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A Kinetic-Potentiometric Method for the Simultaneous Determination of Hydrazine and Acetylhydrazine

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Simultaneous determination of hydrazine (HZ) and acetylhydrazine (AHZ) by H-point standard addition method (HPSAM) and partial least squares (PLS) regression was carried out based on kinetic data of novel potentiometry. The rate of chloride ion production in reaction of HZ and AHZ with N-chlorosuccinimide (NCS) was monitored by a chloride ion-selective electrode. The experimental dada shows not only the good ability of ion-selective electrodes (ISEs) as a detector for the direct determination of chloride ion but also for simultaneous kinetic-potentiometric analysis using HPSAM and PLS methods. The methods are based on the differences observed in the production rate of chloride ions. The results show that simultaneous determination of HZ and AHZ can be performed in their concentration ranges of 0.4-10.0 and 2.0-20.0 μg mL^{-1}, respectively. The total relative standard error for applying the PLS method to 9 synthetic samples in the concentration ranges of 0.0-9.0 μg mL^{-1} for HZ and 2.0-20.0 μg mL^{-1} for AHZ was 2.00. In order for the selectivity of the method to be assessed, the effects of certain foreign ions upon the reaction rate were evaluated and determined. Both methods (HPSAM and PLS) were evaluated using a set of synthetic sample mixtures and then applied for simultaneous determination of HZ and AHZ in water samples.

Key Words: Simultaneous determination, Kinetic-potentiometric, H-point standard addition method, Partial least squares, Hydrazine, Acetylhydrazine.

INTRODUCTION

Hydrazine (HZ) and its derivatives have been used in industry, agriculture and other fields including the manufactureing metal films, photographic chemicals and explosives and as propellants and common precursors in the synthesis of some polymers, plasticizers, pesticides, antioxidants and pharmaceuticals[1]. On the other hand, owing to the toxic nature of HZ and some its derivatives, there is a growing need in both industries and laboratories for the development of highly sensitive methods for low levels determination of HZ and its derivatives. Several methods

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have been reported for the determination of HZ and its derivatives individually such as classic-titrimetry[2], spectrophotometry[3,4], electroanalytical techniques[5,6], fluorometry[7] and chemiluminescence[8]. H-point standard addition method (HPSAM) was reported for simultaneous determination of binaries of HZ and semicarbzide[9], HZ and phenylhydrazine[10], HZ and acetylhydrazine (AHZ)[11], HZ and isoniazid[12]. Recently, we reported a kinetic-spectrophotometric determination of ternary mixture of HZ and its derivatives using principal component regression (PCR) and partial least squares (PLS) methods[13].

In recent years the usage of chemometrics methods in electroanalytical chemistry, as in other areas of analytical chemistry, has received considerable attention as these methods can help with extraction of more information from experimental data. Electroanalytical techniques are well known as excellent and cheap procedures for the determination of trace chemical species. Applications of HPSAM and chemometrics techniques including artificial neural network (ANN), partial least squares (PLS) and principal component regression (PCR) have been frequently reported for the calibration of overlapped voltammetric signals[14-19]. In the field of potentiometry, several methods have been reported based on flow injection system and titration using PLS and ANN as modeling methods[20-25]. Ye *et al.*[26] have also reported a differential kinetic potentiometric method with the Kalman filter for the simultaneous determination of iron(III) and zirconium(IV). It was based on the complexing reaction of iron(III) and zirconium(IV) with fluoride ion that has a differential rate at certain reaction conditions. So iron(III) and zirconium(IV) can be simultaneously determined by measuring the potential change of the fluoride ion-selective electrode. Recently, we reported the first application of PLS and PCR multivariate calibration methods and HPSAM to the simultaneous kinetic-potentiometric determination of binary mixtures of hydrazine and its derivatives and also binary mixture of levodopa and carbidopa drugs[27-29]. Methods were based on the differences observed in the production rate of chloride ions in reaction of these species with N-chlorosuccinimide. The reaction rate of production of chloride ion was monitored by a chloride ion-selective electrode.

This work reports the application of HPSAM and PLS to the simultaneous kinetic-potentiometric determination of binary mixture of HZ and AHZ. The methods are based on the difference observed in the rate of production of chloride ions in the reaction of NCS with HZ and AHZ.

EXPERIMENTAL

A solid-state chloride-selective electrode (Metrohm Model 6.0502.120) was used in conjunction with a double junction Ag/AgCl reference electrode (Metrohm Model 6.0726.100), whose outer compartment was filled with a 10 % (w/v) KNO_3 solution. The metrohm model 780 potentiometer, attached to a Pentium(IV) computer, was used for recording the kinetic potentiometric data. All measurements were carried out in a thermostated (25 ± 0.2 °C), double-walled reaction cell with continuous magnetic stirring. The electrode was stored in 1×10^{-3} M potassium chloride solution when not in use. For pH measurements, a Metrohm Model 780 pH meter with combination glass electrode was used. PLS analysis was performed using PLS toolbox's in MATLAB 7.0 program.

