*Full Paper*

# Simultaneous Kinetic-Potentiometric Determination of Iron(III) and Zirconium(IV) Using H-Point Standard Addition Method and Partial Least Squares

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**Abstract**- A new method for simultaneous kinetic-potentiometric determination of Zr(IV) and Fe(III) at trace levels using partial least-square (PLS) and H-point standard addition method (HPSAM) is described. The methods are based on the difference observed between complex reaction rate of Zr(IV) and Fe(III) with fluoride ion. Therefore, the reaction rate of Zr(IV) and Fe(III) with fluoride ion was monitored by a fluoride ion-selective electrode (FISE). Results have demonstrated that the simultaneous determination of Zr(IV) and Fe(III) can be done in the concentration ranges of 0.2 - 20.0 and 0.5 – 40.0 μg mL$^{-1}$, respectively. The total relative standard error of applying PLS method on 8 synthetic samples in the concentration ranges of 1.0 - 20.0 μg mL$^{-1}$ of Zr(IV) and 1.0 - 35.0 μg mL$^{-1}$ of Fe(III) was 1.85. The effects of certain foreign ions, upon the reaction rate, were determined for assessing the selectivity of the method. The proposed methods (HPSAM and PLS) were successfully applied to the simultaneous determination of Zr(IV) and Fe(III) in different water samples.

## 1. INTRODUCTION

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 [1-5]. In the field of potentiometry, several modeling methods have been reported based on flow injection system and titration using PLS regression and artificial neural networks (ANN) [6-12]. We have 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 [13,14] and binary mixture of levodopa and carbidopa drugs [15]. Recently, we have also reported the application of PLS and HPSAM for the simultaneous determination of binary mixture of PAA and $H_2O_2$ [16].

Zirconium(IV) and iron(III) are metallic ions which appear together in a wide variety of samples. This point indicates a potential interest in simultaneous determination of these metal ions. Different methods have been reported for determination of Zr and Fe individually [17-20]. In relation to the simultaneous analysis of binary mixture of Zr(IV) and Fe(III), Ye et al. were reported a kinetic potentiometric method for using the Kalman filter [21]. However, to the best of our knowledge, there is not any report for the simultaneous determination of Zr(IV) and Fe(III) by electroanalytical techniques using HPSAM and chemometrics methods.

This work reports, for the first time, the application of HPSAM and PLS as chemometrics method for the simultaneous determination of binary mixture of Zr(IV) and Fe(III) using potentiometric technique. The method is based on the difference observed in the reaction rate of fluoride ion with Zr(IV) and Fe(III). Therefore, the rate of fluoride ion reaction with these metallic ions was monitored by a fluoride ion-selective electrode (FISE).


## 2. EXPERIMENTAL

### 2.1. Apparatus and Software

A solid-state fluoride ion-selective electrode (Metrohm Model 6.0502.150) was used in conjunction with a double junction Ag/AgCl reference electrode (Metrohm Model 6.0726.100), with the outer compartment was filled by a 10% (w/v) $KNO_3$ solution. 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 $1\times10^{-3}$ M NaF solution when not in use. For pH measurements, a Metrohm Model 780 pH meter with a combination glass electrode was used. PLS and PCR analysis were performed using the MATLAB 7.0 software.

## 2.2. Materials and reagents

All chemicals were of analytical reagent grade and doubly distilled water was used throughout. The iron(III)  stock solution (1.0 mg mL$^{-1}$) was prepared by dissolving 0.7234 g of $Fe(NO_3)_3.9H_2O$ in 5.0 mL of 0.001 M nitric acid, and diluted to 100 mL. The stock solution of zirconium (1.0 mg mL$^{-1}$) was prepared by dissolving 0.2557 g of $ZrCl_4$ in 5.0 mL of 0.001 M $HNO_3$ and then diluted to 100 mL. A fluoride standard solution (0.1 M) was prepared by dissolving 0.4199 g of sodium fluoride in distilled water and diluted to 100 mL. The salts of Zr(IV) and Fe(III) and fluoride were purchased from Merck company (Germany). A phosphoric acid - nitric acid - sodium hydroxide buffer (pH 2.5) was prepared by mixing the solutions of phosphoric acid (0.20 M) and nitric acid (0.10 M) with a suitable amount of sodium hydroxide (0.15 M) and was adjusted its pH with a pH meter.

## 2.3. Procedure

Twenty five milliliters of buffer solution and 5.0 mL of standard fluoride solution (0.1 M) were added to the reaction cell. One milliliter of the standard or sample solution of Zr(IV), Fe(III) or a mixture of them were injected into the cell quickly, and after the stabilization of the potential (about 30 s), all data were recorded. The potential changes versus time were recorded at the time intervals of 1.0 s. Synthetic samples containing different concentration ratios of Zr(IV) and Fe(III) were prepared and standard additions of Zr(IV) were made. Simultaneous determination of Zr(IV) and Fe(III) was conducted by recording the potential changes for each solution from 30 to 150 s. After each run the cell was emptied and washed twice with doubly distilled water.

