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Development and application of a new sensitive spectrophotometric-multivariate calibration method to the simultaneous determination of hydrazine and acetylhydrazine using silver nanoparticles

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Abstract

In this paper, multivariate calibration methods of partial least squares (PLS) and principle component regression (PCR) were investigated in simultaneously determination of hydrazine (HZ) and acetylhydrazine (AHZ). The aforementioned methods are based on formation of the silver nanoparticles (AgNPs) from the reaction of HZ and AHZ with Ag^+ ions as oxidizing agent in the presence of citrate ions as a stabilizing and catalyzing agent. The reaction was followed by analytical wavelength (420 nm) corresponding to the maximum extinction of surface plasmon resonance (SPR) of AgNPs. These methods were based on the differences observed in the production rate of AgNPs. Differences in the kinetic behavior of the HZ and AHZ were exploited using PLS and PCR to resolve concentration of analytes in their mixture. The obtained results show that simultaneous determination of HZ and AHZ can be performed in the concentration linear ranges of 40.0-1000.0 and 200.0-1000.0 ng mL^{-1}, respectively. The root mean squares errors of prediction (RMSEP) for applying PCR and PLS methods to 9 synthetic samples in these concentration ranges were 0.8307 and 1.9411 for HZ and 1.4407 and 0.9883 for AHZ, respectively. To assess selectivity of the methods, the effects of certain foreign ions upon the reaction rate were determined. Both methods (PLS and PCR) were validated using a set of synthetic sample mixtures and then they were applied for simultaneous determination of HZ and AHZ in different water samples.

Keywords: Silver nanoparticles (AgNPs); surface plasmon resonance (SPR); hydrazine (HZ); acetylhydrazine (AHZ); multivariate calibration methods.

Introduction

There has been growing interest in using nanoparticles in many branches of science and industry [1-3]. Nanoparticles, made of silver and gold, are generating considerable attention in research because of their charming optical properties [4]. Dispersing in liquid media, these nanoparticles exhibit a strong UV-Vis extinction band; even though it is not observed in the spectrum of the bulk metal. This extinction band results when the incident photon frequency is resonant with the collective excitation of the conduction electrons which are known as the surface plasmon resonance (SPR) [5]. SPR excitation findings provide higher sensitivity in colorimetric methods than conventional reagents [6]. Recently, the colorimetric methods using silver nanoparticles (AgNPs) as well as gold nanoparticles (AuNPs) have been developed regarding sensitive and selective

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detection of proteins [7], DNA [8], phenolic compounds [9], thiol-containing amino acids [10], drugs [11,12], ammonia [13], iodide [14], phosphate ion [15], heavy metal ions [16,17], enzymatic activity assay [18], and pH alarm [19], based on optical properties of AgNPs and AuNPs. There are several reported modeling methods in the field of simultaneous analysis of species mixture using artificial neural network (ANN) and method and SPR excitation which belongs to AgNPs and AuNPs. Hormozi Nezhad et al. and Tashkhourian et al. introduced two new methods for simultaneous determination of the binaries of levodopa and benserazide hydrochloride as well as dopamine and ascorbic acid through artificial neural network (ANN) approach [12,20]. The aforementioned methods were based on the differences observed in the production rate of AgNPs in the reaction of these species with the silver nitrate as oxidizing agent in the presence of poly-vinyl pyrrolidone (PVP). The rate of the production of AgNPs was obtained by spectrophotometrically monitoring the changes of SPR band at maximum wavelength of those nanoparticles (440 nm) *vs*. time. Recently, Tashkhourian et al. also defined a new method for simultaneous determination of the binary mixture of peroxyacetic acid (PAA) and hydrogen peroxide (H_2O_2) through ANN model [21]. This method was based on the difference observed in the decomposition rate of PAA and H_2O_2 in the reaction of these species with the AgNPs as reducing and chromogenic reagent.

