Utility of non-steroidal anti-inflammatory for a novel green nano determination of platinum in environmental samples using a cloud point extraction combined with spectrophotometry.

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Abstract

A new ternary surfactant proposal is studied as an extraction strategy for nano amount determination of platinum using tenoxicam (I) or piroxicam (II) as a selective chromogenic reagent in presence of PONPE 5.0 as nonionic surfactant at pH 3.5 has been developed. The analyte was investigated in the enriched solution by spectrophotometry. After examination and optimization of the complexation and extraction conditions, an enrichment factor superior to 500-fold was achieved with improved sensitivity of 342 and 427 using I and II, respectively, times more than the conventional extraction system using only a nonionic surfactant. In the acetonitrile medium, the molar absorptivity of the complex was 4.89×10^5 and 4.45×10^5 L mol^{-1} cm^{-1} at 474 and 482 nm using I and II, respectively. Beer's law is obeyed in the concentration range of 5.0–300 ng mL^{-1}, whereas the optimum range was 15 –275 ng mL^{-1} using Ringbom method. The relative standard deviation (RSD) for 150 ng mL^{-1} Pt^{4+} was 1.67 and 1.32%, respectively. In the original samples, The attained detection and quantification limits amounted to 1.55 and 4.85 using I and 1.42 and 4.50 ng mL^{-1} using II. The proposed procedure was applied successfully for Pt^{4+} determination content in environmental samples such as geological, food and waters samples with excellent results.

Keywords: Platinum determination, Spectrophotometry, Non-steroidal anti-inflammatory, Environmental analysis

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Introduction

Platinum is mainly used as a catalyst in automobile exhaust catalytic converters, in a wide variety of processes such as petroleum reforming and nitric acid production. Platinum also used in electronic industry as a material for electrodes, contacts and resistance wires and in glass and chemical industries as cladding on account of anticorrosion properties. Another application field of platinum is the manufacture of jewels [1]. Some platinum compounds are used as anti-cancer drugs.

Platinum soluble compounds are very toxic, and industrial exposure is responsible for the syndrome called platinosis. The low levels from the abrasion of the catalytic surface can penetrate deeply into human lungs and are toxicological relevant. Moreover, they are able to prepare various organometallic compounds. In these forms they can be solubilised and enter waters, soils, sediments, and plants, and in consequence, they can enter food chain [2].

Therefore, ultra-sensitive and selective analytical procedures are desirable, since low levels of the metal in the real samples are below the limit of detection of most analytical tolls. Various procedures have been investigated separation and preconcentration of platinum from different matrices, e.g., liquid–liquid extraction [3], co-precipitation with tellurium [4], solid phase extraction [5–7] and cloud point extraction [8–10].

Cloud point extraction (CPE) is one of the most simple and versatile methods for preconcentration and extraction of different metal ions [11] considerable attention was attracted due to complies with the “Green Chemistry” principles [12], as the amount of organic solvent is much less than that of traditional liquid extraction. In addition, it is highly efficient, cheap, fast, simple, and of lower toxicity than those using organic solvents. CPE for metal determination was firstly applied and reported by Watanabe and Tanaka [13]. Since it has been used for preconcentration and separation of many metal ions in different matrices [11]. The mechanism of separation is depended on the clouding phenomena of the surfactant. A micellar solution of a non-ionic surfactant was heated and the surfactant will change from water-soluble to oil-soluble. Above a critical temperature, named the cloud point, it will give completely water insoluble and so, the surfactant molecules will separate out from the aqueous phase. The clear solution gives turbid and phase separation occurs and the homogenous surfactant-rich phase contains much of the surfactant at the cloud point, while the other phase, named aqueous phase, contains mostly water and surfactant monomers at a concentration near its critical micelle concentration (CMC). Some organometallic complexes or hydrophobic compounds initially present in the solution and bound to the micelles can favorably be extracted and concentrated in a small amount of the surfactant-rich phase [11].