Using the standard analyte solutions, we can construct a calibration graph of    ($10^{\Delta E/S}$-1) *versus* concentration (fixed-time method) [22], where $\Delta E$ is the potential variation in a selected time interval $\Delta t$ (usually 100 s) and $S$ is the slope of the fluoride electrode response, which is determined periodically by successive additions of micro-amounts of 100 µL of $1.0 \times 10^{-2}$-3.0 M KCl standard solutions in 25.0 mL of water mixed with 2.0 mL of buffer solution. Zr(IV) and Fe(III) standard solutions can be determined simultaneously in the concentration ranges of 0.5-17.0 and 1.0-35.0 µg mL$^{-1}$, respectively.

The simultaneous determination of Zr(IV) and Fe(III) standard solutions with HPSAM was performed by measuring the potential changes ($\Delta E$) at 80 and 120 s after initiation of the reaction for each sample solution. Then plots of HPSAM of ($10^{\Delta E/S}$-1) *versus* added concentration of Zr(IV) were constructed for mixtures of Zr(IV) and Fe(III). Simultaneous determination of Zr(IV) and Fe(III) with PLS method was performed by recording the potential for each solution from 30 to 150 s.

## 3. RESULTS AND DISCUSSION

In this proposed analytical method, use of a suitable reagent to react with both Zr(IV) and Fe(III) under different rates is the most important step. Preliminary studies showed that fluoride ion as reagent using FISE is suitable for our purpose. It is well-known that the reaction rate of $F^-$ is much higher in the presence of Fe(III) as compared to Zr(IV) [22]. When using this ion and FISE, the linear ranges and difference of reaction rates for both two species were suitable. In order to accomplish simultaneous kinetic-potentiometric determination of Zr(IV) by HPSAM and PLS, a series of experiments were conducted to establish the optimum conditions to achieve maximum sensitivities. All experimental parameters affecting the reaction rate of fluoride with Zr(IV) (response-time, pH, concentration of $F^-$ etc.) were carefully optimized.

### 3.1. Study of the electrode characteristics

The characteristics of the fluoride-selective electrode in the $HNO_3$-$H_3BO_3$-NaOH buffer were studied. Typical calibration graphs for the fluoride -selective electrode showed a linear response in the range of $1.0 \times 10^{-6}$–$1.0 \times 10^{-2}$ M fluoride. The slope was found to be 56.8 mV/decade and remained almost constant to 0.2 mV over 7 months of usage in this system at pH 2.5.

### 3.2. Effect of pH

Acidity of the solution influences potential response of FISE and the complexation reaction rate of $F^-$ with Zr(IV) and Fe(III) [23]. If we assume HF to be the predominant fluoride-containing species in acidic solutions, fluoride species present with variation at pH are defined as follows:

$$HF \rightleftharpoons H^+ + F^-$$
$$K = \frac{[H^+][F^-]}{[HF]} = 7.93 \times 10^{-2} \tag{1}$$

The cell potential is given by the equation

$$E = E´ + S \log [F^-] \tag{2}$$

where $E$, $E´$, $S$ and $F^-$ are the potential, formal potential, slope of the fluoride electrode response and free fluoride concentration, respectively. The reaction of zirconium and iron with fluoride is carried out in acidic solution (at pH≤5), where the metallic species are mainly in the form Zr(IV) or Fe(III) (coordinated water has been omitted for simplicity). At this pH, the following reactions may be considered to be the important paths for the initial consumption of Zr(IV) or Fe(III) in the complex formation with fluoride [24]:

$$M^{n+} + F^- \rightleftharpoons MF^{(n-1)+} \tag{3}$$

$$M^{n+} + HF \rightleftharpoons MF^{(n-1)+} + H^+ \tag{4}$$

When the pH was altered from 2 to 5, a moderate decrease in the average rate was recorded (the total potential change was about 5 mV less), apparently owing to the hydrolyzed species of $M^{n+}$ ($MOH^{(n-1)+}$ and $M(OH)_2^{(n-2)+}$ for Zr(IV) and Fe(III)) providing additional paths with a rate proportional to $[F^-]$.