Hydrazine (HZ), a significant industrial chemical, is used as a beginning material for the synthesizing polymers, blowing agents for plastic, pharmaceuticals, and pesticides. Moreover, HZ as a reducing agent is commonly added to steam-boiler water for dissolving oxygen and precipitated metal oxides and its reaction products are nitrogen and water, thus HZ using for inhibiting corrosion or scale build-up in boilers. HZ and its derivatives have been used as Rocket propellant and manufacturer of metal films, photographic chemicals, insecticides and explosives. On the other hand, HZ is highly toxic and may cause skin irritation and poisoned state. Since this substance and its derivatives are applied in a various fields and they are considered as a carcinogen and hepatotoxic agent, their determination is important and very interesting for researchers. Several methods have been recognized for the determination of HZ and its derivatives separately [22,23]. A number of methods have been also introduce for the simultaneous determination of binary and ternary mixtures of HZ and its derivatives using H-point standard addition method (HPSAM) and multivariate calibration methods [24,25]. To the best of our knowledge, chemometrics methods for simultaneous determination of HZ and its derivatives mixture using SPR of AgNPs and/or AuNPs have not been investigated yet. However theory and application of multivariate calibration methods of principal component regression (PCR) and partial least squares (PLS) in spectrophotometry have been discussed by several researchers [26]. The aim of this study was to evaluate the possibility of using PLS and PCR methods for simultaneous determination of HZ and acetylhydrazine (AHZ) as its derivative using SPR of AgNPs. The applied method was based on differences observed in the production rate of AgNPs as chromogenic reagent in the reaction of HZ and AHZ with silver nitrate as oxidizing agent in the presence of trisodium citrate (TSC).

Experimental

Reagents

All chemicals were analytical reagent grade and the solutions were prepared with deionized water. Silver nitrate ($AgNO_3$), TSC, HZ, and AHZ were used for the synthesizing of AgNPs which were purchased from Merck (Darmstadt, Germany). All other common laboratory chemicals were of the best available grade and were used without further purification. All solutions were used within 1 h after preparation. The experiments were performed at ambient temperature (25±2 ºC) and all glassware was cleaned and thoroughly rinsed with deionized water prior to use. Stock solutions of $AgNO_3$ (5.88×10^{-3} mol L^{-1}) were prepared by dissolving 0.050 g of $AgNO_3$ in deionized water and diluting to 50 ml. Stock solutions (100 mg L^{-1}) of HZ and AHZ were prepared in 100 mL flasks by dissolving 0.0406 g of hydrazinium sulfate and 0.1000 g of AHZ in deionized water and then 1 mL of HZ solution were diluted in 10 mL flask to obtain the solution (10 mg L^{-1}) of HZ. A stock solution of tri sodium citrate (0.003 mol L^{-1}) was also prepared by dissolving 0.1000 g of TSC in water and diluting to 100 mL.

Apparatus

The UV-Vis absorbance spectra was recorded on a GBC UV-Visible Cintra 6 spectrophotometer model connected to a Pentium (IV) computer, while 1.0 cm quartz cell was used for the evaluation of the optical characteristics of the Surface Plasmon Resonance (SPR) detection method using AgNPs. Measurements of pH were done with a Denver Instrument Model 270 pH meter equipped with a Metrohm glass electrode. PLSand PCR analyses were performed using PLS and PCR toolboxes in MATLAB program version 7.0. The morphology of the nanoparticles was analyzed applying the image obtained from a transmission electron microscope (Philips Em 208 90 kV). X-ray diffraction (XRD) pattern of dry nanoparticle powder was obtained using X'Pert ProMPD (PANalytical) X-ray diffractometer with CuK_α radiation (λ= 1.51 Ǻ).

Procedure

Appropriate volumes of hydrazine, acetylhydrazine solution, 4.0 mL of TSC 3.4×10^{-3} mol L^{-1}, and 2.0 mL of $AgNO_3$ 5.88×10^{-3} mol L^{-1} were added into a 10 ml volumetric flask and were diluted by deionized water. In order To record the absorbance, it was mixed slowly and a portion of it was transferred into a 1 cm spectrophotometric cell. It should be noted that the order of the addition of the reagents is very important. The absorbencies were measured at 420 nm “that is λ_{max} of SPR peak of AgNPs at this condition, against a reagent blank”.

