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Application of Principle Component Regression and Partial Least Square to the Simultaneous Kinetic-Spectrophotometric Determination of Ternary Mixture of Hydrazine, Phenylhydrazine and Acetylhydrazine

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A method for the simultaneous determination of the hydrazine (HZ) and its derivatives in water samples has been investigated and developed. It is based on reaction kinetics and spectrophotometry and results are interpreted with the aid of partial least squares regression (PLS) and principal component regression (PCR). The analytical method relies on the differential rates of reduction of copper(II) with HZ, phenylhydrazine (PHZ) and acetylhydrazine (AHZ) in the presence of neocuproine (NC) and monitoring the resulted coloured complex of Cu(I)/NC in sodium dodecyl sulfate (SDS) as micellar media at 452 nm. The optimized method was successfully tested by analyzing each of the species independently and linear calibration models are described. The results showed that simultaneous determination of HZ, PHZ and AHZ in ternary mixtures using these chemometrics methods could be performed in their concentration ranges of 0.10-1.0, 0.10-6.0 and 0.50-100 μg mL^{-1}, respectively. The root mean squares errors of prediction (RMSEP) of HZ, PHZ and AHZ were 0.016, 0.026 and 0.054 (for PLS) 0.011, 0.095 and 0.141 (for PCR), respectively. Both the proposed methods (PCR and PLS) were validated using a set of synthetic sample mixtures and subsequently applied to the simultaneous determination of HZ, PHZ and AHZ in water samples.

Key Words: Simultaneous determination, Kinetic spectrophotometric, Hydrazine, Phenylhydrazine, Acetylhydrazine, Partial least squares regression, Principal component regression.

INTRODUCTION

Hydrazine and its derivatives have been used in industry, agriculture and other fields including the manufacture of metal films, photographic chemical, explosive and as propellants and common precursors in the

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synthesis of some polymers, plasticizers, pesticides, antioxidants and pharmaceuticals[1,2]. On the other hand, owing to the toxic nature of hydrazine and some its derivatives[3], there is a growing need in both industries and laboratories for the development of highly sensitive methods for low levels determination of hydrazine and its derivatives.

Several methods have been reported for the determination of hydrazine and its derivatives individually such as titrimetry[4,5], spectrophotometry[6-8], electroanalytical techniques[9,10], fluorometry[11], chromatography[12,13] and chemiluminescence[14]. H-point standard addition method (HPSAM) was reported for simultaneous determination of binaries of hydrazine and semicarbzide[15], hydrazine and phenyl hydrazine (PHZ)[16], hydrazine and acetylhydrazine (AHZ)[17] and hydrazine and isoniazid[18]. To the best our knowledge, it has not been reported any chemometrics methods for simultaneous determination of hydrazine and its derivatives mixture.

The theory and application of principal component regression (PCR) and partial least squares (PLS) in spectrophotometry have been discussed by several workers[19-22]. The aim of this work was to evaluate the possibility of using PLS and PCR methods for simultaneous determination of hydrazine and its derivatives in water samples.

This paper describes two kinetic-spectrophotometric methods for the simultaneous determination of hydrazine, acetylhydrazine and phenyl hydrazine using PCR and PLS models. The methods are based on the difference observe in the rate of reduction of Cu(II) with hydrazine, acetyl hydrazine and phenyl hydrazine in the presence reagent of neocuproine (NC) and buffer of pH 6.0[23-29].

EXPERIMENTAL

All reagents were analytical reagent grade. Triply distilled water was used throughout the study. A stock solution of 0.01 M of neocuproine was prepared by dissolving 0.208 g of neocuproine (Merk) in 16 mL ethanol and diluting with distilled water in a 100 mL volumetric flask. A solution of 0.05 M of Cu(II) was prepared by dissolving 0.6040 g of $Cu(NO_3)_2 \cdot 3H_2O$ (Merk) in water and diluting with water to the mark in 50 mL volumetric flask. A buffer of pH 5 was prepared by using sodium acetate and hydrochloric acid at appropriate concentration. Stock solutions (1000 μg mL^{-1}) of hydrazine, acetyl hydrazine and phenyl hydrazine were prepared in 100 mL flasks by dissolving 0.4061 g hydrazinium sulfate (Merck), 0.1020 g acetylhydrazine (Merck) and 0.1337 g phenylhydrazinium choloride (Merck) in water and diluting with water to the mark.