The effect of pH on the complex formation reaction rate of $F^-$ with Zr(IV) and Fe(III) over the pH range of 1.5 to 5.0 was examined. Maximum differences in kinetic behavior and the exhibition of larger values of potential change ($\Delta E$) between Zr(IV) and Fe(III) were seen at pH 2.5. In addition, each both species of Zr(IV) and Fe(III) had larger values of potential change ($\Delta E$) in this pH. Above pH 2.5, the potential change decreased evidently due to the occurrence of the hydrolysis reaction competing with the complex formation reaction of fluoride with metallic ions, and under pH 2.5, the potential change decreased too, probably owing to the formation of hydrogen fluoride, to which the FISE is insensitive. Thus, pH 2.5 was selected as the optimum pH for further studies.

### 3.3. Effect of fluoride concentration

The effect of $F^-$ concentration over the ranges of $1.0 \times 10^{-5}$–$1.0 \times 10^{-2}$ M on the linear range of calibration graph and reaction rate with Zr(IV) and Fe(III) was investigated. When the concentration of $F^-$ is low, a gentle slope in the calibration graph is realized while a high concentration of $F^-$ causes a steep slope in the calibration graph. The results show that a linear calibration graph can be obtained only when the concentration of $F^-$ is higher than 10 times actual detection limit of the electrode. The results also show that the concentration of $F^-$ has a great effect on the linear range and the change of potential value. The linear range of the calibration graph is about 0.3 - 4.0 times the concentration of $F^-$. Moreover, if the reaction shows a pseudo-first-order, the fluoride concentration must be in excess. However, increasing the fluoride concentration decreases the potential change and causes that the sensitivity to be lower. If the fluoride concentration is too low, the potential may not be steady. Maximum difference in the kinetic behavior of Zr(IV) and Fe(III) and larger values of potential change ($\Delta E$) were observed in the concentration range of $1.0 \times 10^{-3}$ M. Therefore, a concentration of $1.0 \times 10^{-3}$ M fluoride was selected as the optimum concentration for further studies.

### 3.4. The composition of ground buffer solution

The change of the amount of potential ($\triangle E$) was investigated for the reaction of certain amount of $F^-$ with Zr(IV) and Fe(III) in different acidic solutions of $H_3PO_4$ – $H_3BO_3$ – NaOH, KCl – HCl – NaOH, $HNO_3$ – $CH_3COOH$ – NaOH and $HNO_3$ – $H_3BO_3$ – NaOH (Table 1). In the $HNO_3$ – $H_3BO_3$ – NaOH solution (pH 2.5), both species, $\triangle E_{Fe}^{3+}$ and $\triangle E_{Zr}^{4+}$ had larger potential change values. According to obtained results, the mixture of 0.2 M

$H_3BO_3$ - 0.1 M $HNO_3$ - 0.2 M NaOH solutions (pH 2.5) containing $1.0 \times 10^{-4}$ M fluoride was chosen as the ground acidic solution.

**Table 1.** The value of $\triangle E$ for reaction of 10.0 µg mL$^{-1}$ Zr(IV)  or 10.0 µg mL$^{-1}$ Fe(III) with $F^-$ ion in different acidic solutions (pH = 2.5)

| $\triangle E$ | $H_3PO_4 - H_3BO_3$ | KCl – HCl | $HNO_3 - CH_3COOH$ | $HNO_3 - H_3PO_4$ |
|---|---|---|---|---|
| $\triangle E_{Zr(IV)}$ (mv) | 9.3 | 26.8 | 20.5 | 32.6 |
| $\triangle E_{Fe(III)}$ (mv) | 2.7 | 7.6 | 9.1 | 13.4 |

## 3.5. Temperature effect of reaction rate

The temperature of solution evidently affects the reaction rate of the kinetic reaction. But higher temperatures do not have a positive effect on the complex formation reaction of metallic ions with fluoride. Therefore, the temperature of solution was kept at $25 \pm 0.2$ °C by thermostatic water bath in all of the measurements.

## 3.6. Potential-time behavior

The potential–time behavior of reactions of $F^-$ with Zr(IV), Fe(III) and mixtures of them under the optimized conditions is shown in Fig. 1. Fig. 2 shows typical reaction curves for the reaction of $F^-$ with Zr(IV) and Fe(III) at different concentrations. As can be seen in Figs. 1 and 2, the reaction of Fe(III) is faster than Zr(IV) and is almost completed in 10 s after initial reaction but the reaction of Zr(IV) is completed in 150 s. This difference in the reaction rates allowed us to design the HPSAM and PLS method for simultaneous determination of Zr(IV) and Fe(III).

Characteristics of calibration graphs for the determination of Zr(IV) and Fe(III), under the optimum conditions, are given in Table 2.

