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Application of Differential Kinetic Method Using ANN with a New Synthetic Reagent for Simultaneous Spectrophotometric Determination of Mercury and Palladium

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Abstract

A new selective reagent was used for simultaneous determination of mercury and palladium in real samples with their different kinetic spectrophotometric properties. The method is based on the difference in the rate of the oxidation reaction of the recently synthesized reagent, nitro benzoyl diphenylmethylen phosphorane (N-BDMP), with Hg^{2+} and Pd^{2+}. The kinetic profiles were monitored and recorded at maximum wavelength of reagent, and the data obtained from the experiments were processed by a chemometric approach (principal component analysis-artificial neural network models (PCFFNNs)). Performances of the proposed method were tested with regard to relative standard error (RSE), using synthetic solutions. Under the working conditions, the proposed method was successfully applied to the simultaneous determination of Hg^{2+} and Pd^{2+} in water, waste water and urine samples. The results showed that mercury and palladium could be determined simultaneously in the range of 4.00×10^{-7} to 1.00×10^{-4} mol L^{-1}(0.08 to 20.06 µg mL^{-1}) and 1.00×10^{-6} to 1.00×10^{-4} mol L^{-1} (0.11 to 10.64µg mL^{-1}), respectively. Investigation of the effect of other metals on the system shows that this reagent is very selective for these two analytes and other metal ions do not show any interference.

Keywords: *Simultaneous kinetic determination, Artificial neural networks, Hg^{2+} ion, Pd^{2+} ion, Nitro benzoyl diphenylmethylen phosphorane..*

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Introduction

One of the basic requirements for assessing a possible exposure to metals at the workplace or in the environment is the availability of reliable analytical procedures which allow the determination of low concentrations of heavy metals [1]. Mercury is ubiquitous in nature, and the consequences of mercury exposure on human health were recognized from prehistory to the present. The severity of mercury's toxic effects depends on the form and concentration of mercury and the route of exposure. Although its potential for toxicity in highly contaminated areas is well documented, researches have shown that mercury may also be a threat to the health of people and wildlife in many environments that are not obviously polluted. Thus there is no safe level of mercury for humans. The main toxic effects of mercury are known to negatively affect the neurological, renal, cardiovascular and immunological systems. Unlike most other pollutants, mercury is highly mobile, non-biodegradable, and bio-accumulative; as a result, it must be closely monitored to ensure its harmful effects on local populations are minimized [2]. Thus, measurement of mercury in environmental samples, and in particular wastewater, is of great importance as a major tool to protect the environment from mercury released through emissions from manufacturing, use, or disposal activities [3].

Palladium is a steel-white, ductile metallic element resembling and occurring with the nickel. It can form organometallic compounds, only few of which have found industrial uses. Palladium metal is stable in air and resistant to attack by most reagents except aqua regia and nitric acid. Palladiumand its alloys are used as catalysts in the (petro) chemical and, above all, the automotive industries.

Palladium(II) chloride ($PdCl_2$) was poorly absorbed from the digestive tract (<0.5% of the initial oral dose in adult rats or about 5% in suckling rats after 3–4 days). Transfer of small amounts of palladium to offspring via placenta and milk was seen with single intravenous doses of palladium (II) chloride in rats. Information on the elimination and excretion of palladium is scarce and refers mostly to palladium (II) chloride and sodium tetrachloropalladate (II), which were found to be eliminated in faces and urine [4].

The affinity of palladium compounds for amino acids (e.g., L- cysteine, L- cystine, L- methionine), proteins, nucleic acids and other macromolecules (e.g., vitamin B6) was confirmed in many studies [4]. It was indicated that in vitro experiments with palladium (II) chloride and calf thymus DNA, palladium (II) interacts with both the phosphate groups and bases of DNA. Several palladium–organic complexes were observed to form bonds with calf thymus DNA or Escherichia coli plasmid DNA. Most of the complexes appear to interact via non-covalent binding, mainly via hydrogen bonding; in a few cases, however, indications for covalent binding were seen.