In our laboratory, we work on the CPE of many metal ions to preconcentrate, separate, and determine them in different real samples [14-29]. The Goal of the present study was to develop CPE as a preconcentration and separation step for Pt^{4+} prior to its spectrophotometric determination. In the applied system, I or II was used as the complexing agent and PONPE 5.0 as nonionic surfactant. Potential factors affecting the CPE of Pt^{4+} were studied in detail. The accuracy was tested by Pt^{4+} determination in spiked water samples. The developed technique was validated by analyzing Pt^{4+} in geological, food and water samples.

Experimental

Apparatus

An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. A Perkin-Elmer Lambda 12 UV/Vis spectrometer was applied for recording absorbance spectra with 1.0-cm quartz cell. A water bath with temperature control and a centrifuge with 25 mL calibrated centrifuge tubes (Superior, Germany) were used to accelerate the phase separation process.

Reagents and solutions

All solutions were prepared using ultrapure water obtained by a Milli-Q water purification system (Millipore, Bedford, MA, USA). Analytical grade reagents used were obtained from Sigma-Aldrich (St. Louis, MO, USA) or Merck (Darmstadt, Germany). The laboratory glassware was kept overnight in 10% v/v HNO_3 solution. Before the use, the glassware was washed with deionized water and dried in a dust free environment. The standard stock solution (1000 g mL^{-1}) of Pt(IV) was prepared by dissolving an appropriate amounts of Na_2PtCl_6 in 1.0 M HCl. Working standard solutions were prepared daily from the stock solution by dilution with 1.0 M HCl. Solutions of different pH 2.5–11.5 acetate, phosphate, thiel and universal buffers were prepared as described early [30]. Potassium iodide salt and acetonitrile solvent were purchased from Merck.

Egyptian International Pharmaceutical Industries Company (EIPICO) Egypt, kindly provided tenoxicam and piroxicam, Egypt. A 5×10^{-3} M stock solution was prepared by dissolving an appropriate weigh of the solid in minimum volume of glacial acetic acid and is completed to 100 mL with bidistilled water in a 100 mL measuring flask. Acetonitrile solvent and potassium iodide salt were purchased from Merck.

Surfactant PONPE 5.0, (Tokyo Kasei Industries, Chuo-Ku, Tokyo, Japan) 50% (v/v) in ethanol (Sigma Chemical Co.), was employed without further purification.

General procedure

An aliquot of cold Pt^{4+} standard solution was transferred to a 100 mL polypropylene tube, 5.0 mL of the 5×10^{-3} M I or II solution and 10 mL thiel buffer solution of pH 3.5 were added by the Addition of 2.5 mL of 50% PONPE 5.0 solution and 5.0 mL of 0.5 M of KI solution was then added. The total system was placed for 5.0 min in a thermostatic bath at 50°C. The separation of the two phases was obtained by centrifugation for 5.0 min at 3800 rpm using 25 mL calibrated centrifuge tubes. The phases were cooled in an ice bath in order to increase the viscosity of the surfactant-rich phase. The surfactant-rich phase was dissolved and diluted to 0.2 mL with acetonitrile and transferred into a 1.0-mm quartz cell. At 474 or/and 482 nm for I or/and II, respectively, the absorbance was measured. The blank solution was applied to the same procedure without Pt^{4+} ions.

Interferences study

Different concentrations of ions, which may be present in samples, (1/1, 1/10, 1/50 and 1/100 Pt^{4+}/interferent ratio) were submitted to the test solution containing 150 ng mL^{-1} Pt^{4+} and the general above procedure was applied. Tolerance limits were realized in samples without addition of masking or anticoagulant agents.

Accuracy study

Adequate volume of each sample was spiked with increasing amounts of Al^{3+} (100 and 150 ng mL^{-1}). Analyte concentrations were determined by proposed methodology.