**Table 2.** Characteristic of calibration graphs for the determination of Zr(IV) and Fe(III)

| Species | Linear range (µg mL$^{-1}$) | Slope (mL µg$^{-1}$) | Intercept | Correlation coefficient (n = 10) | Detection limit[a] (µg mL$^{-1}$) |
|---|---|---|---|---|---|
| Zr(IV) | 0.2 – 20.0 | 0.3135 | 0.1611 | 0.9991 | 0.1 |
| Fe(III) | 0.5 – 40.0 | 0.0754 | 0.1482 | 0.9992 | 0.2 |

[a] concentration corresponding to an analytical signal equal to three times the standard deviation of the blank.

## 3.7. Potential-time behavior

We have 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 [13,16].
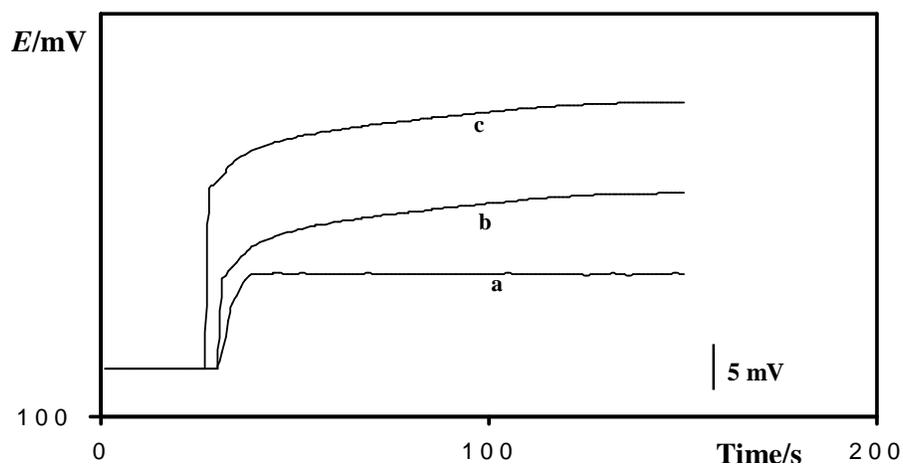
**Fig. 1.** Potential-time curves for the reaction of $F^-$ with 10.0 µg mL$^{-1}$ of Fe(III) (a), 10.0 µg mL$^{-1}$ of Zr(IV) (b) and a mixture of them (c)
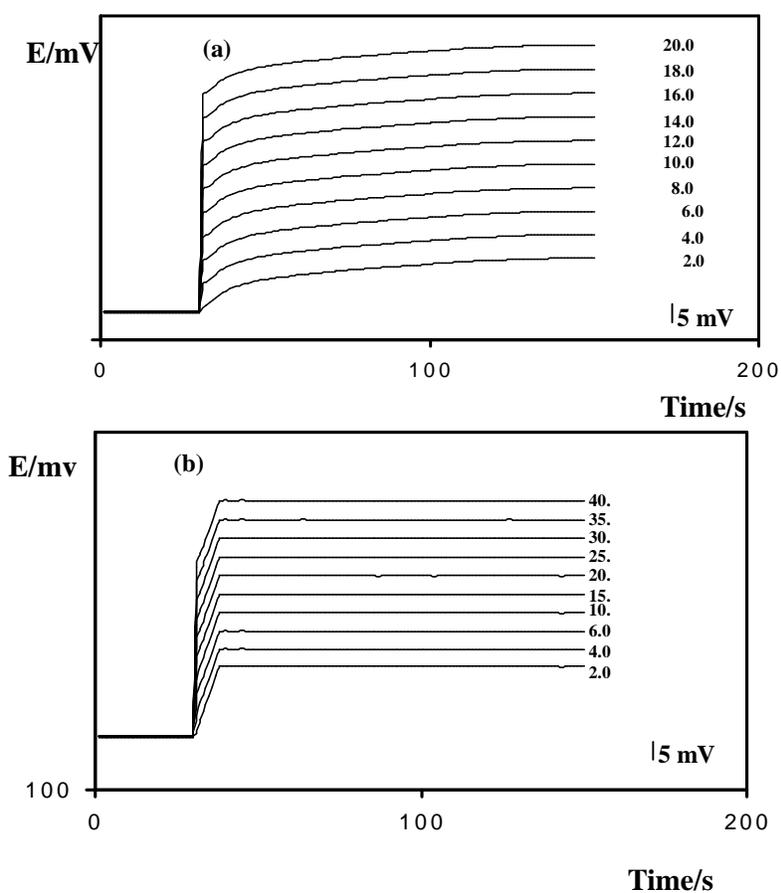


**Fig. 2.** Typical potential-time curves for the reaction of $F^-$ with Fe(III) (a) and Zr(IV) (b) at different concentrations (µg mL$^{-1}$)