Signs of acute toxicity of several palladium salts in rats or rabbits included death, decrease in feed and water uptake, emaciation, cases of ataxia and tiptoe gait, clonic and tonic convulsions, cardiovascular effects, peritonitis or biochemical changes (e.g., changes in activity of hepatic enzymes, proteinuria or ketonuria) [4]. Differences in kinetic behavior have been used extensively for the determination of components in mixtures. Many differential kinetic methods have been proposed for the analysis of mixtures of closely related species without prior separation. The kinetic determination of analytes is usually based on the difference in their reaction rate constants. Several methods based on the kinetic spectrophotometric method have been reported for determination of binary and ternary mixtures [5-7]

The simultaneous determination of several analytes in a given sample is now an interesting area in Chemometrics [8, 9]. In recent years, artificial neural network (ANN) has attracted increasing interest as a powerful non-parametric non-linear modeling technique [10-12].

Mercury and palladium are metals that appear together in many real samples, such as waste water, therefore determination of low levels of mercury and palladium is very important in environmental and biological samples. Few reports have been published on the simultaneous determination of these ions in different samples [1, 13 -16]

In this study, we use a new synthetic selective reagent for simultaneous kinetic spectrophotometric determination of mercury and palladium in the presence of other metal ions. Determination is based on the oxidation of bidentate phosphorus ylide, nitro benzoyl methylene diphenyl methyl phosphorane (N-BDMP), by Hg^{2+} and Pd^{2+} ions with the aid of chemometric approach, feed forward neural networks (FFNNs).

Experimental

Reagent and standard solutions

All solutions were prepared with analytical grade reagents. Stock solutions of Hg^{2+} and Pd^{2+}ions (1.00×10^{-3}mol L^{-1}) were prepared by dissolving $HgCl_2$ and $PdCl_2$ (Fluka,Buchs, Switzerland) in doubly distilled water. The solution of N-BDMP (4.50×10^{-3}mol L^{-1}) was prepared by dissolving appropriative amount of it in extra pure ethanol (Merck Company, Darmstadt, Germany).

Preparation of Nitro Benzoyl Diphenylmethylen Phosphorane (N-BDMP)

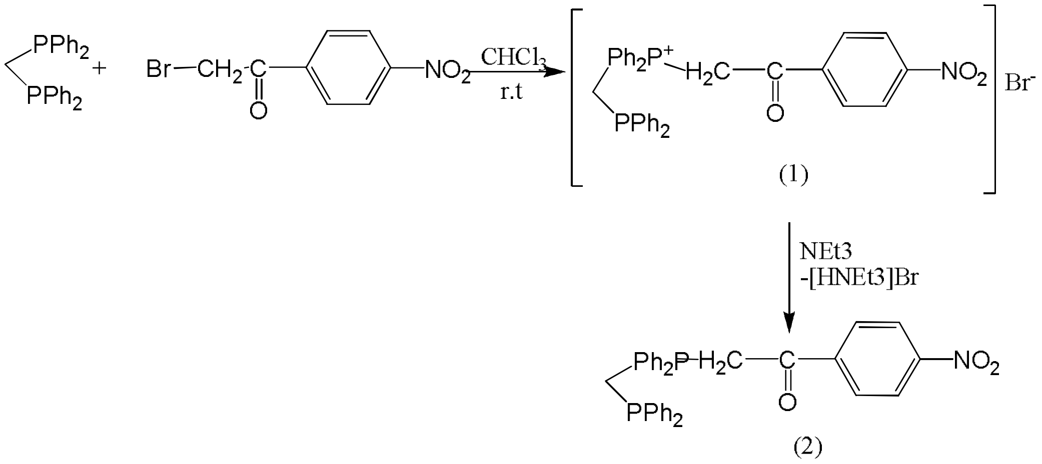
N-BDMP was synthesized based on scheme 1 according to Ref. [17]