A GBC UV-Visible Cintra 6 Spectrophotometer model, with 1 cm glass cells was used for recording the kinetic spectrophotometric data. A Metrohm 691 pH-meter furnished with a combined glass-saturated calomel electrode

was calibrated with at least two buffer solutions at pH 3 and 9. The data were treated in an AMD 2000 XP (256 Mb RAM) microcomputer using MATLAB software. PLS and PCR analysis were performed using PLS and PCR toolboxes in MATLAB program version 7.0.

Procedure: A volume of 7.5 mL of buffer solution (PH 5), 2.0 mL of stock Cu(II) solution and 5.0 mL stock solution of NC were added to a 25 mL volumetric flask and then diluting with water to the mark. The temperature was kept constant at 25 ºC by a thermostat for 10 min, 3.0 mL of solution was transferred into a glass cell of the spectrophotometer and the absorbance of this solution was zeroed before injecting the analyte(s). Then, an appropriate volume of hydrazine, acetyl hydrazine and phenyl hydrazine or mixture of them in their concentration ranges was injected to the cell by microsyringe and absorbance was recorded at 452 nm at the time intervals of 2.0 s.

RESULTS AND DISCUSSION

The Cu(II)- neocuproine (NC) system allows the spectrophotometric determination of a reducing agent, A_{red}, as follows[23-29]:

$$nCu^{2+} + 2nNC + A_{red} \longrightarrow n[Cu(NC)_2]^{+} + A_{ox}$$

Above reaction is complete with the formation of an equivalent amount of $[Cu(NC)_2]^{+}$ with respect to the *n*-electron reductant, A_{red}. The reduction of Cu(II) to Cu(I) in the presence of NC and subsequent complex formation between Cu(I) and NC (with λ_{max} = 452 nm) takes in the presence of suitable reducing agents such as hydrazine and its derivatives in few minutes. The reduction rate of Cu(II) with hydrazine, acetyl hydrazine and phenyl hydrazine is different. The difference provides the possibility of resolving their mixtures using PLS and PCR methods. Characteristics of calibration graphs of hydrazine, acetyl hydrazine and phenyl hydrazine are given in Table-1.

TABLE-1
CHARACTERISTIC OF CALIBRATION GRAPHS FOR THE DETERMINATION HYDRAZINE, ACETYL HYDRAZINE AND PHENYL HYDRAZINE

Analyte	Slope (mL μg^{-1})	Intercept	CC (n = 10)	LR ($\mu g\ mL^{-1}$)	DL ($\mu g\ mL^{-1}$)
Hydrazine	0.1563	0.0384	0.9992	0.10-1.0	0.01
Acetyl hydrazine	0.0063	0.1067	0.9991	0.50-100.0	0.10
Phenyl hydrazine	0.7422	0.0393	0.9999	0.10-6.0	0.02

CC = Correlation coefficient, LR = Linear range, DL = Detection limit

A series of experiments were conducted to establish the optimum analytical to achieve maximum sensitivity in the simultaneous determination of hydrazine, acetyl hydrazine and phenyl hydrazine. The experimental parameters, such as reagents concentration, temperature and pH of solutions were optimized. Optimization process gave similar results for both individual analytes and mixture of three analytes.

Effect of neocuproine concentration: Fig. 1 shows the effect of neocuproine concentration on the absorbance in the concentration range of 5×10^{-4} to 3×10^{-3} M. As it is seen, at high concentrations of neocuproine, the absorbance due to Cu(I)-neocuproine complex decreases. This might be due to the fact that high concentrations of neocuproine would result in a positive interference from Cu(II) that could have arisen from incomplete conversion of Cu(I) to Cu(I)-neocuproine complex *via* mixed ligand complex formation[23,24]. Thus, a concentration of 2×10^{-3} M neocuproine was chosen as the optimum neocuproine concentration.