Results and discussion

In this study, the system consists of an aqueous $AgNO_3$ solution including TSC as stabilizer and catalyst, HZ and AHZ as effective reducing agents for reduction of silver ions to the AgNPs as chromogenic reagent without addition of any seeds (Eq. 1).The reaction of Ag^+ and N_2H_4 is represented by equation 1:

$$4Ag^+ + N_2H_4 \rightarrow 4Ag\,(s) + 4H^+ + N_2\,(g) \quad (1)$$

In the absence of reducing agents, there was no absorption peak in the visible region (380-700 nm). Upon addition of HZ or AHZ, which acted as reducing agents, silver ions were reduced to AgNPs and then the absorbance characteristic to the plasmon of the AgNPs was observed. Figure 1 shows the absorption spectra of the AgNPs that was produced by the HZ and AHZ against the reagent blank.

Based on the peaks appearance, a method was proposed for the detection of HZ and AHZ. Furthermore, a series of experiments were conducted to establish the optimum analytical conditions. Also the reduction reaction rate of $AgNO_3$ with HZ and AHZ were different. The difference suggested the possibility of resolving their mixtures through PLS and PCR methods.

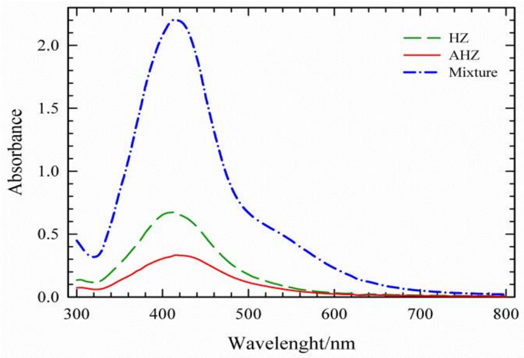


Figure 1. Absorption spectra of AgNPs in the solutions containing 200 ng mL^{-1} HZ (a), 500 ng mL^{-1} AHZ (b) and the mixture of them (c) in the presence of 0.001 mol L^{-1} TSC, 0 .001 mol L^{-1} $AgNO_3$ and 25 °C

The extracted parameters from the calibration graphs of HZ and AHZ are given in Table 1. As is shown in Table 1, the linear ranges of HZ and AHZ determinations are acceptable.

Table 1. Extracted parameters derived from the calibration graphs for the determination of HZ and AHZ

Parameter	HZ	AHZ
Slope (ng^{-1} mL)	2.179	2.305
Intercept	0.072	-0.038
Correlation coefficient	0.9992	0.9995
Linear range (ng mL^{-1})	40.0-1000.0	200.0-1000.0
Detection Limit (ng mL^{-1})	36.1	34.0

The experimental parameters, such as metal ion concentration, concentration of TSC, temperature, time, and pH of the solution were optimized. The optimization process showed similar results for each of analytes and their mixture.

Effect of Ag^{+} concentration

The effect of Ag^{+} concentration on the reaction rate of HZ and AHZ and mixture of them was investigated at constant conditions of analytical wavelength corresponding to the maximum extinction of was related to surface plasmon resonance (SPR) of AgNPs (420 nm), neutral pH and room temperature (25 ºC).

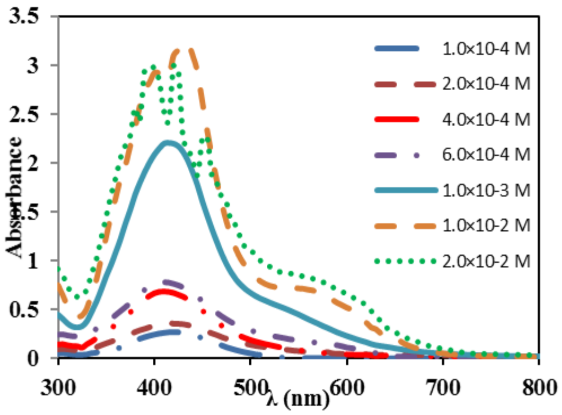


Figure 2. SPR of AgNPs synthesized by mixing HZ and AHZ in different concentrations of silver nitrate solution in the presence of 0.001 mol L^{-1} TSC

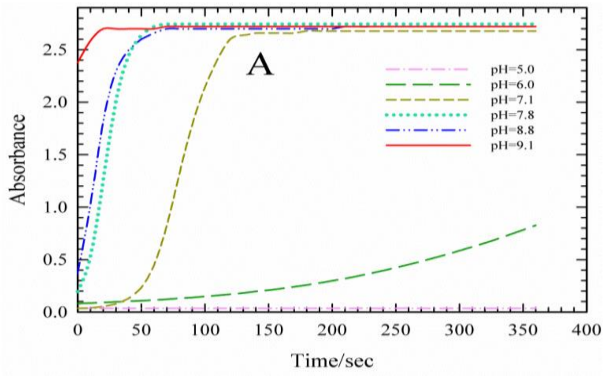
As is shown in Figure 2, the reaction rate and absorbance change of both species and their mixture increase with increasing the concentration of Ag^+ ions up to 0.001 mol L^{-1}, whereas, above this concentration the color solution became dark. Therefore, 0.001 mol L^{-1} silver nitrate was selected as the optimum concentration for further studies.