Considering a binary mixture of Zr(IV)-Fe(III), as an example, we can assume that the amount of $(10^{\Delta E/S}-1)$ during reaction of Zr(IV) with $F^-$ was $P_i$ and $Q_i$ at times $t_1$ and $t_2$, respectively. While those of the reaction of Fe(III) with $F^-$, under the same conditions, was $P$ and $Q$, respectively (Fig. 3). Both of them are equal in this case. The following equations demonstrate the relation between them:

For Zr(IV):          $Q_i = P_i + m_i t_j \ (t_1 \leq t_j \leq t_2; \ i=0,1,...,n)$                               (5)

For Fe(III):          $Q = P + mt_j \ (m=0)$                                                        (6)

where, subscripts $i$ and $j$ denote number of additions of Zr(IV) concentration (prepared to apply to HPSAM) and the time in the range of $t_1$-$t_2$, respectively.
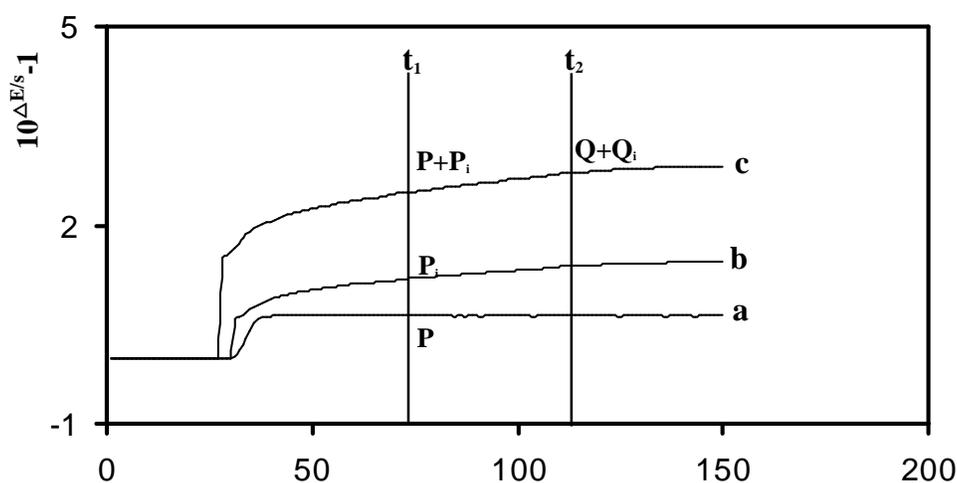


**Fig. 3.** Plot of potential changes $(10^{\Delta E/S}-1)$ for the reaction of $F^-$ with 10.0 µg mL$^{-1}$ of Fe(III) (a), 10 µg mL$^{-1}$ of Zr(IV) (b) and a mixture of them (c)

Thus, the overall amounts of $(10^{\Delta E/S}-1)$ (or $R$) of the Zr(IV)-Fe(III) mixture are:

At      $t_1$          $Rt_1 = P + P_i$                                                              (7)

At      $t_2$          $R_{t2} = Q + Q_i$                                                            (8)

To select the appropriate times, the following principles were observed. At the two selected times $t_1$ and $t_2$, the amount of $R$ of the Zr(IV) must be linear with the concentrations, and the amount of $R$ for Fe(III) must remain constant even if the Zr(IV) concentrations are changed. The amount of $R$ for the mixture of Zr(IV) and Fe(III) should be equal to the sum of individual $Rs$ of the two compounds. In addition, the slope difference of the two straight lines obtained at both $t_1$ and $t_2$ must be as large as possible to achieve good accuracy. Then known amounts of Zr(IV) are successively added to the mixture and resulting potential changes are measured at the two times and expressed:

$R_{t1} = (10^{\Delta E(t1)/S}-1)_{t1} = P_0 + P + M_{t1}C_i$                                        (9)

$$R_{t2} = (10^{\Delta E(t2)/S}-1)_{t2} = Q_0 + Q + M_{t2}C_i \tag{10}$$

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 $Q_0$ are the amounts of $R$ for Zr(IV) at a sample at $t_1$ and $t_2$, respectively. $P$ and $Q$ are the amounts of $R$ for Fe(III) at $t_1$ and $t_2$, respectively (Fig. 4). $M_{t1}$ and $M_{t2}$ are the slopes of the standard addition calibration lines at $t_1$ and $t_2$, respectively. $C_i$ is the added Zr(IV) concentration. The two obtained straight lines intersect at the so-called H-point $(-C_H, R_H)$, which at point H (Fig. 4), since $R_{t1} = R_{t2}$, $H(-C_H, R_H) \approx (-C_{Zr}, R_{Fe})$ from Eqs. (5) and (6) we have:

$$P_0 + P + M_{t1}(-C_H) = Q_0 + Q + M_{t2}(-C_H) \tag{11}$$

$$-C_H = [(Q - P) + (Q_0 - P_0)]/(M_{t1} - M_{t2}) \tag{12}$$

as species Fe(III) is assumed not to evolve over the considered range of time,

$$Q = P$$

and

$$C_H = (Q_0 - P_0)/(M_{t1} - M_{t2}) \tag{13}$$

which is equal to the existing $C_{Zr} (=P_0/M_{t1} = Q_0/M_{t2})$. Combining this with Eq. (9) yields $R_H = P$. The overall equation for the potential at the H-point is simply represented by:

$$Q = P = R_H = R_{Fe} \tag{14}$$

The intersection of the straight lines (Eqs. (9) and (10)) directly yields the unknown Zr(IV) concentration $(C_{Zr})$ and the $R$ for Fe(III) species $(R_{Fe})$ corresponding 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 enables us to calculate the concentration of Fe(III) from a calibration curve.
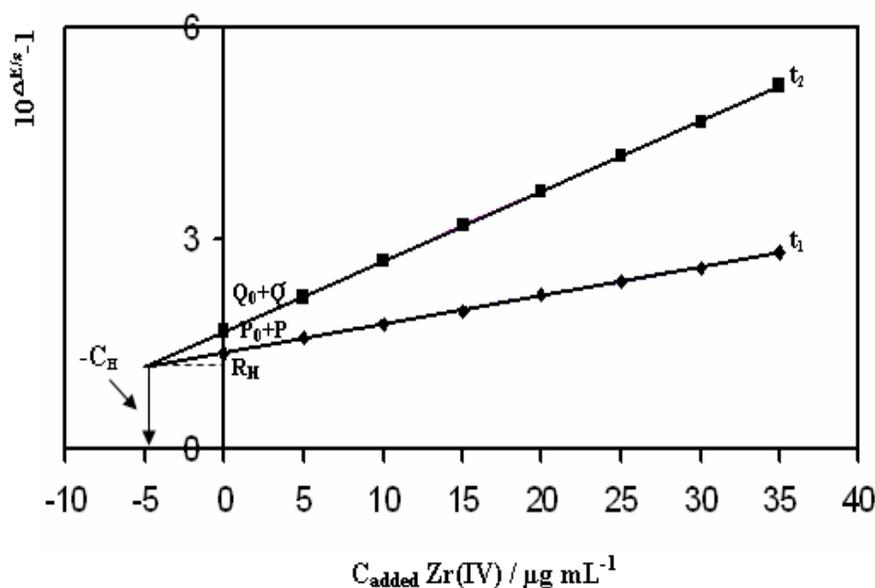


**Fig. 4.** Plot of HPSAM for simultaneous determination of a mixture of Zr(IV) (10 µg mL$^{-1}$) and Fe(III) (10 µg mL$^{-1}$)

Since, Zr(IV) is selected as the analyte, it is possible to select several pairs of time ranges which present the same *R* for Fe(III). Some of the selected time pairs were 50-100, 60-100, 80-120, 80-100 and 100-150 seconds. However, the time pair, which gives the greatest slope increment, lower error and shortest analysis time, was selected [25]. For this reason, the time pair of 80-120 seconds was employed.

A summary of the obtained results for various analyte concentrations is given in Table 3. 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.

**Table 3.** Results of six replicate experiments for analysis of Zr(IV) and Fe(III) mixtures in different concentration ratios using HPSAM (T = 25°C)

| *R-C* equation | r | Spiked ($\mu g\ mL^{-1}$) | | Found ($\mu g\ mL^{-1}$) | | Recovery (%) | |
|---|---|---|---|---|---|---|---|
| | | Fe(III) | Zr(IV) | Fe(III) | Zr(IV) | Fe(III) | Zr(IV) |
| $R_{120} = 0.1783\ C_i + 0.2450$ | 0.9985 | | | | | | |
| $R_{80} = 0.0371\ C_i + 0.0800$ | 0.9988 | 18 | 1 | 18.21(±0.14) | 0.96(±0.04) | 101.1 | 96.0 |
| $R_{120} = 0.1400\ C_i + 0.2213$ | 0.9987 | | | | | | |
| $R_{80} = 0.0291\ C_i + 1.2212$ | 0.9986 | 15 | 3 | 15.12(±0.15) | 2.91(±0.11) | 100.8 | 97.0 |
| $R_{120} = 0.1385\ C_i + 0.1665$ | 0.9988 | | | | | | |
| $R_{80} = 0.0251\ C_i + 0.7834$ | 0.9979 | 12 | 5 | 11.84(±0.23) | 5.11(±0.10) | 98.6 | 102.2 |
| $R_{120} = 0.1303\ C_i + 1.3602$ | 0.9989 | | | | | | |
| $R_{80} = 0.0291\ C_i + 0.7205$ | 0.9991 | 9 | 7 | 9.13(±0.10) | 7.07(±0. 08) | 101.4 | 101.0 |
| $R_{120} = 0.1086\ C_i + 0.9101$ | 0.9993 | | | | | | |
| $R_{80} = 0.0280\ C_i + 0.5812$ | 0.9983 | 4 | 9 | 3.92(±0.07) | 9.16(±0.14) | 98.0 | 101.7 |
| $R_{120} = 0.1020\ C_i + 0.6730$ | 0.9993 | | | | | | |
| $R_{80} = 0.0269\ C_i + 0.5401$ | 0.9979 | 2 | 12 | 1.98(±0.06) | 12.15(±0.15) | 99.0 | 101.2 |