Water samples

Tap, river, brackish, sea and industrial waste water samples used for development of the method were collected in polytetrafluoroethylene containers, filtered using a 0.45 mm Millipore cellulose nitrate membrane to remove the suspended particulate matter, and stored in the dark at 4°C. Tap water was obtained from our laboratory, and river water was collected from river Nile water from Benha City (Egypt). Brackish water was taken from Rasheed Bridge (Egypt). Sea water was collected from Mediterranean sea from Port Said City (Egypt). The domestic wastewater was provided from Port Said Sewage Wastewater Treatment Plant (Egypt).

Geological samples

The rock and road dust samples were obtained and collected from different areas in Geology Department, Faculty of Science, Benha, Egypt. The samples were dried at 90°C for 2.0 h, ground, passed through a sieve of 100 meshes and homogenized. 2.0 g of each sample was accurately weighed in a 100 mL beaker. In order to dissolve, 10 mL of aqua regia was added into the beaker and the mixture was heated almost to dryness. Then, 5.0 mL of aqua regia and 2.0 mL of H_2O_2 were added again to the residue and the mixture was evaporated to dryness. Double distilled water was added into the beaker and then the insoluble part was filtered through a filter paper and finally washed with double distilled water. The pH was adjusted to about 3.5 using 1.0 M of NaOH and the total volume was made up to 10.0 mL with double distilled water in a measuring flask. 5.0 mL of the digested samples were subjected to the CPE methodology for Pt^{4+} determination as described above.

Food samples

An accurately weighed sample (about 5.0 g) was placed in a 100 mL beaker, and a solution of concentrated $HClO_4$–HNO_3 1 : 2 (v/v) (10 mL) was added. This mixture was heated gradually until the solution became clear. Near dryness about 10 mL of double distilled water were added, the solution was filtered off then cooled and diluted to 50 mL with double distilled water. Then Pt^{4+} was determined as described above for 10 mL of this solution.

Results and Discussion

Reagent I and II is often applied as a chromgenic reagent for the determination of Pd^{2+} [31]. Pt^{4+} form a complex with I or/and II in the presence of PONPE 5.0 which has a maximum wavelength at 452 or/and 459 nm, respectively. By addition of iodide ion, the solution became turbid and can be extracted by CPE procedure. The ternary complex formed in surfactant-rich phase indicates a maximum absorbance at 474 or/and 482 nm, respectively (Figure 1). The absorbance was measured at 474 or/and 482 nm, respectively, against blank reagent, after separation of surfactant-rich phase.

Optimization

To take full advantage of the method, experimental reaction conditions must be examined and optimized. Variable parameters were investigated to achieve optimum experimental conditions. All parameters were optimized by setting these parameters to be constant and optimizing one each time.

In the pH range of 2.5 – 11.5, the effect of pH on the developed colour at a constant concentration of complex in surfactant-rich phase was studied. Different buffer solutions (acetate, borate, phosphate, universal and thiel) were examined. The absorbance of the Pt^{4+}– {I or II} – PONPE 5.0 system at 474 or/and 492 nm, respectively, in surfactant-rich phase was investigated against blank reagent. Thiel buffer solution gave the highest and constant absorbance. In the range of 3.0–4.0, the absorbance was nearly constant. So, pH 3.5 was selected as the optimum (Figure 2). The amount of pH 3.5 was investigated to choose the optimum volume. The highest absorbance value was achieved by addition of 8.0–12 mL of pH 3.5. For all further studies, 10 mL of pH 3.5 per 100 mL was selected.

The separation and determination of Pt^{4+} was affected with the reagent I or/and II concentration which investigated in the range of $0.5–5.0 \times 10^{-4}$ M. The formed complex increased by increasing reagent concentration up to 2.5×10^{-4} M and decreased at higher concentrations. It was expected that increasing I or/and II causes an increase in the absorbance of complex. At concentrations $\geq 3.0 \times 10^{-4}$ M, the concentration of uncomplexed reagent in surfactant-rich phase increases significantly. Therefore, much probably decrease of absorbance change at concentrations $\geq 3.0 \times 10^{-4}$ M is due to this fact that the free reagent competes with the complexes in extraction to surfactant-rich phase. The optimum reagent concentration of 2.5×10^{-4} M was selected.

