sum_{i=1}^{N} \left( \hat{C}_i - C' \right)^2}{\sum_{j=1}^{N} (C_i - C')^2}
\]  

(17)

Where \( \hat{C}_i \) represents the estimated concentration, \( C_i \) and \( n \) are the actual analyte concentration and the number of samples, respectively.
Table 4 demonstrates the values of RSEP, RMSEP and $R^2$ for each component using PLS and PCR. It is shown that the obtained values, for the statistical parameters, are almost the same for both PLS and PCR methods.

3.9. Interference study

The study of interfering ions was performed by a standard mixture solution containing 5 µg mL$^{-1}$ of each H$_2$O$_2$ and PAA and a certain amount of added ions. The following excess of ions did not interfere the reaction (i.e., caused a relative error of less than 5%): more than a 1000-fold (largest amount tested) amount of Na$^+$, K$^+$, Zn$^{2+}$, Cd$^{2+}$, Mg$^{2+}$, Pb$^{2+}$, Bi$^{3+}$, Al$^{3+}$, F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$; a 100-fold amount of Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Br$^-$, Cr$^{3+}$, Ca$^{2+}$; a 10-fold amount of PO$_4^{3-}$; a 1-fold amount of MnO$_4^-$, S$^{2-}$ and a 0.5-fold amount of SCN$^-$.  

<table>
<thead>
<tr>
<th>Table 3. Prediction set for constructing PLS and PCR methods in determination of PAA and H$_2$O$_2$</th>
</tr>
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<tbody>
<tr>
<td><strong>Solution</strong></td>
</tr>
<tr>
<td><strong>PAA</strong></td>
</tr>
<tr>
<td>1</td>
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<td>2</td>
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<td>3</td>
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<td>8</td>
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$^a$ Predicted mean (recovery percent)

<table>
<thead>
<tr>
<th>Table 4. Statistical parameters calculated for the prediction set using PLS and PCR methods</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Component</strong></td>
</tr>
<tr>
<td><strong>RSE (%)</strong></td>
</tr>
<tr>
<td><strong>PLS</strong></td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
</tr>
<tr>
<td>PAA</td>
</tr>
</tbody>
</table>
3.10. Real sample analysis

To evaluate the analytical applicability of the proposed methods (PCR, PLS and HPSAM), we spiked the known amounts of both H$_2$O$_2$ and PAA into waste water samples, which were obtained after the treatment with peroxides. In Table 5, the results obtained for different samples using this method together with the recovery studies are shown. As can be seen, the recoveries were about 100%, which validates the method.

Table 5. Simultaneous determination of H$_2$O$_2$ and PAA in different water samples$^a$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spiked $^{(\mu g , mL^{-1})}$</th>
<th>Recovery$^b$ (%)</th>
<th>PCR</th>
<th>HPSAM</th>
<th>PLS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$O$_2$</td>
<td>PAA</td>
<td>H$_2$O$_2$</td>
<td>PAA</td>
<td>H$_2$O$_2$</td>
</tr>
<tr>
<td>1</td>
<td>1.2</td>
<td>3.0</td>
<td>104 ± 4</td>
<td>101 ± 2</td>
<td>106 ± 4</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>1.0</td>
<td>103 ± 2</td>
<td>102 ± 5</td>
<td>101 ± 3</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>6.0</td>
<td>102 ± 2</td>
<td>103 ± 5</td>
<td>104 ± 5</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>3.0</td>
<td>104 ± 5</td>
<td>104 ± 6</td>
<td>103 ± 4</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>2.0</td>
<td>97 ± 3</td>
<td>100 ± 3</td>
<td>100 ± 4</td>
</tr>
<tr>
<td>6</td>
<td>1.8</td>
<td>8.0</td>
<td>105 ± 3</td>
<td>102 ± 4</td>
<td>98 ± 4</td>
</tr>
</tbody>
</table>

$^a$Each sample was analyzed four times. Samples 1, 2 were drinking water samples, 3, 4 were river water samples and 5, 6 were well water samples, containing H$_2$O$_2$ and PAA mixture

$^b$Mean of recovery percent ± S.D (four replicates)

4. CONCLUSION

This work, as the pioneer application of HPSAM, PLS and PCR methods for the simultaneous determination of the binary mixture of H$_2$O$_2$ and PAA has shown an excellent performance of ISEs, as the detectors not only for the individual determination of products or consumed ions, but also in the simultaneous kinetic-potentiometric analysis. In addition, this study has also demonstrated that the ability and advantages of the HPSAM and chemometrics methods such as; PLS and PCR, ISEs and kinetic methods produce a very attractive and excellent technique for the analysis of multi-component mixtures. Other chemometrics approaches like ANN, ISEs (fluoride, bromide, iodide and etc.) and the other kinetic
reactions, in which the production or consumption rate of the corresponding ion is different, can also be useful. Our team has obtained good results for the simultaneous determination of other species using HPSAM, chemometric methods, different ISEs and various reaction systems and further results will be presented for publication in the near future.

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REFERENCES