Effect of acidity

In the present study, the influence of pH on the reaction rate of Ag^+ reduction by HZ and AHZ over the range of 5.0 to 10.3 was investigated. Figure 3 shows the effect of pH on the reaction rate of HZ and AHZ in the presence of TSC and silver nitrate. Because buffered conditions prevent from silver nanoparticles formation, enough HNO_3 or NaOH was added to regulate acidity or alkalinity. At low pH range, up to 20 min the solution was colorless and would not formed any nanoparticles. When the pH increased up to 8.0, the reaction rate was enhanced for both of the analytes. At the higher pHs, the solution was dark which is due to the Ag_2O formation. Thus, pH of 8.0 was selected as the optimum pH for both of analytes.

Effect of TSC amount

Protective agent or stabilizer plays a vital role in stabilizing the colloidal metal nanoparticles from agglomeration [27]. In this study, TSC was selected as stabilizer for prevention of AgNPs agglomeration and as catalyst for this reaction. In order to optimize the TSC amount, different TSC quantities were used for the synthesizing AgNPs. The variation of the absorbance at 420 nm versus time in different volumes of TSC (3.4×10^{-3} mol L^{-1}) is shown in Figure 4. The result shows that 3.0 mL is containing the best amount of TSC.



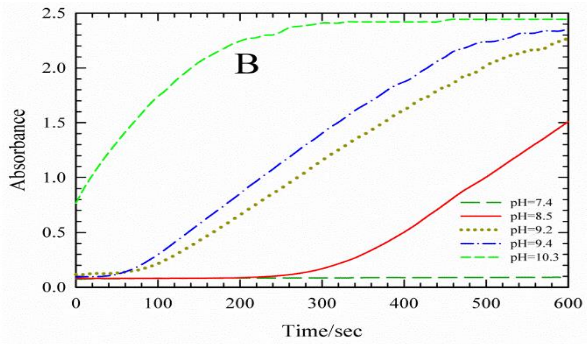


Figure 3. Effect of pH on the reaction rate in the solutions containing 200 ng mL^{-1} HZ (A) and 500 ng mL^{-1} AHZ (B) in the presence of 0.001 mol L^{-1} TSC, 0.001 mol L^{-1} $AgNO_3$, and 25 ºC

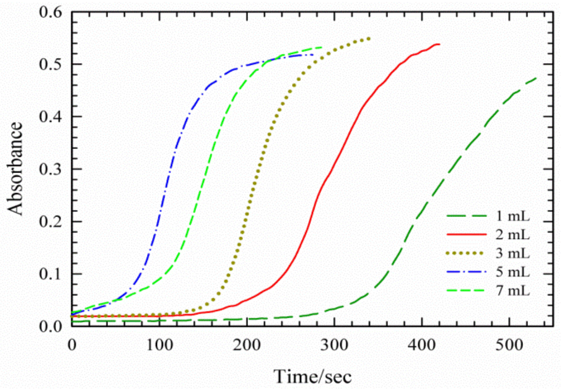


Figure 4. Effect of TSC amount (3.4×10^{-3} mol L^{-1}) on the production of AgNPs in the solution containing 200 ng mL^{-1} HZ, 500 ng mL^{-1} AHZ, 0.001 mol L^{-1} $AgNO_3$ and 25 ºC

Effect of temperature

The effect of temperature on the reaction rate of HZ and AHZ was studied in the range of 10-40 ºC. As is shown in Figure 5, the reaction rate of both species increases with increasing the temperature. However, for simplicity and better control of the temperature effect on the accuracy of the measurements, 25 °C was chosen as the optimized temperature. So, this temperature was used in further studies.