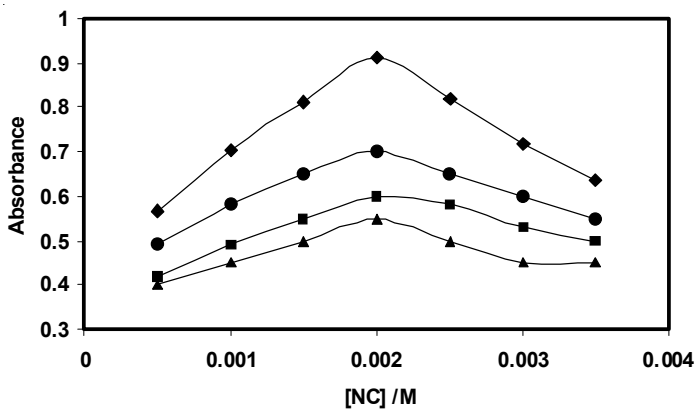

Fig. 1. Effect of concentration of neocuproine on the reaction of 0.30 μg mL^{-1} of hydrazine (■), 0.90 μg mL^{-1} of PHZ (▲), 4.5 μg mL^{-1} of AHZ (●) and mixture of them (◆), Conditions: 4×10^{-3} M Cu(II), pH 6.0, 25 °C

Effect of Cu(II) concentration: The effect of Cu(II) concentration was examined over the range of 1.5×10^{-3} to 5.5×10^{-3} M of Cu(II) (Fig. 2). The oxidizing power of Cu(II) in a solution containing neocuproine is dependent on the ease of formation of $[Cu(NC)_2]^+$. An excess of Cu(II) can exhibit an affinity for neocuproine[23,24]. Therefore, large excess of Cu(II) competes with Cu(I) for complex formation with neocuproine. A concentration of 4.0×10^{-3} M Cu(II) was chosen as the optimum Cu(II) concentration.

Effect of pH: The effect of pH over the ranges of 1.0 to 7.0 on the reaction rate and absorbance of hydrazine, acetyl hydrazine and phenyl hydrazine with Cu(II) in the presence of neocuproine was studied (Fig. 3).

The results showed that at pH 5, the reaction rate and absorbance for phenyl hydrazine was highly increased so that the reaction was completed within 30 s. But, as shown in Fig. 3, hydrazine at pH between 5 to 6 and acetyl hydrazine at pH 6 have maximum absorbance and also maximum increase in reaction rate. It was found that pH 6 was most suitable pH for the resolving their mixtures using PLS and PCR methods. Thus, pH 6.0 was chosen as optimization pH value.

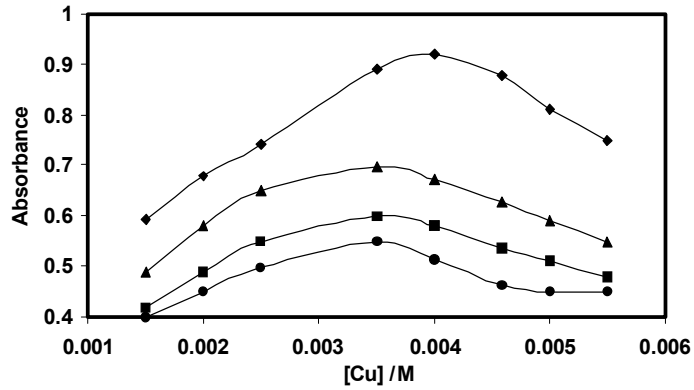

Fig. 2. Effect of concentration of Cu(II) on the reaction of 0.30 μg mL^{-1} of HZ (■), 0.90 μg mL^{-1} of PHZ (▲), 4.5 μg mL^{-1} of AHZ (●) and mixture of them (◆). Conditions: 2×10^{-3} M neocuproine, pH 6.0, 25 °C