All chemicals were of analytical reagent grade and double distilled water was used throughout. A 0.05 M N-chlorosuccinimide (NCS) stock solution was prepared by dissolving 0.6667 g of NCS (Serva) in water and diluting to 100 mL. The solution was prepared daily and kept at 4 ºC in an amber-coloured bottle in the darkness. Stock solutions (1000 μg mL^{-1}) of HZ and AHZ were prepared in 100 mL volumetric flasks by dissolving 0.4063 g of hydrazinium sulfate (Merck) and 0.1000 g of acetylhydrazine (Merck) in water and diluting with water to the mark. AHZ stock solution was prepared on a daily basis. Acetate buffer solution (0.05 M, pH 5.0) was prepared using acetic acid and NaOH solutions and was adjusted its pH with a pH meter.

Procedure: 25.0 mL of double distilled water, 2.0 mL of buffer solution and 1.0 mL of 0.05 M NCS solution were added to the thermostated (25 ºC) reaction cell. 10.0 mL of the standard or sample solution of HZ, AHZ or mixture of them was injected into the cell quickly and after the stabilization of the potential all data were recorded. The potential changes *versus* time were recorded at the time intervals of 1.0 s. Simultaneous determination of HZ and AHZ was conducted by recording the potential changes for each solution from 10.0 to 100 s. After each run the cell was emptied and washed twice with double distilled water.

Using the standard analyte solutions, construct a calibration graph of ($10^{\Delta E/S}$-1) *versus* concentration (fixed-time method)[30], where ΔE is the potential change in a selected time interval Δt (usually 90 s) and S is the slope of the chloride electrode response, which is determined periodically by successive additions of micro-amounts of 100 μL of 1.0×10^{-2}–3.0 M KCl standard solutions in 25.0 mL of water mixed with 2.0 mL of buffer solution. HZ and AHZ standard solutions can be determined simultaneously in the concentration ranges of 0.5-20.0 and 0.6-20.0 μg mL^{-1}, respectively. The potentiometric slope of the electrode response (S) was checked periodically by successive addition of 100 μL of 1.0×10^{-3} and 1.0×10^{-2} M KCl standard solutions in 10.0 mL of water mixed with 2.0 mL of buffer.

The simultaneous determination of HZ and AHZ standard solutions with HPSAM was performed by measuring the potential changes (ΔE) at 55 and 100 s after initiation of the reaction for each sample solution. Then plot of HPSAM of ($10^{\Delta E/S}$-1) *versus* added concentration of HZ were constructed for mixture of HZ and AHZ. Simultaneous determination of HZ and AHZ with PLS method was performed by recording the potential for each solution from 10 to 100 s.

RESULTS AND DISCUSSION

A series of experiments were conducted to establish the optimum conditions to achieve maximum sensitivities. In the proposed analytical method, using a suitable reagent to react with HZ and AHZ under different rates is the first and important step. Under these conditions, the rate of halide ion production through reactions of the reagent with HZ and AHZ are different and consequently, the potentiometric response for HZ and AHZ will be different. Different reactants such as NBS, NCS, FDNB, 1-chloro-2,4-dinitrobenzene (CDNB), 1-bromo-2,4-dinitrobenzene (BDNB) and sodium dichloroisocyanurate (SDCC) were investigated as reagents for reaction with HZ and AHZ to produce halide ion. Preliminary studies showed that NCS is a suitable reagent for present purpose. By using this reagent, the linear range and differences of reaction rate for both two species (HZ and AHZ) were better than any others.

NCS, as a chlorinating and oxidizing agent is more stable than alkali hypochlorite which contains chlorine in the same oxidation state but disproportionates easily to chlorate and chloride ions[1]. In oxidation reactions, NCS undergoes a $2e^-$ reduction to succinimide (NHS) and chloride ion. Alternatively, NCS may be regarded as a source of hypochlorous acid, which is generated by hydrolysis:

$$\text{NCS} + \text{H}_2\text{O} \longrightarrow \text{NHS} + \text{HOCl}$$

Hypochlorous acid is probably responsible for the oxidizing properties of NCS. HZ and AHZ are oxidized by NCS to NHS, N_2, H_2O and Cl^-.[30,31]

All experimental parameters affecting the reaction rate of NCS with HZ and AHZ (electrode characteristics, concentration of NCS, pH, *etc.*) were carefully optimized.

Study of the electrode characteristics: The characteristics of the chloride-selective electrode in the acetate buffer were studied. Typical calibration graphs for the chloride-selective electrode showed a linear response in the range of 3×10^{-6}-1 M chloride. The slope was found to be 56.4 mV/decade and remained almost constant to within 0.4 mV over 9 months of usage in this system. The fast response of chloride ISE and its nernstian behaviour with respect to chloride ions in medium acidic solutions indicated that this electrode might be employed effectively in kinetic studies of reaction involving changes in the chloride ion concentration.