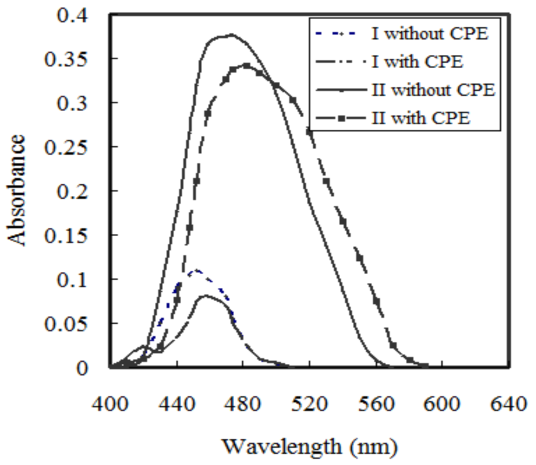

***Figure 1**. Absorption spectra for Pt^{4+} complexed with I and II using mgmL^{-1} Pt^{4+} without CPE and 150 ng mL^{4+} with CPE at the optimum.*

Effect of 50% PONPE 5 concentration on the complexation of Pt^{4+} was studied in the volume range 0.5 - 5.0 mL. The absorbance increased by increasing PONPE 5 concentration up to 2.5 mL of 50% and decreased at higher concentrations. The absorbance of blank also increased by increasing PONPE 5 concentration. This is due to more extraction of reagent by increasing PONPE 5 concentration, whereas the difference between the sample and blank (ΔA) increased by increasing PONPE 5 concentration up to 2.5 mL of 50% and decreased at higher concentrations (Figure 3). Therefore, 2.5 mL of 50% PONPE 5 was selected.

Salt addition can cause non-ionic surfactant solutions to separate into immiscible surfactant-rich and surfactant-poor phases. Various inorganic salts KCl, KBr, KI, NaCl, NaF, and KNO_3, were examined and KI was found as the best. Therefore, addition of iodide was induced micelle growth and extraction of complex. The iodide concentration effect was studied in the range of 0.005–0.04 M. Addition of 0.025 M iodide in the final 100 mL solution sufficed for maximum extraction and separation of the complex formed and the absorbance decreased at higher concentrations. A 0.025 M iodide was selected for further studies.

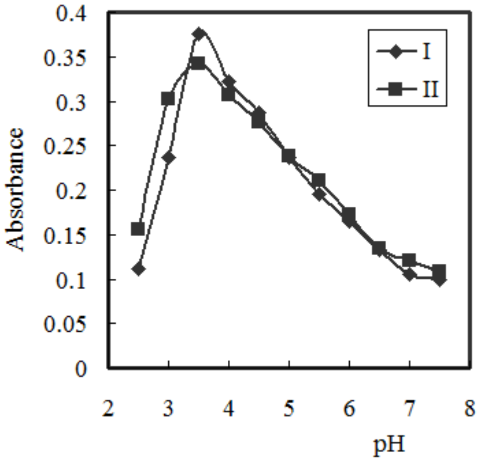

***Figure 2.** Effect of pH on the CPE of 150 ng ml^{-1}Pt^{4+} complexed with I and II at the optimum conditions.*

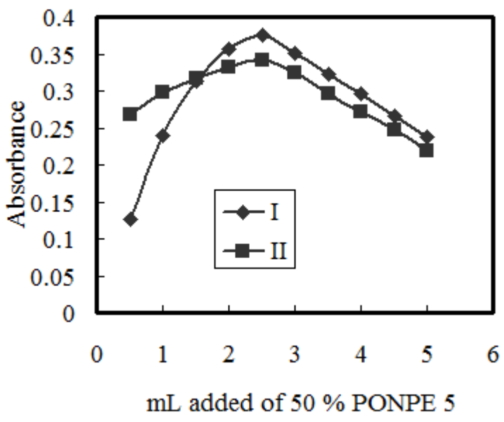

***Figure 3.** Effect of 50% PONPE 5 volume on the CPE of 150 ng mL^{-1} Pt^{4+} complexed with I and II at the optimum conditions.*