Absorbance- Time behavior

Under the optimized conditions, the reaction of HZ and AHZ with the silver nitrate in the presence of TSC showed different kinetic behavior. As is shown in Figure 6, the spectra of the HZ and AHZ are nearly the same, and the spectrophotometric determination of each compound interferes with the other one. However, it was observed that the reaction of HZ with $AgNO_3$ in the presence of TSC completed in 5 minutes after mixing, while in the same conditions, the reaction of AHZ with $AgNO_3$ was relatively slow (Figure 6). The reaction could be monitored spectrophotometrically by measuring the absorbance of solutions at 420 nm. These differences in the reaction rates allowed us to design multivariate calibration methods as a technique for simultaneous determination of HZ and AHZ. The linearity of the analysis was studied individually under the optimum conditions (Table 1).

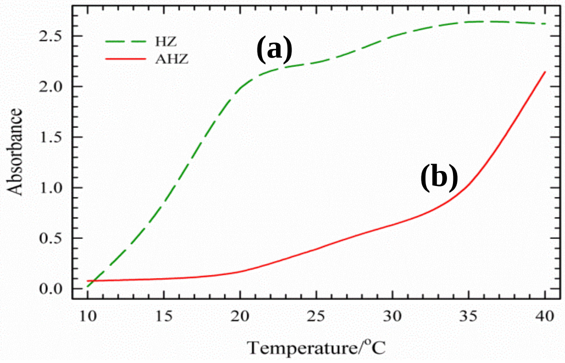


Figure 5. Effect of temperature on the reaction rate of 200 ng mL^{-1} HZ (a) and 500 ng mL^{-1} AHZ (b). Conditions: 0.001 mol L^{-1} $AgNO_3$ in the presence of 0.001 mol L^{-1} TSC

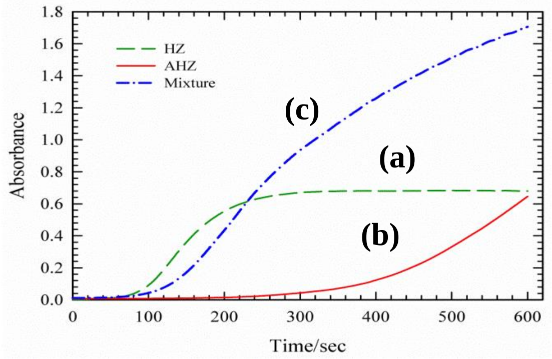


Figure 6. Absorbance changes of AgNPs against time in the reaction of 200 ng mL^{-1} HZ (a), 500 ng mL^{-1} AHZ (b) and the mixture of them (c) with 0.001 mol L^{-1} $AgNO_3$ in the presence of 0.001 mol L^{-1} TSC

Characterization *of AgNPs*

The size and the shape of AgNPs were investigated by transmission electron microscopy (TEM) operating at an accelerating voltage of 90 kV. The nanoparticles which are observed in Figure 7 are spherical and have a narrow particles size distribution with the largest diameter of 18 nm.

The experimental powder diffraction (XRD) pattern of the prepared AgNPs is shown in Figure 8. In the XRD pattern of AgNPs, diffraction peaks at 38.13º, 44.21º, 64.47º and 77.37º can be assigned to face-centered cubic (fcc) metallic silver corresponding to the (111), (200), (220) and (311) faces of the silver crystals.