Effect of NCS concentration: The effect of NCS concentration on the reaction rate of HZ and AHZ was investigated. The reaction rate of both species increases with increasing the concentration of NCS in the range of 5×10^{-5}–5×10^{-2} M. Further increase in oxidizing agent concentration was avoided due to the limited solubility of NCS in water. Therefore, a concentration of 5×10^{-2} M NCS was selected as the optimum concentration for further studies.

Effect of pH: Acidity of the solution influences both potential response of chloride ISE and the reaction rates of HZ and AHZ. The effect of pH on the reaction rate of HZ and AHZ with NCS over the pH range of 2.0 to 9.0 was examined. Moreover, maximum differences in kinetic behaviour of HZ and AHZ were observed in pH 3.0. In addition to this, both HZ and AHZ had larger values of potential change (ΔE) in this pH. Thus, pH 3.0 was selected as the optimum pH for both analytes.

The electrode potential was also evaluated in different pHs. The electrode potential is stable in pure NCS solutions. Therefore, NCS solutions behave as dilute chloride solutions. The concentration of chloride, equivalent to NCS (having the same potential), increases with pH and provides a constant background response before injection of the sample solutions. In pH 3.0, concentration of chloride was minimized.

Effect of surfactants: The effect of surfactants on the reaction rate of NCS with HZ and AHZ was investigated. According to the obtained results, anionic (sodium dodecyl sulfate, SDS) and cationic (cetyl trimethyl ammonium bromide, CTAB) surfactants decrease thereaction rate of NCS with HZ and AHZ while, non-ionic surfactants (Triton-X-100) do not have any considerable effect on the reaction rate. Therefore, it was preferred that the reaction be performed without the presence of surfactants.

Potential-times behaviour: The potential-time behaviour of reaction of NCS with HZ, AHZ and mixture of them under the optimized conditions is shown in Fig. 1. Fig. 2 shows typical reaction curves for the reaction of NCS with HZ and AHZ at different concentrations. As it is seen from Figs. 1 and 2, the reaction of HZ is faster than the reaction of AHZ and was almost completed in 30 s after initial reaction but the reaction of AHZ is completed in 100 s. This difference in reaction rates allowed to design the HPSAM and PLS method for simultaneous determination of HZ and AHZ.

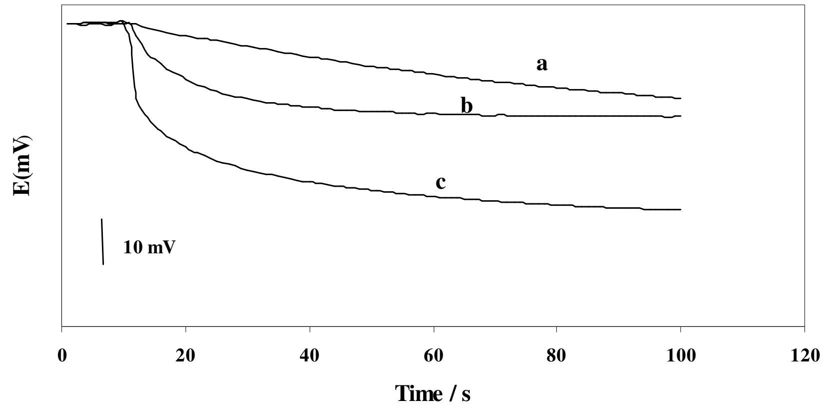

Fig. 1. Potential-time curves for the reaction of NCS with 10 μg mL^{-1} of AHZ (a), 5 μg mL^{-1} of HZ (b) and mixture of them (c)

Under the optimum conditions, the characteristics of calibration graphs for determination of HZ and AHZ are given in Table-1.

Requirements for applying HPSAM: HPSAM as a modified standard addition method is suggested as a method to obtain an unbiased analyte concentration when both analyte and interference are present in a sample. This method can be applied to kinetic data for the simultaneous determination of binary mixtures or calculation