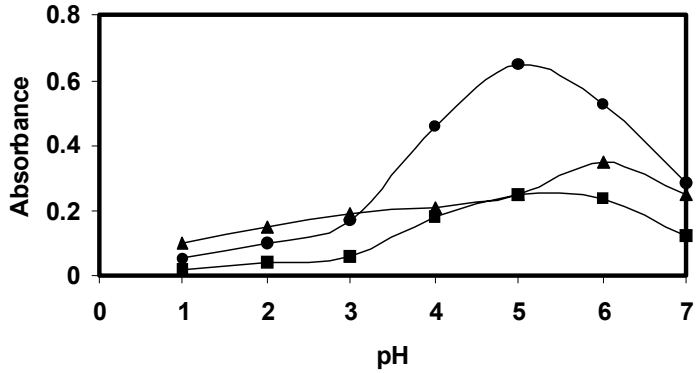

Fig. 3. Effect of pH on the reaction of 0.30 μg mL^{-1} of HZ (■), 0.90 μg mL^{-1} of PHZ (▲), 4.5 μg mL^{-1} of AHZ (●) Conditions: 2×10^{-3} M neocuproine, 4×10^{-3} M Cu(II), pH 6.0, 25 °C

Effect of surfactants: The effect of three kinds of surfactants (anionic, cationic and non-ionic) and their concentrations on the reaction rates of hydrazine, acetyl hydrazine and phenyl hydrazine with Cu(II) in

the presence of neocuproine was investigated. The results showed that each three kinds of surfactants of sodium dodecyle sulfate (SDS), Triton X-100 (TX-100) cause a few decrease on the reaction rate of hydrazine, acetyl hydrazine and phenyl hydrazine and cetyl trimethyl ammonium bromide (CTAB) increased rate of reaction of hydrazine and its derivatives. Therefore, any surfactant was not used for further studies in this work.

Effect of temperature: The effect of temperature on the reaction rate of hydrazine, acetyl hydrazine and phenyl hydrazine with Cu(II) in the presence of neocuproine was studied in the range of 20-70 °C. An increase in the temperature caused an increase in the reaction rates for each three analytes. However, for simplicity and better control of the temperature effects on the precision of determinations, 25 °C was chosen as an optimum temperature.

Absorbance-time behaviour: Under the optimized conditions, reactions of hydrazine, acetyl hydrazine and phenyl hydrazine with Cu(II)-neocuproine system showed different kinetic behaviours (Fig. 4). The reaction of phenyl hydrazine was faster than hydrazine and acetyl hydrazine and was almost completed in 1 min, while reactions both hydrazine and acetyl hydrazine were completed in almost 5 min. The reaction of thiosemicarbazide also was faster than hydrazine. These differences in the reaction rates allowed designing multivariate calibration methods as a technique for simultaneous determination of hydrazine, acetyl hydrazine and phenyl hydrazine. The linearity of the analytes was studied individually under the optimum conditions (Table-1).

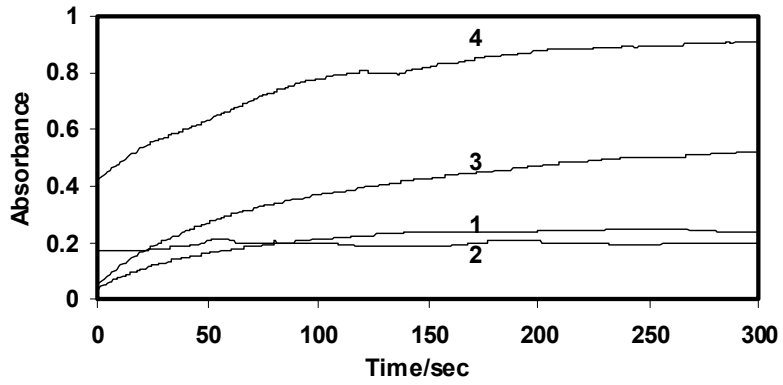

Fig. 4. Absorbance changes of Cu(II)/neocuproine complex *vs.* time in the reaction with: (1) 0.30 μg mL^{-1} of HZ, (2) 0.90 μg mL^{-1} of PHZ and (3) 4.5 μg mL^{-1} of AHZ and mixture of them (4). Conditions: 2.0×10^{-3} M neocuproine, 4.0×10^{-3} M Cu(II), pH 6.0, 25 °C

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 prediction. In this research, a synthetic set of 40 solutions containing different concentrations of hydrazine, phenyl hydrazine and acetyl hydrazine were constructed. The concentration ranges of 0.1-1.0, 0.1-6.0 and 0.5-100.0 μg mL^{-1} were used for hydrazine, phenyl hydrazine and acetyl hydrazine, respectively. The numbers of 30 solutions were selected as a calibration set (Table-2) and the other 10 were used as a prediction set (Table-3). Their composition was randomly chosen for obtaining more information from the calibration set. Changes in the absorbance of the solutions were recorded during a time period of 300 s.