Synthesis of $[Ph_2PCH_2PPh_2CH_2C(O)C_6H_4NO_2]Br$ *(1)*

A solution of bis (diphenylphosphino) methane (dppm) (0.192 g, 0.50mmol) and 4-nitrophenacyl bromide (0.152 g, 0.50 mmol) in chloroform (17 ml) was stirred at room temperature for 2 h. The yellow solution was concentrated under reduced pressure to 5 ml, and diethyl ether (20 ml) was added. The orange solid formed was filtered, washed with diethyl ether (20 ml) and dried under reduced pressure. Yield: 0.276 g, 88%. M.p. 210–212 °C. Anal. Calc. for $C_{33}H_{28}BrNO_3P_2$: C, 63.07; H, 4.49; N, 2.23. Found: C, 62.98; H, 4.40; N, 2.39%.IR (cm^{-1}): 1684 (νC=O).^{1}HNMR ($CDCl_3$): δ 6.10 (PCH_2CO $^2J_{P\text{-}H}$=12.81). ^{31}P NMR ($CDCl_3$): δ-29.52 (d, PPh_2, $^2J_{P\text{–}P}$=64.57), 20.70 (d PCH, $^2J_{P\text{–}P}$ = 64.54).

Synthesis of $[Ph_2PCH_2PPh_2{=}C(H)C(O)C_6H_4NO_2]$ *(2)*

The resulting phosphonium salts (1) (0.314 g, 0.50 mmol) were treated with triethyl amine (0.5 ml) in toluene (15 ml). The triethyl amine hydrobromide was filtered off. Concentration of the toluene layer to 5 ml and subsequent addition of petroleum ether (25 ml) results in the precipitation of reagent as yellow solids. Yield:0.222 g, 81%. M.p. 144–147 °C. Anal. Calc. for $C_{33}H_{27}NO_3P_2$: C, 72.39; H, 4.97; N, 2.56. Found: C, 72.57; H, 5.11; N, 2.78%.IR (cm^{-1}): 1524 (νC=O). ^{1}HNMR ($CDCl_3$): δ 4.34 (PCH $^2J_{P\text{-}H}$=22.94). ^{31}P NMR ($CDCl_3$): δ -30.31 (d, PPh_2, $^2J_{P\text{–}P}$=62.47), 11.52 (d PCH, $^2J_{P\text{–}P}$ = 65.63)[17].



Scheme 1. Preparation of Nitro Benzoil Diphenylmethylen Phosphorane.

Apparatus and materials

The absorbance spectra were recorded on an Agilent 8453 UV–Vis spectrometer using 1-cm quartz cells and a slit of 0.5 cm. A short program was written in MATLAB 7.1 for performing principal component analysis of the data and the networks calculations were performed using nnet–Toolbox for MATLAB 7.1.

Procedure

A 1.0 ml of N-BDMP solution was transferred into a 5.0mL volumetric flask containing an appropriate amount of Hg^{2+} or Pd^{2+}ions or their mixture. The solution was mixed and diluted to the mark with 2 mL ethanol and doubly distillated water. Then 2.0mL of this solution was transferred into a cleaned cell in sample holder and kinetic measurements were begun in 25 °C at 365 nm. The kinetic measurementcontinued for a period of 15 min with the intervals of 1 min by measuring the decrease in absorbance at 365 nm. Calibration and prediction sets contained 15 and 6 samples, respectively. Table 1 shows the two sample sets.

Table 1. Concentration data for the different mixtures used in the calibration set and prediction set for the simultaneous determination of Hg^{2+} and Pd^{2+} ions.

Sample No.	Calibration set/mol L^{-1}		Prediction set/mol L^{-1}	
	Hg^{2+}	Pd^{2+}	Hg^{2+}	Pd^{2+}
1	2.00×10^{-6}	1.80×10^{-5}	1.50×10^{-5}	1.80×10^{-5}
2	2.00×10^{-6}	1.00×10^{-5}	2.00×10^{-6}	3.00×10^{-5}
3	1.00×10^{-5}	1.80×10^{-5}	9.00×10^{-5}	1.80×10^{-5}
4	1.00×10^{-5}	3.60×10^{-5}	2.00×10^{-5}	5.00×10^{-5}
5	8.00×10^{-6}	1.80×10^{-5}	3.00×10^{-6}	4.00×10^{-6}
6	3.00×10^{-5}	1.00×10^{-5}	1.00×10^{-4}	1.00×10^{-5}
7	4.00×10^{-5}	1.80×10^{-5}		
8	2.00×10^{-5}	6.00×10^{-6}		
9	5.00×10^{-6}	7.20×10^{-5}		
10	4.00×10^{-6}	3.00×10^{-5}		
11	2.00×10^{-6}	3.00×10^{-5}		
12	3.00×10^{-5}	3.60×10^{-5}		
13	8.00×10^{-6}	1.00×10^{-5}		
14	2.00×10^{-4}	5.00×10^{-5}		
15	1.00×10^{-4}	8.00×10^{-6}		