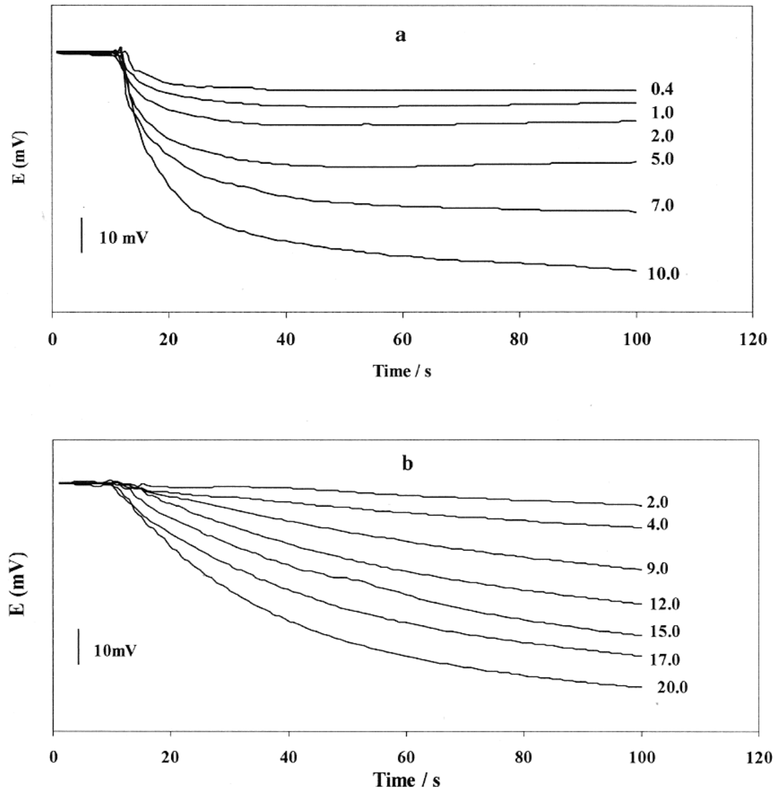

Fig. 2. Typical potential-time curves for the reaction of NCS with HZ and AHZ at different concentrations (μg mL^{-1})

TABLE-1
CHARACTERISTIC OF CALIBRATION GRAPHS FOR THE DETERMINATION OF HZ AND AHZ

Species	Linear range (μg mL^{-1})	Slope (mL $μg^{-1}$)	Intercept	Correlation coefficient (n = 10	Detection limit* (μg mL^{-1})
HZ	0.4-10.0	0.9873	0.1801	0.9992	0.22
AZH	2.0-20.0	0.1038	0.3743	0.9999	0.16

*Concentration corresponding to a net analytical signal equals to three times the standard deviation of the blank.

of analyte concentration completely free from bias[32,33]. In this case, the time variables to be fixed were t_1 and t_2, at which the product of the reaction of AHZ had the same amount of $(10^{\Delta E/S}-1)$ over the range between these two time variables and there is also an appropriate distinction between the slopes of the calibration lines.

Considering a binary mixture of HZ-AHZ, for example, assume that, the amount of ($10^{\Delta E/S}$-1) produced in the reaction of AHZ with NCS at time variables t_1 and t_2 are P_i and R_i, respectively, while those for the HZ-NCS reaction under the same conditions are P and R′, respectively (Fig. 3). They are equal in this case. The following equations show the relation between them:

For AHZ: $R_i = P_i + m_i t_j$ ($t_1 \leq t_j \leq t_2$; i = 0,1,…,n) (1)

For HZ: $R' = P + mt_j$ (m=0) (2)

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

At t_1 $R_{t1} = P_0 + P_i$ (3)

At t_2 $R_{t2} = R' + R_i$ (4)

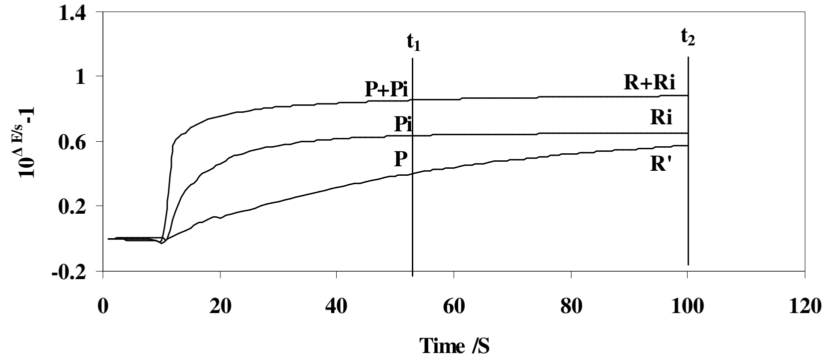

Fig. 3. Plot of potential changes ($10^{\Delta E/S}$-1) for the reaction of NCS with 10 μg mL^{-1} AHZ (a), 5 μg mL^{-1} HZ (b), mixture of them (c)