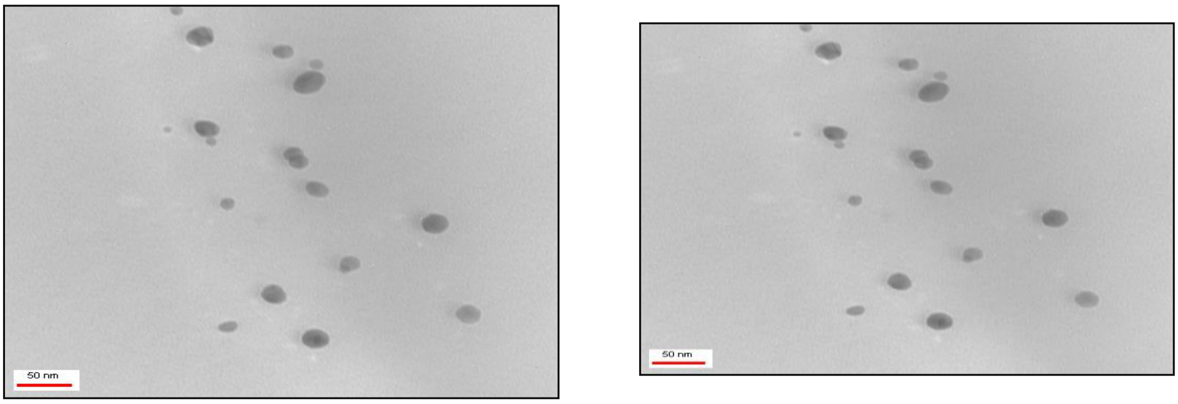


Figure 7. TEM image of spherical AgNPs

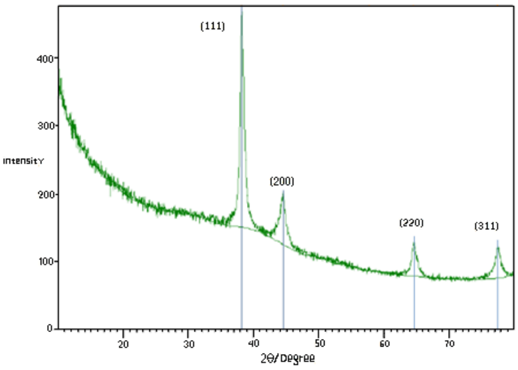


Figure 8. XRD pattern of AgNPs

Multivariate calibration

Multivariate calibration methods such as PLS and PCR require a suitable experimental design of the standard belonging to the calibration set in order to provide good predictions. In this research, a synthetic set of 39 solutions containing different concentrations of HZ and AHZ was constructed. The concentration ranges of 40-1000 and 200-1000 ng mL^{-1} were used for HZ and AHZ, respectively. The numbers of 30 solutions (Table 2) were selected as a calibration set and the other 9 solutions were used as a prediction set (Table 3).

Table 2. Calibration set for construction of PLS and PCR methods in determination of HZ and AHZ

Sample	HZ (ng mL^{-1})	AHZ (ng mL^{-1})
1	400.0	300.0
2	400.0	500.0
3	800.0	400.0
4	600.0	200.0
5	60.0	600.0
6	400.0	700.0
7	800.0	200.0
8	400.0	400.0
9	600.0	700.0
10	1000.0	0.0
11	80.0	700.0
12	1000.0	300.0
13	600.0	500.0
14	80.0	800.0
15	1000.0	500.0
16	200.0	600.0
17	200.0	200.0
18	600.0	400.0
19	0.0	1000.0
20	800.0	300.0
21	800.0	700.0
22	400.0	600.0
23	100.0	600.0
24	800.0	600.0
25	40.0	700.0
26	600.0	300.0
27	100.0	400.0
28	1000.0	400.0
29	60.0	700.0
30	40.0	800.0

Table 3. Prediction set for construction of PLS and PCR methods in determination of HZ and AHZ

Sample	Added (ng mL^{-1})		Predicted (ng mL^{-1})			
			PLS		PCR	
	HZ	AHZ	HZ	AHZ	HZ	AHZ
1	200.0	300.0	202.3	299.0	201.5	299.4
2	60.0	800.0	58. 9	799.6	60.1	798.4
3	400.0	200.0	402.3	201.0	399.6	202.1
4	80.0	600.0	81.1	600.4	80.3	598.4
5	600.0	600.0	596.9	600.6	600.4	601.7
6	100.0	400.0	99.1	399.1	100.2	401.0
7	800.0	500.0	802.8	498.9	798.5	498.5
8	1000.0	700.0	998.8	702.2	1001.1	701.1
9	40.0	1000.0	41.1	1000.3	39.8	1001.2

Their composition was randomly chosen to obtain more information from the calibration set. Changes in the absorbance of each solution were recorded during a time period of 600 s, which implies working with 600 experimental points (1 point every 1 second). In this region, the maximum differences in kinetic behavior are observed. Kinetic-spectrophotometeric data were collected through the Excel program and fed into the MATLAB program.