### 3.8. Partial least squares regression

PLS model is a powerful multivariate statistical tool, which is successfully applied to the quantitative analysis of spectrochemical and electrochemical data [13-16,26-27]. The first step in the simultaneous determination of species by PLS methodology involves constructing

the calibration matrix for the binary mixture of Zr(IV) and Fe(III). 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 Zr(IV) and Fe(III) was prepared. A collection of 25 solutions were selected as the calibration set and the other 8 solutions were used as the prediction set (Table 4). Their composition was randomly designed to obtain more information from the calibration procedure. Changes in the potential of the solutions were recorded during a time period of 150 s.

**Table 4.** Prediction set of PLS method in determination of Zr(IV) and Fe(III)

| Sample | Synthetic ($\mu g\ mL^{-1}$) | | Prediction ($\mu g\ mL^{-1}$) | | Recovery (%) | |
|--------|---------|--------|---------|--------|---------|--------|
| | Fe(III) | Zr(IV) | Fe(III) | Zr(IV) | Fe(III) | Zr(IV) |
| 1 | 1 | 35 | 1.05 | 35.73 | 105.0 | 102.0 |
| 2 | 5 | 30 | 5.34 | 31.08 | 106.8 | 103.6 |
| 3 | 8 | 25 | 7.65 | 25.91 | 95.6 | 103.6 |
| 4 | 10 | 20 | 10.54 | 20.90 | 105.4 | 104.5 |
| 5 | 10 | 15 | 10.17 | 14.62 | 101.7 | 97.4 |
| 6 | 15 | 10 | 15.47 | 10.04 | 103.1 | 100.4 |
| 7 | 18 | 5 | 16.62 | 4.70 | 92.3 | 94.0 |
| 8 | 20 | 5 | 20.47 | 4.77 | 102.3 | 95.4 |
| Mean recovery | -- | -- | -- | -- | 101.5 | 99.9 |
| RSE (%) | -- | -- | -- | -- | 1.58 | 2.07 |
| $RSE_t$ (%) | -- | -- | -- | -- | 1.85 | |

To select the number of factors in the PLS algorithm, as a cross-validation method, leaving out one sample method was employed [13-16]. The prediction error was calculated for each species for the prediction set. This error was expressed as the prediction residual error sum of squares (PRESS):

$$PRESS = \sum_{i=1}^{m} \left( \hat{C}_i - C_i \right)^2 \tag{15}$$

where m is the total number of calibration sample, $\hat{C}_i$ represents the estimated concentration, and $C_i$ is the reference concentration for the $i$th sample left out of the calibration during cross validation. To find minimum factors, we used the F-statistic to carry

out the significant determination [28]. The optimal number of factors for the two components was obtained as 2.

For evaluating the prediction 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 [13-16]:

$$RMSEP = \left( \sum_{i=1}^{N} \left( \hat{C}_i - C_i \right)^2 / n \right)^{1/2} \tag{16}$$

$$RSEP(\%) = \left( \sum_{i=1}^{N} \left( \hat{C}_i - C_i \right)^2 / \sum_{i=1}^{N} (C_i)^2 \right)^{1/2} \times 100 \tag{17}$$

$$R^2 = \sum_{i=1}^{N} \left( \hat{C}_i - C' \right)^2 / \sum_{j=1}^{N} (C_i - C')^2 \tag{18}$$

where $N$ is number of samples, $C_i$ the concentration of the component in the $i$th mixture and $\hat{C}_i$ the estimated concentration.

### 3.9. Interference study

The study of interference ions was performed by a standard mixture solution containing 10 µg mL$^{-1}$ each of Zr(IV) and Fe(III) and a certain amount of foreign ions. The following excesses of ions do not interfere (i.e., caused a relative error of less than 5%): more than a 1000-fold (largest amount tested) amount of Na$^+$, K$^+$, , Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Mg$^{2+}$, Be$^{2+}$, Bi$^{3+}$, As$^{3+}$, IO$_3^{3-}$, I$^-$, Br$^-$, Cl$^-$, NO$_3^-$, BO$_3^{3-}$, C$_2$O$_4^{2-}$, CH$_3$COO$^-$; a 100-fold amount of Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Pb$^{2+}$, Cr$^{3+}$; a 10-fold amount of SO$_4^{2-}$, PO$_4^{3-}$, Hg$^{2+}$ and a 1-fold amount of Al$^{3+}$, Ti$^{4+}$, Mo$^{6+}$.