Optimal incubation time equilibration and temperature were necessary to complete the reaction and to achieve as sufficient as possible for easy phase preconcentration and separation of Pt^{4+}. The effect of equilibration temperature on the extraction recovery of Pt^{4+} was investigated in the range of 30–60°C. It was found that the extraction recovery increased with equilibration temperature from 45–55°C and stabilized up to 55°C. Thus 50°C was ensured to get maximum absorbance. Therefore, the temperature of 50°C was employed in continuing the experiment, keeping the equilibration temperature as 50°C and the influence of the incubation time on cloud point extraction was monitored in the range of 1.0–15 min thus the obtained result showed that the 5.0 min of incubation time was sufficient for the separation process. Also, a successful CPE was found to be enough after centrifugation at 3800 rpm for 5.0 min.

Regarding sensitivity, various solvents were examined to choose the one producing the optimal results because the surfactant-rich phase was precipitated. Among methanol, ethanol, acetone, acetonitrile, and DMF, acetonitrile gave the optimum results due to low overlapping of spectra of components and high sensitivity. Therefore, acetonitrile was selected in order to have appropriate amount of sample for transferring and measurement of the absorbance and also a suitable preconcentration factor. Therefore, a preconcentration factor of 500 was achieved using the proposed procedure.

Stoichiometric ratio

At the optimum conditions described early, the nature of the complex was established using the continuous variation and molar ratio procedures. The plot of absorbance versus the molar ratio of I or/and II to Pt^{4+}, obtained by varying the I or/and II concentration, indicated inflection at molar ratio 2.0, indicating presence of two I or/and II molecules in the formed complex. Moreover, the Job method showed a ratio of I or/and II to Pt^{4+} = 2.0. Consequently, the results indicated that the stoichiometric ratio was (2 : 1) [I or/and II : Pt^{4+}]. The conditional formation constant (log K), calculated using Harvey and Manning equation applying the data obtained from the above two procedures, was found to be 3.74, whereas the true constant was 3.57.

For the ternary complex with PONPE 5.0, the obtained results implied that a 1: 1 complex is formed between the [(I or/and II)$_2$Pt] complex and PONPE 5.0. Consequently, the results indicated that the stoichiometric ratio was 2 : 1 : 1 [(I or/and II)$_2$Pt][PONPE 5.0], as recorded in the following equations. The conditional formation constant (log K), calculated using the Harvey and Manning equation applying the data obtained from the above two procedures, was found to be 4.04, whereas the true constant was 4.00.

$$\text{2 I or/and II} + Al^{3+} \rightleftarrows [(\text{I or/and II})_2Pt]$$

$$[(\text{I or/and II})_2Pt] + \text{PONPE 5.0} \rightleftarrows [(\text{I or/and II})_2Pt][\text{PONPE 5.0}]$$

Selectivity

Various cations and anions effect on 150 ng mL^{-1} Pt^{4+} determination by the proposed method was investigated. An ion was considered to be an interference when it caused difference in absorbance greater than ± 5.0%. For the determination of 150 ng mL^{-1} Pt^{4+}, the foreign ions can be tolerated at the levels recorded in Table 1. I or/and II forms stable complexes with different metal ions, including transition metal ions. Most of the cations and anions tested do not interfere with the extraction and determination of Pt^{4+}. These results demonstrate that excess amounts of some common cations and anions do not interfere on the determinations of the analyte, putting in evidence the adequate selectivity of the developed methodology. The interferences from Ni^{2+}, Pd^{2+}, and Au^{3+} were removed by using masking agent as NaF, EDTA, and $SnCl_2$. The masking agent was added to the sample before addition of reagent solution. The masking agent form highly stable water soluble charged complexes with interfering ions and prevent them from complexing with I or/and II, thus removing their interference.