Simultaneous kinetic determination of concentration of AHZ and HZ by HPSAM requires the selection of two time variables t_1 and t_2. To select the appropriate time variables, the following principles were observed. At the two selected time variables t_1 and t_2, the amount of R for AHZ must be linear with the concentrations and the amount of R for HZ must remain equal, even if AHZ concentrations are changed. The amount of R for the mixture of AHZ and HZ 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 t_1 and t_2 must be as large as possible to achieve good accuracy[32]. Then known amounts of AHZ are successively added to the mixture and resulting potential variations are measured at both time variables and expressed:

$$R_{t1} = (10^{\Delta E(t1)/S}-1)_{t1} = P_0 + P + M_{t1}C_i \quad (5)$$

$$R_{t2} = (10^{\Delta E(t2)/S}-1)_{t2} = R_0 + R' + M_{t2}C_i \quad (6)$$

where $\Delta E(t_1)$ and $\Delta E(t_2)$ are the potential variations measured at t_1 and t_2, respectively. P_0 and R_0 are the amounts of R for AHZ at a sample at t_1 and t_2, respectively. P and R′ are the amounts of R for HZ at t_1 and t_2, respectively (Fig. 3). 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 AHZ concentration. Two straight lines obtained intersect at the so-called H-point ($-C_H$, R_H), as shown in Fig. 4, since $R_{t1} = R_{t2}$, $C_i = -C_H$, $H(-C_H, R_H) \approx (-C_{AHZ}, R_{HZ})$ from eqns. 1 and 2 we have,

$$P_0 + P + M_{t1}(-C_H) = R_0 + R' + M_{t2}(-CH) \tag{7}$$

$$-C_H = [(R' - P) + (R_0 - P_0)]/(M_{t1} - M_{t2}) \tag{8}$$

as species HZ is assumed not to evolve over the considered range of time,

$$R' = P$$

and

$$C_H = (R_0 – P_0)/(M_{t1} – M_{t2}) \tag{9}$$

which is equivalent to the existing C_{AHZ} ($=P_0/M_{t1} = R_0/M_{t2}$). Combining this with eqn. 5 yields $R_H = P$. The overall equation for the absorbance at the H-point is simply represented as:

$$R' = P = R_H = R_{HZ} \tag{10}$$

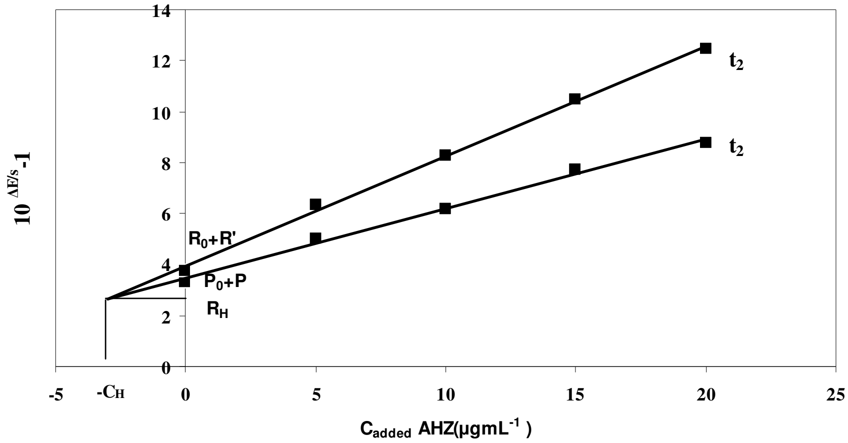

Fig. 4. Plot of HPSAM for simultaneous determination of a mixture of HZ (3.0 µg mL^{-1}) and AHZ (3.0 µg mL^{-1}).

The intersection of the straight lines (eqns. 5 and 6) directly yields the unknown AHZ concentration (C_{AHZ}) and the R for HZ species (R_{HZ}) corresponding to t_1 and t_2 in the original samples, as the two time varibles were chosen in such a way that the later species had the same R at both times. This analytical signal enables the calculation of the concentration of HZ from a calibration curve.

Since AHZ is selected as the analyte, it is possible to select several pairs of time ranges which present the same R for HZ. Some of the selected time pairs were 50-90, 60-90, 65-95, 50-100 and 55-100. Fig. 5 shows the H-point standard addition plots for sample solution at some of the different pairs of time ranges chosen when AHZ was added. Greater time increments caused higher sensitivity and steeper slope of the two time axes, as shown previously by Campins-Falco *et al.*[34] Also, the accuracy of determinations was affected by the slope increments of H-point plots. However, the time pair that gives the greatest slope increment, lower error and shortest analysis time was selected. For this reason, the time pair of 55-100 s was employed.

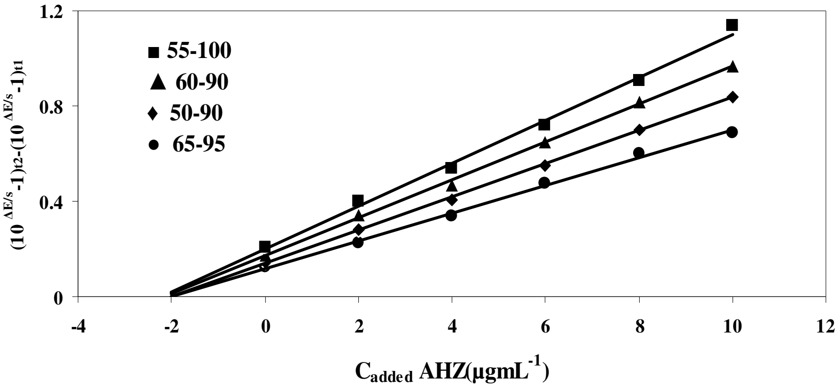

Fig. 5. ΔR *vs.* added AHZ concentration at different time intervals for synthetic mixtures containing 3.0 µg mL^{-1} of HZ and 10.0 µg mL^{-1} of AHZ