### 3.10. Application

After the proposed method was found to provide good results in the determination of Zr(IV) and Fe(III) in laboratory-made samples, it was applied to the determination on Zr(IV) and Fe(III) in four spiked water samples. For this purpose, 5.0 mL water was spiked at three concentration levels within the linear ranges of solutions of each metal ion, and the proposed method was then applied as described in the Experimental section. The results are shown in Table 5. The results show that the proposed HPSAM and PLS method could accurately determine the concentration of the metal ions under investigation in real water samples, and there is no significant difference between the results of HPSAM and PLS method for their simultaneous determination. The most important characteristics of this method are that it is very suitable for the simultaneous determination of Zr(IV) and Fe(III) in complex samples, and that no extraction step is required, hence the use of organic solvents is avoided.

**Table 5.** The results of analysis of different water samples, spike simultaneously with different amounts of Fe(III) and Zr(IV), using the proposed HPSAM and PLS method

| Sample | Added ($\mu$g mL$^{-1}$) | | Found ($\mu$g mL$^{-1}$) | | | |
| | | | HPSAM | | PLS | |
| | Fe(III) | Zr(IV) | Fe(III) | Zr(IV) | Fe(III) | Zr(IV) |
|---|---|---|---|---|---|---|
| **Tap water** | 14 | 2 | 14.82($\pm$0.40) | 2.10($\pm$0.10) | 13.87($\pm$0.23) | 2.08($\pm$0.12) |
| | 8 | 8 | 7.87$\pm$0.28) | 8.17($\pm$0.16) | 7.91($\pm$0.23) | 8.21($\pm$0.23) |
| | 3 | 15 | 3.18($\pm$0.13) | 14.76($\pm$0.44) | 3.12($\pm$0.10) | 14.86($\pm$0.40) |
| **River water** | | | | | | |
| | 14 | 2 | 14.78($\pm$0.26) | 2.12($\pm$0.04) | 14.83($\pm$0.20) | 2.10($\pm$0.03) |
| | 8 | 8 | 7.83($\pm$0.20) | 8.18($\pm$0.26) | 7.88($\pm$0.18) | 8.12($\pm$0.30) |
| | 3 | 15 | 2.91($\pm$0.18) | 15.28($\pm$0.32) | 2.94($\pm$0.07) | 15.17($\pm$0.40) |
| **Spring water** | 14 | 2 | 14.27($\pm$0.32) | 1.93($\pm$0.05) | 14.21($\pm$0.31) | 1.97($\pm$0.14) |
| | 8 | 8 | 8.24($\pm$0.21) | 7.83($\pm$0.20) | 8.36($\pm$0.12) | 7.87($\pm$0.17) |
| | 3 | 15 | 3.17($\pm$0.10) | 14.75($\pm$0.37) | 3.28($\pm$0.11) | 14.84($\pm$0.28) |
| **Well water** | 14 | 3 | 14.35($\pm$0.27) | 1.90($\pm$0.10) | 14.25($\pm$0.23) | 1.92($\pm$0.02) |
| | 8 | 8 | 8.28($\pm$0.23) | 7.81($\pm$0.18) | 8.21($\pm$0.22) | 7.86($\pm$0.21) |
| | 3 | 15 | 3.21($\pm$0.12) | 17.72($\pm$0.30) | 3.12($\pm$0.13) | 14.81($\pm$0.36) |

## 5. CONCLUSION

This work as the first application of HPSAM and PLS method in the simultaneous determination of the binary mixture of Zr(IV) and Fe(III) shows the ability and excellent performance of ISEs as detectors not only for individually determination of produced or consumed ions, but also in the simultaneous kinetic-potentiometric analysis. This is a valuable result that a simpler bi-variate method such as HPSAM is comparable with the powerful multivariate PLS method. Although PLS is a full data method, the results clearly show that the HPSAM, as a bi-variate method, produces almost the same accuracy. However, HPSAM as a standard addition method is more time consuming for analyzing a large number of unknown samples in comparison with PLS. The most important characteristics of this work are as follows: (I) The proposed method is very suitable for simultaneous determination of Zr(IV) and Fe(III) in complex samples. (II) This method is cheaper than spectrometric or other electrochemical methods. (III) No extraction step was required and hence the use of toxic organic solvents is avoided. In other words, this method belongs to green chemistry.

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