Analytical characteristics

The analytical characteristics of the optimized method summarized in Table 2, including regression equation,

Table 1. *Effect of diverse ions on the determination of 150 ng mL^{-1} Pt^{4+}.*

Ion added	Tolerance limit, mg mL^{-1}		Ion added	Tolerance limit, mg mL^{-1}	
	I	II		I	II
Na+, K+, Li+	15000	7500	Co2+, Rh3+	125	150
Mg2+, Ca2+, Ba2+	12500	6000	Pd2+ a	100	129
Al3+, Cr3+, Au3+	10500	5000	Au3+ b	75	60
Pb2+, Mn2+, Hg2+	8750	4000	Acetate, citrate	12000	10500
Cd2+, Zn2+, Sn2+,	5000	3300	Sulphate, oxalate	9000	8000
V5+, V4+, Sn4+	2250	2500	Nitrate, tartrate	7500	7000
Ag+, Hg+	3700	3000	Chloride, nitrite	5000	5000
W6+, Mo6+, Cr6+	2250	1750	Phosphate, benzoate	3000	2750
Th4+, Zr4+	1800	1500	Fluoride, iodide	2250	2500
Rh3+, Ir3+	1250	800	Carbonate, bicarbonate	1750	2000
Ru3+, Os8+	800	600	Thiosulphate,	1000	1000
Ce3+, Ce4+	250	200	Thiocyanate	750	800
Ni2+a	150	80	Iodate, sulphide	600	600

Note: [*]: Cations added as chloride, nitrate and sulphate, anions added as sodium or potassium states, unless otherwise stated

[a]: In the presence of 300 µg mL^{-1} of oxalate; NaF or EDTA

[b]: In the presence of 1200 µg mL^{-1} $SnCl_2$

linear range and limit of detection, reproducibility, and preconcentration and improvement factor. The limit of detection [32], defined as $C_L = 3S_B/m$ (where C_L, S_B, and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 1.55 and 1.42 using I and II, respectively. Because the amount of Py^{4+} in 100 mL of sample solution is measured after preconcentration in a final volume of 0.2 mL acetonitrile, the solution is concentrated by a factor of 500. The improvement factor, obtained as the ratio of the slope of the calibration graph for the CPE procedure to that of the calibration graph in micellar media without preconcentration, was 342 and 427 for I and II, respectively. The relative standard deviation (RSD) and relative error for six replicate measurements of 150 ng mL^{-1} of Pt^{4+} was 1.67% and 1.32%, respectively.

The proposed procedure characteristics have been compared with those of other methods. Table 3 compares analytical quality parameters of the proposed procedure with those reported previously for Pt^{4+} determination. It was shown that the proposed method is comparable in detection limit to the previous studies for Pt^{4+} determination. Therefore, CPE combined with spectrophotometric detection is a very simple and sensitive method for the preconcentration and determination of Pt^{4+}.