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 two straight lines. HZ concentrations were calculated in each test solution by the calibration method with a single standard and ordinate value of R. To check the reproducibility of the method, 5 replicate experiments were performed and the relative deviation (RSD) was obtained for the mixtures. The results are given in Table-3. The precision of results is satisfactory.

Partial least squares regression (PLS): Multivariate calibration methods such as PLS require a suitable experimental design of the standard belonging to the calibration set in order to provide good prediction. For constructing the calibration set, factorial design was applied to 5 levels to extract a great deal of quantitative information using only a few experimental trials. In this research, a synthetic set of 32 solutions including different concentrations of HZ and AHZ was prepared. A collection of 23 solutions were selected as the calibration set and the other 9 s were used as the prediction set (Table-4). Their composition was randomly designed (Table-5) to obtain more information from the calibration procedure. Changes in the potential of the solutions were recorded during a time period of 90 s.

To select the number of factors in the PLS algorithm a cross-validation, leaving out one sample methods was employed[35]. 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):

$$\text{PRESS} = \sum_{i=1}^{m} \left(\hat{C}_i - C_i\right)^2 \tag{11}$$

TABLE-2
RESULTS OF SEVERAL EXPERIMENTS FOR THE ANALYSIS OF HZ AND AHZ MIXTURES AT DIFFERENT CONCENTRATION RATIOS BY HPSAM

R-C equation	r	Spiked ($\mu g\ mL^{-1}$)		Found ($\mu g\ mL^{-1}$)	
		HZ	AHZ	HZ	AHZ
$R_{100} = 0.2345C_i + 2.7135$	0.993	2.0	2.0	2.10	1.95
$R_{55} = 0.0849\ C_i + 2.4209$	0.997				
$R_{100} = 0.2198C_i + 2.1344$	0.997	1.0	4.0	1.05	4.05
$R_{55} = 0.0861C_i + 1.5730$	0.996				
$R_{100} = 0.1314C_i + 1.4224$	0.995	0.5	5.0	0.54	5.30
$R_{55} = 0.0644C_i + 1.0636$	0.998				
$R_{100} = 0.0854C_i + 2.0408$	0.998	1.0	9.0	1.07	9.36
$R_{55} = 0.0320C_i + 1.5406$	0.999				
$R_{100} = 0.1955C_i + 6.4788$	0.997	6.0	2.0	5.96	2.08
$R_{55} = 0.0092C_i + 6.0910$	0.996				
$R_{100} = 0.1231C_i + 2.9833$	0.998	2.0	5.0	2.20	4.92
$R_{55} = 0.04231C_i + 2.5854$	0.998				
$R_{100} = 0.5646C_i +0.8493$	0.999	3.0	5.0	2.93	4.90
$R_{55} = 0.3685C_i + 4.8876$	0.999				
$R_{100} = 0.1986C_i + 2.1586$	0.999	1.0	5.0	0.95	5.20
$R_{55} = 0.1261C_i + 1.7810$	0.998				

TABLE-3
RESULTS OF FIVE REPLICATE EXPERIMENTS FOR ANALYSIS OF HZ AND AHZ MIXTURES USING HPSAM (T = 25 °C)

R-C equation	r	Spiked ($\mu g\ mL^{-1}$)		Found ($\mu g\ mL^{-1}$)	
		HZ	AHZ	HZ	AHZ
$R_{100}=0.4020\ C_i + 3.005$	0.9924	2.00	2.00	2.01	2.09
$R_{55} = 0.2223\ C_i + 2.6294$	0.9931				
$R_{100} =0.3533\ C_i + 3.0363$	0.9967	2.00	2.00	2.14	2.07
$R_{55} = 0.1680\ C_i + 2.6510$	0.9906				
$R_{100}=0.9330\ C_i + 2.3393$	0.9957	2.00	2.00	1.98	2.09
$R_{55} = 0.0357\ C_i + 2.2184$	0.9986				
$R_{100}=0.0666\ C_i + 2.4084$	0.9963	2.00	2.00	2.10	2.03
$R_{55} = 0.0218\ C_i + 2.3171$	0.9993				
$R_{100} =0.01669C_i +2.5077$	0.9964	2.00	2.00	2.00	2.1
$R_{55}= 0.1222\ C_i + 2.4134$	0.9984				
Mean				2.04	2.07
Standard deviation				0.07	0.08

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 ith sample left out of the calibration during cross validation. Fig. 6 shows a plot of PRESS against the number of factors for mixture of components. To find minimum factors, the F-statistic was also used to carry out the significant determination[35]. The optimal number of factors for the two components were obtained as 3.