TABLE-2
CALIBRATION SET FOR CONSTRUCTING PLS AND PCR MODELS IN DETERMINATION OF HYDRAZINE, PHENYL HYDRAZINE AND ACETYL HYDRAZINE

No. of sample	Concentration (μg mL^{-1})			No. of sample	Concentration (μg mL^{-1})		
	HZ	PHZ	AHZ		HZ	PHZ	AHZ
1	0.06	0.2	1.0	16	0.90	5.0	13.5
2	0.13	0.4	2.0	17	0.93	2.8	14.0
3	0.20	0.6	3.0	18	0.97	2.9	14.5
4	0.26	0.8	4.0	19	1.00	3.0	15.0
5	0.33	1.0	5.0	20	0.06	0.2	0.5
6	0.40	1.2	6.0	21	0.13	0.4	1.0
7	0.48	1.4	7.0	22	0.20	0.6	1.5
8	0.53	1.6	8.0	23	0.26	0.8	2.0
9	0.60	1.8	9.0	24	0.33	1.0	2.5
10	0.67	2.0	10.0	25	0.40	1.2	3.0
11	0.73	2.2	11.0	26	0.47	1.4	3.5
12	0.76	4.0	11.5	27	0.53	1.6	4.0
13	0.80	2.4	12.0	28	0.60	1.8	4.5
14	0.83	3.0	12.5	29	0.67	2.0	5.0
15	0.86	2.6	13.0	30	0.20	0.8	3.0

To select the number of factors in the PLS and PCR algorithm a cross-validation, leaving out one sample methods was employed[30]. 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):

$$PRESS = \sum^{m}_{i=1} (\hat{C}_i - C_i)^2$$

TABLE-3
PREDICTION SET FOR CONSTRUCTING PLS AND PCR MODELS IN DETERMINATION OF HYDRAZINE, PHENYL HYDRAZINE AND ACETYL HYDRAZINE

Sample	Actual (μg mL^{-1})			Predicated (μg mL^{-1})					
				HZ		PHZ		AHZ	
	HZ	PHZ	AHZ	PLS	PCR	PLS	PCR	PLS	PCR
1	0.10	0.30	1.50	0.11	0.11	0.31	0.32	1.52	1.6
2	0.17	0.50	2.50	0.15	0.18	0.49	0.51	2.45	2.4
3	0.23	0.70	3.50	0.24	0.22	0.69	0.68	3.46	3.6
4	0.30	0.90	4.50	0.29	0.28	0.92	0.88	4.45	4.3
5	0.37	1.10	5.50	0.39	0.36	1.09	1.30	5.51	5.2
6	0.43	1.30	6.50	0.45	0.44	1.28	1.40	6.55	6.6
7	0.50	1.50	7.50	0.49	0.51	1.48	1.60	7.45	7.5
8	0.57	1.70	8.50	0.58	0.56	1.70	1.60	8.48	8.4
9	0.64	1.90	9.50	0.65	0.63	1.85	1.80	9.42	9.6
10	0.70	2.10	10.5	0.67	0.71	2.15	2.00	10.4	10.6

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 of the calibration during cross validation. Fig. 4 shows a plot of PRESS against the number of factors for mixture of components. For finding the fewest number of factors, the F-statistic was used to carry out the significant determination[30]. The optimum number of factors for three components were obtained 4 and 5 for PLS and PCR, respectively.

Statistical parameters: 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[31]:

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

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

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

The squares of correlation coefficient (R^2), which is an indication of the quality fit of all the data to a straight line is presented by:

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

where C' represents the mean of the actual concentration in the prediction set[32].

Table-4 shows values of RSE, 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.