Preparation of waste water and urine samples

The real samples in this study were collected from Analytical Laboratory of Bu-Ali Sina University (laboratory waste waters). The impurities of collected water and urine sample were first removed by filter paper.

Results and discussion

Kinetic study of the system

Figure 1 shows the spectra of the N-BDMP in the absence and presence of Hg^{2+}. As Figure 1 shows, the absorbance of the N-BDMP solution at 365 nm decreased with time in the presence of Hg^{2+}.

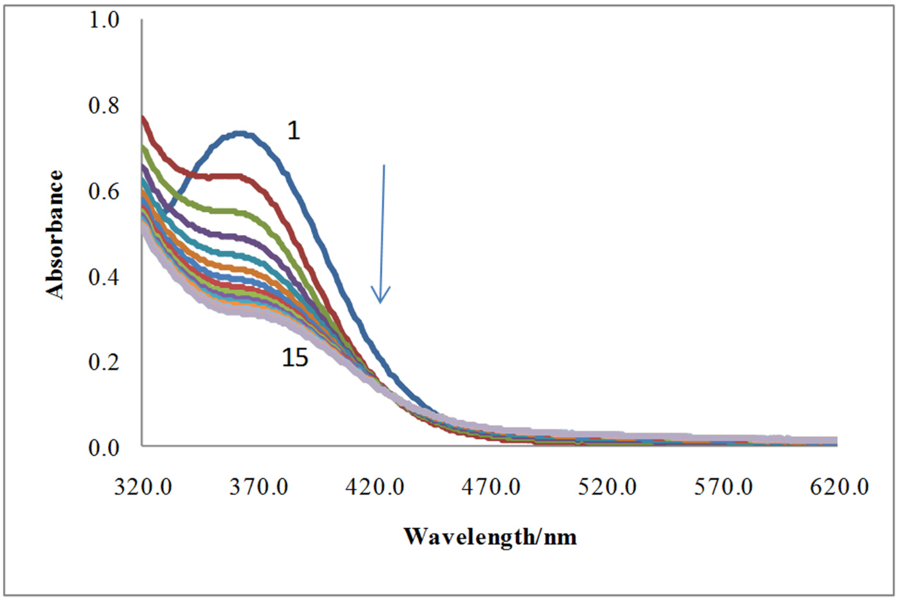


Figure 1. Theabsorption spectra for (1) 1.00 × 10^{-4}mol L^{-1}N-BDMP,(2-15)1.00× 10^{-4} mol L^{-1}N-BDMP in the presence 1.0 ×10^{-4} mol L^{-1} Hg^{2+}, time interval 1 min.

Catalytic effect of Hg^{2+} on the oxidation of benzoyl methylene diphenyl phosphino Methyl phosphorane (BDEP) has been reported previously [18]. The scheme 2 shows the reaction between Hg^{2+} ion and BDEP.

$$2Ph_2PCH_2PPh_2{=}CHCOPh \xrightarrow[\substack{HgX_2\\ [O]}]{H_2O} 2O{=}PPh_2CH_2P^+Ph_2CH_2COPhX^- + Hg$$

Scheme 2. The reaction between Hg^{2+} ion and BDEP.

It is likely that Hg (0) is produced following the oxidation of phosphine by the trace amount of water, leading to the formation of phosphonium salt as shown below.

By Comparison of the N-BDMPand BDEP structures and considering the spectrophotometric results (absorbance reduction at 365 nm) the pathway in Scheme 2 for the reaction of N-BDMP with Hg^{2+}can be proposed.