TABLE-4
CALIBRATION AND PREDICATION SETS FOR CONSTRUCTING PLS MODEL AND DETERMINATION OF HZ AND AHZ (μg mL^{-1})

Calibration set		Prediction set	
HZ	AHZ	HZ	AHZ
0	2	0	4
0	6	1	6
0	10	1	10
0	16	2	8
1	2	3	6
1	8	3	16
1	14	5	20
2	6	7	2
2	12	9	12
2	18	-	-
2	20	-	-
3	4	-	-
3	12	-	-
3	14	-	-
5	6	-	-
5	10	-	-
5	12	-	-
7	4	-	-
7	12	-	-
7	16	-	-
9	2	-	-
9	8	-	-
9	20	-	-

TABLE-5
PREDICTION SET FOR CONSTRUCTING PLS METHOD IN DETERMINATION OF HZ AND AHZ

Sample	Synthetic (μg mL^{-1})		Prediction (μg mL^{-1})		Recovery (%)	
	HZ	AHZ	HZ	AHZ	HZ	AHZ
1	0.0	4.0	–	4.21	–	105.2
2	1.0	6.0	1.01	5.91	101.0	98.5
3	1.0	10.0	0.96	10.34	96.0	103.4
4	2.0	8.0	2.00	7.89	100.0	98.6
5	3.0	6.0	3.05	6.13	101.6	102.1
6	3.0	16.0	3.09	16.32	103.0	102.0
7	5.0	20.0	4.93	19.69	98.6	98.4
8	7.0	2.0	6.87	2.04	98.1	102.0
9	9.0	12.0	9.24	11.85	102.6	98.8
Mean recovery	–	–	–	–	100.1	101.0
RSE (%)	–	–	–	–	0.022	0.020
RSE_t(%)	–	–	–	–	0.020	0.020

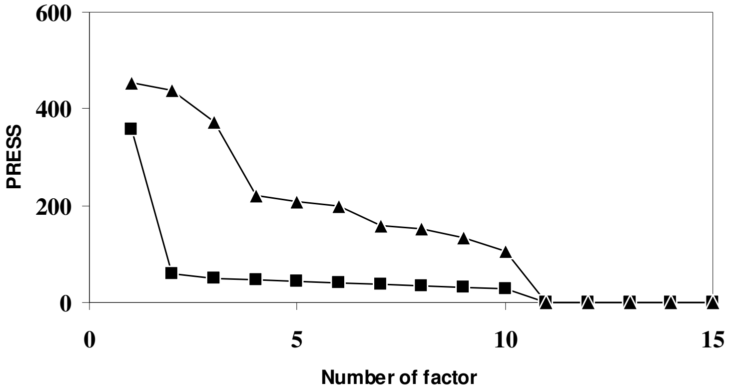

Fig. 6. Plot of PRESS against the numbers of factors for HZ (■) and AHZ (▲)

For the evaluation of the predictive ability of a multivariate calibration model, the root mean square error of prediction (RMSEP) and relative standard error of prediction (RSEP) can be used[36-38].

$$\text{RMSEP} = \left(\sum_{i=1}^{N} \left(\hat{C}_i - C_i \right)^2 / n \right)^{1/2} \qquad (12)$$

$$\text{RSEP}(\%) = \left(\sum_{i=1}^{N} \left(\hat{C}_i - C_i \right)^2 / \sum_{i=1}^{N} (C_i)^2 \right)^{1/2} \times 100 \qquad (13)$$

where $\hat{C}_i$ represents the estimated concentration, C_i and n are the actual analyte concentration and the number of samples, respectively.

Interference study: To study the selectivity of the proposed methods, the effect of various ions on the determination of a mixture of 2.0 μg mL^{-1} for both HZ and AHZ was tested under the optimum conditions. The results are shown in Table-6. The tolerance limit was defined as the maximum concentration of the added ion causing less than 5 % relative error.

TABLE-6
EFFECT OF INTERFERING IONS ON THE DETERMINATION OF 1.0 μg mL^{-1} OF BOTH HZ AND AHZ

Species	Tolerance ratio*
Li^+, K^+, Na^+, Fe^{3+}, Cr^{3+}, $H_2PO_4^-$, SO_4^{2-}, PO_4^{3-}, F^-	1000**
Pb^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, $C_2O_4^{2-}$,CO_3^{2-}, CH_3COO^-, NO_3^-, TX-100	100
I^-, SDS, CTAB	10
Br^-	0.5

*Tolerance ratio is the ratio of the interfering species to HZ and AHZ mixture, which causes less than 5 % relative error. **Largest amount tested.