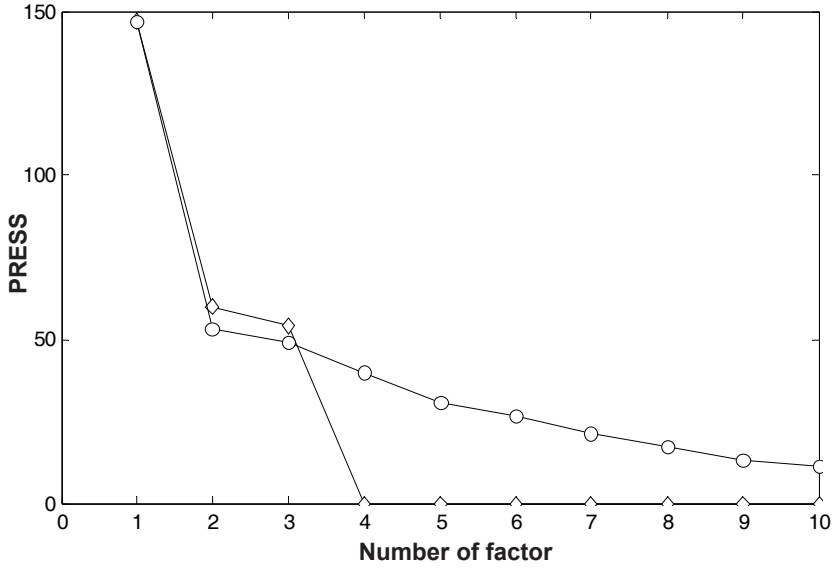

Fig. 5. Plot of PRESS against the number of factors for mixture of hydrazine, phenyl hydrazine and acetyl hydrazine for PLS (O) and PCR (◇) methods

TABLE-4
STATISTICAL PARAMETERS CALCULATED FOR THE PREDICTION SET USING PLS AND PCR METHODS

Component	RSE (%)		RMSEP		R^2	
	PLS	PCR	PLS	PCR	PLS	PCR
Hydrazine	3.69	2.56	0.016	0.011	0.9964	0.9918
Phenyl hydrazine	1.93	3.18	0.026	0.095	0.9938	0.9924
Acetyl hydrazine	0.81	2.13	0.054	0.141	0.9889	0.9956

Application: To evaluate the analytical applicability of proposed methods (PLS and PCR), known amounts of hydrazine, phenyl hydrazine and thiosemicarbazide were spiked into some water samples. The proposed methods were applied to determine analytes simultaneously and satisfactory results were obtained. The results are given in Table-5.

Conclusion

In this work, it is shown that PLS and PCR methods can be well adopted for simultaneous determination of hydrazine and its deivatives. The PLS and PCR methods based on kinetic-spectrophotometric data were developed for the simultaneous determination of hydrazine, phenyl hydrazine and acetyl hydrazine in synthetic ternary mixture. The proposed methods

TABLE-5
SIMULTANEOUS DETERMINATION OF HYDRAZINE, PHENYL HYDRAZINE AND ACETYL HYDRAZINE IN DIFFERENT WATER SAMPLES (n = 4)

Sample	Amount added (μg mL^{-1})			Predicated (μg mL^{-1})					
				HZ		PHZ		AHZ	
	HZ	PHZ	AHZ	PCR	PLS	PCR	PLS	PCR	PLS
Spring water	0.7	2.0	10	0.68 (±0.21)	0.68 (±1.10)	1.90 (±0.45)	1.70 (±0.64)	9.90 (±0.55)	9.10 (±0.72)
River water	0.7	2.0	10	0.71 (±0.50)	0.65 (±0.48)	1.70 (±0.64)	1.50 (±0.87)	9.50 (±1.10)	9.20 (±0.82)
Tap water	0.7	2.0	10	0.68 (±0.45)	0.67 (±0.67)	1.80 (±0.89)	1.60 (±0.27)	9.70 (±0.56)	9.50 (±0.37)
Well water	0.7	2.0	10	0.69 (±0.71)	0.64 (±0.93)	1.80 (±0.25)	1.90 (±1.10)	9.60 (±0.78)	9.40 (±0.52)

as new, inexpensive and sensitive methods offer good accuracy and precision that can be applied for a wide range of hydrazine, phenyl hydrazine and acetyl hydrazine concentrations. Both methods are cheaper than chromatographic separation methods, furthermore, in these methods, we do not need to use complex pretreatment or toxic organic solvents. In other words they belong to green chemistry.

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