In order to select of the number of factors in the PLS and PCR algorithm, an across-validation leaving out one sample method was employed [9]. The prediction error was calculated for each species for the prediction set. This error was expressed as the prediction of the residual error sum of square (PRESS):

$$\mathrm{PRESS} = \sum_{i=1}^{m}(\hat{C}_i - C_i)^2 \qquad (2)$$

where m is the total number of calibration samples, $\hat{C}_i$ represents the estimated concentration and C_i is the reference concentration for the ith sample left out the calibration during cross validation. Figure 9 shows a plot of PRESS against the number of factors for mixture of components. In order to find the fewest number of factors and carry out significant determination, the F-statistic test was used [22]. The optimum number of factors for two components were obtained 5 for both PLS and PCR.

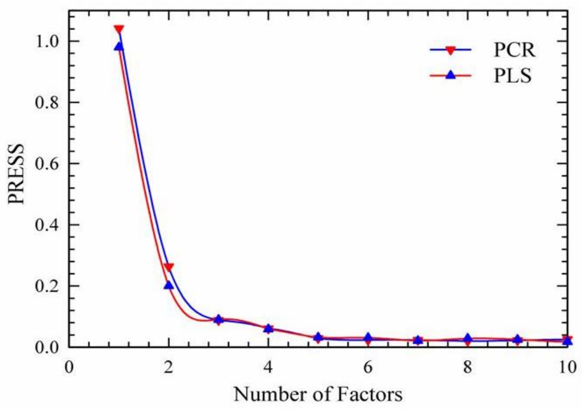


Figure 9. Plot of PRESS against the number of factors for mixtures of HZ and AHZ for PLS and PCR methods

In order to evaluate 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 [6].

$$RMSEP = \left[\sum_{i=1}^{N} (\hat{C}_i - C_i)^2 / n) \right]^{1/2} \tag{3}$$

$$\%RSEP = \left[\sum_{i=1}^{N} (\hat{C}_i - C_i)^2 / \sum_{i=1}^{N} (C_i)^2 \right]^{1/2} \times 100 \tag{4}$$

Where n is the number of samples. The squares of correlation coefficient (R^2), which indicate the fit quality of all the data to a straight line is presented by:

$$R^2 = \sum_{i=1}^{N} (\hat{C}_i - C')^2 / \sum_{j=1}^{N} (C_i - C')^2 \tag{5}$$

Where C′ represents the mean of the actual concentration in the prediction set [21]. Table 4 shows the values of RSEP(%), RMSEP and R^2 for each component used in PLS and PCR methods. It shows that the obtained values of the statistical parameters are almost the same for both PLS and PCR methods.

Table 4. Statistical parameters calculated for the prediction set using PLS and PCR methods

Statistical parameter	**HZ**		**AHZ**	
	PLS	PCR	PLS	PCR
RMSEP	1.9411	0.8307	0.9883	1.4407
RSEP (%)	0.3907	0.1672	0.1610	0.2347
R^2	0.9987	0.9996	1.0019	0.9985

Interference study

To study the selectivity of the proposed methods of PLS and PCR, the effect of various ions on the determination of a mixture of 200 ng mL^{-1}HZ and 500 ng mL^{-1}AHZ was tested under the optimum conditions. The results are shown in the Table 5.

Table 5. Effect of interference ions on the determination of 1000 ng mL^{-1} of both HZ and AHZ

Species	**Tolerance ratio**[a]
K^+, Na^+, Li^+, Zn^{2+}, NO_3^-, Cu^{2+}, Ni^{2+}, Cd^{2+}	1000
Ca^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+}, $C_2O_4^{-2}$, SO_4^{-2}, HSO_4^-	100
CH_3COO^-, Fe^{3+}, NH_4^+, CO_3^{-2}, HCO_3^-	10
SO_3^{-2}, HPO_4^{-2}, $H_2PO_4^-$, Pb^{2+}, Co^{2+}	1

[a] Tolerance ratio is the ratio of the interfering species of HZ and AHZ mixture which causes less than 5% relative error.

The tolerance limit was defined as the maximum concentration of added ion causing less than 5% relative error.

Application

In order to evaluate the analytical applicability of the proposed PLS and PCR methods, these methods were applied to the simultaneous determination of HZ and AHZ in water samples from Yazd power generation management company. The tested samples were found to be free of AHZ and thus, synthetic samples were prepared for adding known amount of HZ and AHZ to some water samples. The proposed methods were applied to determine analytes simultaneously, and satisfactory results were obtained. The results are given in Table 6.