We also studied the behavior of N-BDMP in the presence of Pt (II), Pd(II) and Rh(I) too. It was observed that, similar to Hg^{2+}, Pd^{2+} reacts with N-BDMP and causes a decrease in the absorbance of the solution at 365 nm. The reaction of N-BDMP with Pd^{2+} was slower than its reaction with Hg^{2+}. It should be noted that in the previous studies, reduction of Pt (II), Pd (II) [19] and Rh (I) [20] with BDEP in aqueous media was not reported. Absorbance changes with time of the N-BDMP in the presence of 1.00 × 10^{-4} mol $L^{-1}$$Hg^{2+}$ and Pd^{2+}were recorded at 365 nm and are shown in Figure 2. According to this Figure, two analytes in the same concentration have different kinetic profiles and the simultaneous determination of these ions was done using this difference.

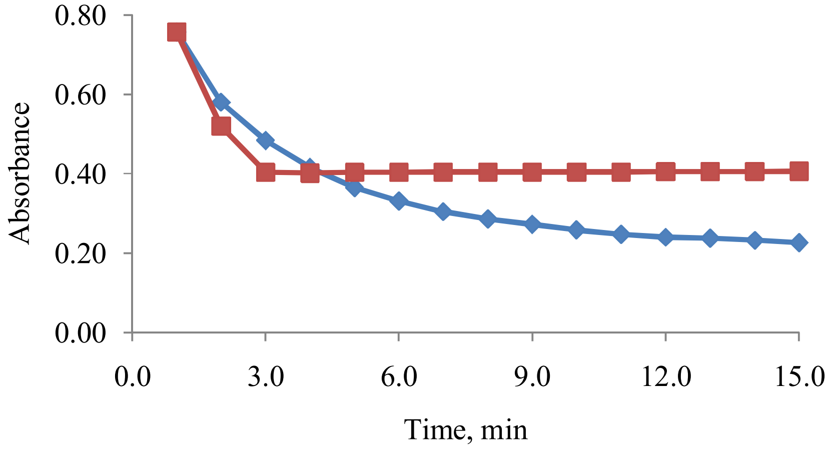


Figure 2. Kinetic proiles for 5.00 × 10^{-5} mol L^{-1}N-BDMP at 365 nm in the presence of 1.00 × 10^{-4} mol $L^{-1}Hg^{2+}$(a) and 1.00 × 10^{-4} mol $L^{-1}Pd^{2+}$ (b), time interval, 1min.

Influence of experimental factors

Effect of pH

The influence of pH on the reaction was studied in acidic, neutral and alkaline media. It is well known that using buffer solution for pH adjustment causes an increase in the ionic strength of the solution. We found that N-BDMP precipitated in the solutions with high ionic strengths. Therefore, low concentration of buffer solutions was used to avoid precipitation of N-BDMP. In the strong acidic and alkaline media the sensitivity of the method decreased strongly as in low pH values, N-BDMP was destroyed and in high pH values Hg^{2+} and Pd^{2+}were eliminated from the reaction media by the precipitation caused by hydroxide form. Investigation of neutral pHs effect showed that the sensitivity of the system does not improve therefore we do not use any buffers solution.

Effect of N-BDMP concentration

The effect of N-BDMP concentration over the range 1.0×10^{-5} to 1.5×10^{-4}mol L^{-1} on the determination of 3.0×10^{-5} mol l^{-1} of Hg^{2+} and Pd^{2+} ions was studied to obtain the maximum sensitivity. As Fig. 3 shows, it is apparent that with the addition of concentrations of N-BDMP up to 1.0×10^{-4} mol L^{-1} the difference between reagent absorbance in the absence and in the presence of metal ions (ΔA) increased and then remained constant at higher concentration. Therefore 1.0×10^{-4} mol l^{-1}N-BDMP was chosen as the optimal value.