Determination of Pt(IV) in spiked water samples

To test the accuracy of the studied separation method, it has been applied to determine Pt^{4+} in spiked water samples from different sources. The results (Table 4) indicated that the recoveries are quantitative at reasonable levels for trace Pt^{4+} analysis, ranging from 98–103%. The method is then applied

Table 2. *Analytical features of the proposed method.*

Parameters	without CPE		Using CPE	
	I	II	I	II
Amount of acetonitrile	--	--	0.2	0.2
pH	3.5	3.5	3.5	3.5
Optimum reagent (M)	1.6 × 10^{-4}		1.6 × 10^{-4}	
Reaction time (min)	20	20	5	5
Stirring time (min)	10	10	5	5
Beer's range (ng mL^{-1})	500 - 3850	750-5000	5.0–300	5.0–300
Ringbom range (ng mL^{-1})	1000 - 3600	1500-5750	15 –275	15-270
Molar absorptivity (L mol^{-1}cm^{-1})	2.28 × 10^4	2.04 × 10^4	4.89 × 10^5	4.45 × 10^5
Sandell sensitivity (ng cm^{-2})	27.9	25.7	0.004	0.0044
Regression equation				
Slope (µg mL$^{-1)}$	0.021	0.018	2.51	2.28
Intercept	-0.012		0.04	
Correlation coefficient (r)	0.998	0.9888	0.999	0.9995
RSD a (%)	3.1	3.5	1.67	1.82
Detection limits (ng mL^{-1})	160	230	1.55	1.42
Quantification limits (ng mL^{-1})	490	725	4.82	4.5
Enhancement factor	--		500	500
Improvement factor	--		342	427

Table 3. *Comparison of some spectrophotometric methods for platinum.*

Reagents	$\lambda_{\mu\alpha\xi}$	ε ξ 10^4 Λ	Beer's	Ref.
	(nm)	mol^{-1} cm^{-1}	µg mL^{-1}	
2-(6-Aminoquinoxaline-2, 3-dithiol	625	2.75	0.0 - 2.0	[33]
5-Chloro2-hydroxythiobenzhydrazide	680	2.4	1.0 - 7.0	[34]
2, 2'-Diaminodiphenyldisulphide	725	5.48	0.25 - 5.0	[35]
N-(3,5-dimethylphenyl)-N'-(4-amino-benzenesulfonate)-thiourea	755	9.51	0.1 - 3.0	[36]
Pyronine G	575	10.7	0.0 - 0.80	[37]
Promethazine hydrochloride	406	1	0.0 - 7.5	[38]
NPTSQ	640	13.7	0.0 - 1.0	[39]
5-Chloro2-hydroxythiobenzhydrazide	510	1.06	1.8 - 14.4	[40]
Butyl rhodamine B	570	92.6	0.0 - 1.20	[41]
o-Hydroxythiobenzhydrazide	690	2.78	0.46 - 9.2	[42]
Bis(2-hydroxynaphtaldehyde) ethylendiamine	355	1.4	1.0 - 5.0	[43]
Rhodamine 6G	530	28	0.08 - 0.6	[44]
TMK	530	29.5	0.0 – 0.48	[45]
1-Phenyl-4-ethyl thiosemicarbazide	715	5	0.2 – 2.6	[46]
5-Br-PADAP	570	15.4	1.0 – 3.6	[47]
CEABT	390	2.05	0.8 – 3.2	[48]
5-(2',4'-Dimethylphenylazo)-6-hydroxy-pyrimidine-2,4-dione	634	149	0.03–0.13	[29]
I	474	48.9	0.005 -0.3	This work
II	482	44.5	0.5-0.300	This work

for the analysis of synthetic mixtures. A suitable liquid of the synthetic mixture was analyzed by the proposed procedure and the results are displayed in Table 4. The agreement between the actual and found values confirmed the accuracy of the procedure.

Applications

In order to investigate the validity of the proposed method, the described procedure was applied to determine Pt^{4+} in food and geological samples. The results obtained in five individual determinations and their standard deviations are shown in Table 5. The same batch of samples was also analysed by ICP-MS after solvent extraction with APDC/MIBK [49]. The paired t-test was applied to the results obtained by the proposed and the reference methods, and it indicated that the calculated t values were lower than the tabulated t value (t=2.36, n=5, P=0.05). This suggested that at the 95% confidence level, the difference between the results obtained by the two methods were statistically not significant. These results demonstrate the applicability of the method for the determination of Pt^{4+} in real samples.