Table 6. Simultaneous determination of HZ and AHZ in different water samples (n=3) analysis and recovery results from main cooling tower of Yazd power generation management company

Added/ng mL^{-1}		**Predicted/ng mL^{-1}**							
		PLS				**PCR**			
HZ	**AHZ**	**HZ**	**Recovery (%)**	**AHZ**	**Recovery (%)**	**HZ**	**Recovery (%)**	**AHZ**	**Recovery (%)**
0	0	105.4(±0.1)	-	0.0(±0.2)	-	107.5(±0.2)	-	0.0(±0.2)	-
100	300	206.2(±0.3)	100.8	301.2(±0.4)	100.4	203.7(±0.5)	96.2	297.5(±0.8)	99.2
300	500	414.3(±0.1)	102.9	501.6(±0.1)	100.3	409.4(±0.8)	100.6	502.1(±0.3)	100.4
500	700	608.7(±0.4)	100.7	700.9(±0.3)	100.1	610.0(±0.1)	100.5	698.8(±0.4)	99.8

Conclusion

In this work, it is shown that the PLS and PCR models can be well adopted for simultaneous determination of HZ and AHZ using SPR of AgNPs. The PLS and PCR methods based on kinetic-spectrophotometric data were developed for the simultaneous determination of HZ and AHZ in synthetic binary mixtures. The proposed approach is new, inexpensive and sensitive that offers good accuracy and precision and can be applied to a wide range of HZ and AHZ concentrations. Table 7 shows a comparison of the proposed method with some other reported methods of the individual and simultaneous determination of HZ and AHZ. It could be seen that some obtained values for the proposed method are as or better than some of the previously reported methods.

Table 7. Comparative data from proposed method with some other reported methods of the individual and simultaneous determination of HZ and AHZ

Technique	**Analytes**	**Linear range**	**Detection limit**	**Reference**
Kinetic Spectrophotometric	HZ, TSC and PHZ[a]	1.0–70.0, 0.2–6.0 and 0.1–10.0 µg mL^{-1}, respectively	0.4, 01, and 0.07 µg mL^{-1}, respectively	[17]
Kinetic-Potentiometric	HZ and TSC[b]	0.5-20.0 and 0.7-20.0µg mL^{-1}, respectively	0.10 and 0.4 µg mL^{-1}, respectively	[18]
kinetic spectrophotometric	HZ	$4.7\times10{-}6\sim3.1\times10{-}5$ mol L^{-1}	3.1×10^{-6} mol L^{-1}	[28]
kinetic spectrophotometric	HZ	3.0×10^{-7}–3.2×10^{-5} mol L^{-1}	8.5×10^{-8} mol L^{-1}	[29]
Kinetic Spectrophotometric	HZ and PHZ	0.020–0.50 and 0.20–10.0 µg ml^{-1}, respectively.	-	[30]
Kinetic Spectrophotometric	HZ, AHZ and	0.10-1.0, 0.10-6.0, and 0.50-	-	[31]

	PHZ	100 µg mL^{-1}, respectively		
Kinetic-Spectrophotometric	HZ and AHZ	0.020 - 0.70 and 0.20 - 5.0 mg L^{-1}, respectively	HZ-AHZ 0.01, 0.08 mg L^{-1} respectively	[32]
Kinetic-Potentiometric	HZ and AHZ	0.4-10.0 and 2.0-20.0 µgmL^{-1}, respectively	0.22 and 0.16 µg mL^{-1}, respectively	[33]
Spectrophotometric-multivariate calibration method	HZ and AHZ	40.0-1000.0 and 200.0-1000.0 ng mL^{-1}, respectively	36.1, 34.0 ng mL^{-1} respectively	In this work

[a] Phenylhydrazine
[b] Thiosemicarbazide

The PLS and PCR models were validated with the use of synthetic binary mixtures of HZ and AHZ and the figures of merit, RSEP (%), RMSEP and R^2. This method is cheaper than previous spectrophotometric methods and also conventional chromatographic separation methods. Furthermore, in this method, we do not need to use complex pretreatment or toxic organic solvents. In other words they belong to green chemistry. Finally, this work shows ability of AgNPs for simultaneous determination of important analytes.

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