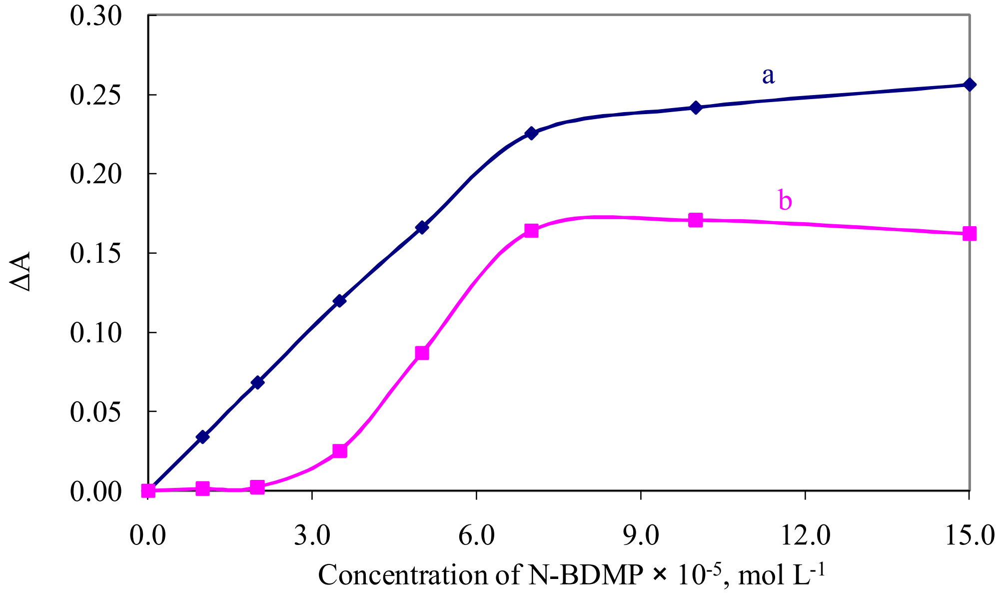


Figure 3. Effect of N-BDM concentration on □A signals of 3.0 × 10^{-5}mol L^{-1}Hg^{2+} (a) and 3.0 × 10^{-5}mol L^{-1}Pd^{2+} (b).

Optimizing the network variables in PCFFNNs

ANNs are mathematical or computational models based on biological neural networks. They consist of an interconnected group of artificial neurons and process information using a connectionist approach to computation. For the optimization of a neural network, a trial and error method has to be used to find the best neural network architecture. One layer of nodes in the output layer is a common topological suggestion, when an ANN is used as a model of calibration. In this study some factors such as number of principal components, number of nodes (neurons) in the hidden layer, learning function and the number of epochs were optimized. The overall predictive capacity of the model was compared in terms of relative standard error (RSE), defined as

$$\text{RSE (\%)} = 100 \times (\sqrt{\frac{\sum_{i=1}^{n}(\hat{C}_i - C_i)^2}{\sum_{i=1}^{n}(C_i)^2}})^{0.5} \qquad (1)$$

Where $\hat{C}_i$ and C_i are the desired output and the actual output sets, respectively, and n is the number of prediction set samples. Reducing the data volume before using ANNs for multivariate calibration was suggested as a preprocessing step in many of the previous studies [21]. If the number of weights exceeds the number of samples for the training of ANN to some extent, “over fitting” may be caused [22]. Also, in the case of a high number of input variables, meaningful variables could become hidden [23], the probability of chance correlation increases [24], and may prevent ANN from finding optimized models [25]. Therefore, PCA input selection is necessary in order to improve the predicted results of different ANN.

In this work, kinetic data were employed in ANN to predict the concentrations of the corresponding analytes. The kinetic data, before building the ANNs models, were subjected to the principal component analysis and decomposed to PC scores. The numbers of input nodes were selected as optimal numbers of PC scores. The PCFFNN including one to ten PC scores was trained. The lowest RSE% values were obtained with three input factors for Hg^{2+} and Pd^{2+} ions. In order to determine the optimal number of hidden layer networks, neural networks with different numbers of hidden nodes were trained. The number of hidden nodes varied from one to ten to train the networks. According to RSE% values versus the number of hidden layer nodes, the best numbers of hidden layer nodes were three for $Hg^{2+}$and four for Pd^{2+} ions. To get the best network architecture, different transfer functions in hidden and output layer were also tested. The best transfer functions as well as some other parameters such as number of epochs, learning rate and momentum are summarized in Table 2. In order to predict metals concentrations in prediction set, the program was performed in optimum conditions and finally the RSE% values were calculated and applied for comparing the applicability of the methods. Table 3 shows the prediction results obtained with a model having optimized parameters.