Conclusion

The results of this work demonstrate the possibility of using drug I and II as an effective complexing agent for the CPE and separation of Pt^{4+} prior to its determination using spectrophotometry. The method can be applied successfully determination of Pt^{4+} in environmental samples. The procedure proved to be sensitive, selective, rapid, and convenient to determine Pt^{4+} in environmental samples without interferences. Furthermore, the proposed procedure was compared with other reported methods. As is demonstrated, the proposed procedure presents superior or comparable analytical figures of merit to the reported procedures.

Table 4. *Determination of Pt^{4+} in spiked water samples by the proposed procedure^{a}.*

Sample	**Concentration of Pt(IV) (ng mL^{-1})**						
	Added	**Found ± S.D.**		**% Recovery**		**RSD**	
		I	II	I	II	I	II
Tap water	—	BDL	BDL	—			
	10	10.1 ± 0.07	9.85 ± 0.06	101	98.5	1.7	1.5
	20	20.0 ± 0.05	19.75 ± 0.07	100	98.75	1.9	2.2
	50	50.5 ± 0.08	50.50 ± 0.05	101	101	2.4	1.9
River Nile water	—	BDL	BDL	—			
	20	19.80 ± 0.03	20.25 ± 0.07	99	101.25	2.1	2.6
	40	40.75 ± 0.07	40.60 ± 0.08	101.9	101.5	2.7	2.9
	60	59.85 ± 0.05	60.75 ± 0.03	99.75	101.25	1.4	1.6
Brackish water	—	BDL	BDL	—			
	30	29.80 ± 0.08	30.50 ± 0.07	101.7	101.67	2.2	1.8
	60	60.60 ± 0.07	59.40 ± 0.05	99	99	1.7	1.6
	90	89.50 ± 0.04	91.10 ± 0.06	101.2	101.22	1.5	1.9
Sea water	—	BDL	BDL	—			
	40	39.55 ± 0.07	40.50 ± 0.09	101.3	101.25	2.9	2.6
	80	81.00 ± 0.05	80.07 ± 0.80	101.3	101.25	2.5	2.8
	120	121.2 ± 0.07	119.0 ± 0.06	101	99.16	2.1	2.2
Waste water	—	BDL	BDL	—			
	60	59.40 ± 0.06	60.75 ± 0.08	101.3	101.25	2.6	2.8
	120	118.6 ± 0.09	121.5 ± 0.05	98.83	101.25	1.8	2.9
	180	182.2 ± 0.07	178.4 ± 0.08	101.2	99.11	2.7	2.6

Note: BDL: below detection limit. The results are the mean of five measurements ± standard deviation

Table 5. *Determination of Pt^{4+} in food and geological samples by the recommended procedure.*

Sample	**Pt(IV) concentrationa (ng g^{-1})**			**t-test**	**F-value**
	The present work				
	I	**II**	**ICP-MSb**		
Rice	0.23 ± 0.04	0.24 ± 0.03	0.25 ± 0.02	1.78	
Tomato	0.13 ± 0.06	0.14 ± 0.05	0.14 ± 0.07		2.98
Flour	0.35 ± 0.08	0.31 ± 0.04	0.37 ± 0.03	2.11	
Flour	0.3 ± 0.04	0.34 ± 0.08	0.37 ± 0.03		3.47
Beans	0.26 ± 0.05	0.25 ± 0.04	0.24 ± 0.07	2.25	
Tobacco	0.56 ± 0.09	0.43 ± 0.11	0.44 ± 0.21		3.65
Road dust	16.75 ± 0.25	16.50 ± 0.70	15.95 ± 1.11	1.93	
Rock	33.7 ± 0.75	32.42 ± 0.45	34.33 ± 1.75		3.13

Note: [a] Mean ± S.D. (n = 5). [b] After solvent extraction with APDC/MIBK

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