Application: To evaluate the analytical applicability of the proposed methods (PLS and HPSAM), known amounts of HZ and AHZ were spiked into some water samples. The proposed methods were applied to determine analytes simultaneously. The results were compared with those obtained by kinetic-spectrophotometric methods[11,13]. The kinetic-spectrophotometric methods are based on the based on the difference observed in the reaction rate of 4-dimethylaminobenzaldhyde (DAB) with HZ and AHZ using HPSAM[11] and difference reaction rate of their with iron(III) in the presence of 2,2-bipyridine (Bpy) using PLS method[13]. The results (Table-7) demonstrate that the proposed methods can be employed satisfactorily for the simultaneous determination of HZ and AHZ in water samples.

TABLE-7
SIMULTANEOUS KINETIC-POTENTIOMETRIC AND –SPECTROPHOTOMETRIC [Ref. 11,13] DETERMINATION OF HZ AND AHZ IN DIFFERENT WATER SAMPLES USING HPSAM AND PLS METHOD

Sample	Amount added (μg mL^{-1})		Predicted (μg mL^{-1})			
			Kinetic-potentiometric			
			HPSAM		PLS	
	HZ	AZH	HZ	AHZ	HZ	AHZ
Tap water	2	2	2.08(±0.10)	2.05(±0.12)	2.05(±0.08)	1.97(±0.13)
	4	5	4.18(±0.14)	5.20(±0.28)	3.88(±0.13)	5.14(±0.20)
	8	12	8.37(±0.40)	11.74(±0.26)	8.40(±0.34)	12.36(±0.30)
River water	2	2	2.16(±0.15)	2.18(±0.10)	2.09(±0.11)	2.05(±0.08)
	4	5	4.24(±0.20)	5.28(±0.22)	4.20(±0.25)	5.24(±0.20)
	8	12	8.30(±0.35)	12.34(±0.24)	8.24(±0.22)	11.82(±0.30)
Spring water	2	2	2.12(±0.13)	2.08(±0.10)	2.14(±0.12)	2.20(±0.18)
	4	5	4.10(±0.11)	5.17(±0.20)	4.28(±0.22)	4.84(±0.24)
	8	12	8.40(±0.30)	12.35(±0.32)	7.86(±0.25)	12.24(±0.18)
Well water	2	2	2.10(±0.14)	2.14(±0.08)	2.15(±0.13)	2.10(±0.08)
	4	5	4.16(±0.16)	4.98(±0.12)	3.74(±0.20)	5.10(±0.20)
	8	12	8.23(±0.26)	12.26(±0.22)	7.66(±0.25)	12.34(±0.20)
Sample	Amount added (μg mL^{-1})		Kinetic-spectrophotometric			
			HPSAM [Ref. 11]		PLS [Ref. 13]	
	HZ	AZH	HZ	AHZ	HZ	AHZ
Tap water	2	2	2.15(±0.14)	2.12(±0.10)	2.16(±0.13)	2.06(±0.11)
	4	5	4.16(±0.23)	5.24(±0.26)	4.25(±0.23)	5.26(±0.28)
	8	12	7.88(±0.32)	12.64(±0.52)	8.35(±0.34)	12.45(±0.26)
River water	2	2	1.87(±0.12)	2.20(±0.17)	2.16(±0.14)	2.74(±0.22)
	4	5	4.19(±0.23)	5.30(±0.28)	4.22(±0.27)	5.38(±0.32)
	8	12	8.30(±0.34)	12.32(±0.26)	8.30(±0.40)	12.67(±0.45)
Spring water	2	2	2.14(±0.10)	2.16(±0.15)	2.10(±0.16)	1.88(±0.14)
	4	5	4.15(±0.16)	5.20(±0.23)	4.22(±0.18)	5.30(±0.25)
	8	12	8.34(±0.32)	12.64(±0.42)	8.24(±0.24)	12.54(±0.34)
Well water	2	2	2.18(±0.15)	2.16(±0.17)	2.22(±0.14)	2.08(±0.10)
	4	5	4.26(±0.13)	5.46(±0.33)	4.30(±0.27)	5.22(±0.26)
	8	12	8.20(±0.23)	12.86(±0.36)	8.42(±0.24)	12.37(±0.25)

Conclusion

This work using HPSAM and PLS method in the simultaneous determination of the binary mixture of HZ and AHZ 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. In addition, this paper has also demonstrated that the ability and advantages of the HPSAM and chemometrics methods such as PLS, ISEs and kinetic methods produce a very attractive and excellent technique for the analysis of multi-component mixtures. Other chemometrics approaches like PCR or ANN, ISEs (flouride, bromide, iodide, *etc.*) and other kinetic reactions in which the rate of production or consumption of the corresponding ion is different can also be used. Present team has obtained good results for the simultaneous determination of other species using HPSAM, chemometrics methods, different ISEs and various reaction systems and its complete results will be presented for the publication in future.

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