Table 2. Optimized parameters used for construction of PC-FFN network for Hg^{2+} and Pd^{2+} determination.

Parameter	Hg^{2+} ion	Pd^{2+} ion
Number of PCs	3	3
Input nodes	3	3
Hidden nodes	3	4
Output nodes	1	1
Learning rate	0.1	0.1
Number of iteration(epoch)	54	25
Hidden layer transfer function	Logsig	Tansig
Output layer transfer function	Purelin	Purelin

Table 3. Prediction results obtained with PC-FFNN for Hg^{2+} and Pd^{2+} ions.

Sample No.	Added /mol L^{-1}		Found /mol L^{-1}	
	Hg^{2+} ion	Pd^{2+} ion	Hg^{2+} ion	Pd^{2+} ion
1	1.50×10^{-5}	1.80×10^{-5}	1.48×10^{-5}	1.76×10^{-5}
2	2.00×10^{-6}	3.00×10^{-5}	2.06×10^{-6}	2.53×10^{-5}
3	9.0×10^{-6}	1.80×10^{-5}	8.90×10^{-6}	1.73×10^{-5}
4	2.00×10^{-5}	5.00×10^{-6}	1.97×10^{-5}	4.96×10^{-6}
5	3.00×10^{-6}	4.00×10^{-6}	3.02×10^{-6}	3.65×10^{-6}
6	1.00×10^{-4}	1.00×10^{-5}	1.04×10^{-4}	1.03×10^{-5}
RSE %			3.88	2.69

Validity of the method

Linearity and sensitivity

A set of sample solutions with different concentrations of metal ions was prepared and measurements were carried out under the optimum conditions.

The calibration curves of two analytes were linear in the ranges 4.00×10^{-7} mol L^{-1} to 1.00×10^{-4} mol L^{-1} and 1.00×10^{-6} mol L^{-1} to 1.00×10^{-4} mol L^{-1} for Hg^{2+} and Pd^{2+}ions, respectively. The triplicate signals demonstrated good reproducibility. Equations for calibration graphs were obtained versus analyte concentrations as: $\Delta A = 7034.3C + 0.0021$with a correlation coefficient 0.996 for Hg^{2+} and $\Delta A= 6558.3C - 0.0055$ for $Pd^{2+}$with a correlation coefficient 0.994 where ΔA is the difference between reagent absorbance before and after addition of metal ions(after 15 min) and C is the concentration of analyte in mol L^{-1}. The limit of detection (LOD) of the method, defined as the concentration that produced a signal-to-noise ratio of 3, was2.71×10^{-7} mol L^{-1} (0.054 μg mL^{-1}) and 2.94×10^{-7} mol L^{-1} (0.031 μg mL^{-1}) for $Hg^{2+}$and Pd^{2+} ions, respectively.

Study of interferences

A systematic study was carried out on the effects of foreign species on the determination of 2.00×10^{-7} mol L^{-1} Hg^{2+} ion and 1.00×10^{-6} mol L^{-1} Pd. The tolerance limit of a compound was taken as the maximum amount of species causing an error not greater than ±5%. It was found that 1000-fold excess of K^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, Ba^{2+}, Ni^{2+}, Al^{3+},NO^{3-}, CO^{32-}, HCO^{3-}, Cl^{-}, F^{-}, $S2^{-}$, I^{-}; 500- fold excess ofZn^{2+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, 300-fold excess of $Fe^{3+}$and 200-fold excess of Ag^{+} and Pt^{2+} did not interfere with the determination of metals.

According to these results many of metal ions do not show any interference effect on the determination of the two analytes.

Therefore the reagent is very selective for the determination of Hg^{2+} and Pd^{2+} ions in the presence of other metal ions.

Applications

In order to evaluate the analytical applicability of the proposed method, the method was applied to the determination of Hg^{2+} and Pd^{2+} ions in tap water. Known amount of these metal ions were added to the samples and their concentrations were estimated with the proposed method. Simultaneous determination of ions in the home waste water and urine samples was also performed. The samples were found to be free from Hg^{2+} and Pd^{2+} ions. Therefore different amounts of Hg^{2+} and Pd^{2+} were added to the sample and analyzed by the proposed method. The results for determination of the two species in real samples are given in Table 4. Satisfactory recoveries of the experimental results were found for Hg^{2+} in the range of 96.0 –104.0% and in the range of 95.6–102.0% for Pd^{2+}. The reproducibility of the method was demonstrated by the mean relative standard deviation (R.S.D.). The results obtained indicate that the R.S.D. values for Hg^{2+} and Pd^{2+} ions in real samples were between 1.24 – 2.52 % and 1.27 – 3.06 %, respectively.

Table 4. The application of the proposed method for simultaneous determination of Hg^{2+} and Pd^{2+} ions in real samples.

Sample	Spiked (mol L^{-1})		Found (mol L^{-1})		Recovery (%)		RSD (%)	
	Hg^{2+}	Pd^{2+}	Hg^{2+}	Pd^{2+}	Hg^{2+}	Pd^{2+}	Hg^{2+}	Pd^{2+}
Tap water	-	-	ND[a]	ND	-	-		
	2.00×10^{-5}	1.00×10^{-5}	1.96×10^{-5}	0.98×10^{-5}	98.0	99.8		
	3.00×10^{-5}	2.00×10^{-6}	2.89×10^{-6}	2.04×10^{-6}	96.4	102.0		
					97.2	100.9	1.24	2.03
Waste water	-	-	ND[a]	ND[a]	-	-		
	3.00×10^{-6}	3.00×10^{-5}	2.92×10^{-6}	2.97×10^{-5}	97.3	99.0		
	4.00×10^{-5}	8.00×10^{-6}	3.94×10^{-5}	7.89×10^{-6}	98.5	98.6		
					97.9	98.8	1.86	1.27
Laboratory waste water	-	-	1.00×10^{-5}	6.00×10^{-6}	-	-		
	1.00×10^{-5}	3.00×10^{-5}	1.96×10^{-5}	3.47×10^{-5}	96.0	95.6	2.51	3.06
Urine sample	-	-	ND	ND	-	-		
	4.00×10^{-6}	6.0×10^{-5}	3.86×10^{-6}	5.86×10^{-5}	96.5	97.6		
	1.00×10^{-5}	2.50×10^{-5}	1.04×10^{-5}	2.43×10^{-5}	104.0	97.2		
					101.2	97.4	1.97	2.42

[a] ND: not detected

Conclusions

Most spectrophotometric methods for the determination of mercury and palladium are based on the formation of complexes between these metal ions with chromogenic reagents, however, separation of mercury and palladium from each other is required in advance because the absorption maxima for mercury- and palladium-complexes are very close to each other for most chromogenic reagents [16], but in this case we use a new synthetic reagent using a chemometrics method for simultaneous determination of the two analytes. New synthetic reagent shows an interaction with Hg2+ and Pd2+ that allows us to determine these metal ions without interference from other metals. Moreover the calculated results proved that the proposed neural networks approach is suitable for the simultaneous determination of Hg2+ and Pd2+ in complex mixtures such as urine and waste water samples.

As shown in this work, the use of kinetic data as inputs to ANNs provides an effective calibration method for the kinetic determination of Hg2+ and Pd2+ mixtures by using a new synthetic reagent and spectrophotometric detection. A comparison between the proposed method and the previously reported methods [14-16] for simultaneous determination of Hg2+ and Pd2+ ions (Table 5) indicates that the result obtained from proposed method is in a good agreement with the other methods.

Table 5. Analytical methods for simultaneous determination of Hg^{2+} and Pd^{2+} ions

Analytical method	Linear range (μg mL^{-1})		Ref.
	Hg^{2+}	Pd^{2+}	
Derivative spectrophotometric determination	0.40 – 1.40	0.08 - 0.18	15
Spectrophotometric determination	0.025 – 1.60	0.05 – 0.50	16
Cathodic stripping voltammetry	0.04 – 1.40	0.025 – 1.20	14

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