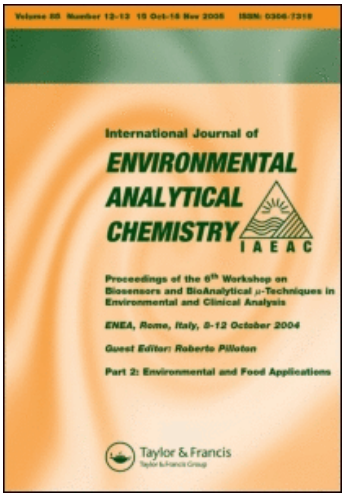

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Cloud-point extraction, preconcentration, and spectrophotometric determination of palladium in water samples

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Cloud-point extraction, preconcentration, and spectrophotometric determination of palladium in water samples

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The possibility of using Thio-Michler's Ketone (TMK), 4,4′-bis(dimethylamino) thiobenzophenone, for palladium(II) concentrated by micellar extraction at the cloud-point temperature, and later spectrophotometric determination, was investigated. Under the optimum conditions, preconcentration of 50 mL of water samples in the presence of 0.1% (w/v) octylphenoxy polyethoxy ethanol (Triton X-114), 2×10^{-6} mol L^{-1} TMK and 1×10^{-3} mol L^{-1} buffer solution (pH = 3.0) gave the limit of detection of 0.47 ng mL^{-1}, and the calibration graph was linear in the range of 2–50 ng mL^{-1}. The recovery under optimum working conditions was higher than 97%. The proposed method has been applied to the spectrophotometric determination of palladium(II) in natural water samples after cloud-point extraction with satisfactory results.

Keywords: Micellar extraction; Spectrophotometric determination; Natural water samples; Palladium

1. Introduction

Palladium has been used in different areas of science and technology, including agents, brazing alloys, petroleum, electrical industries, and catalytic chemical reactions [1, 2]. The metal may enter the environment and interact with complexing materials, such as humic substances [3]. Palladium has no biological role, and all palladium compounds should be regarded as highly toxic and carcinogenic. Thus, because of its increasing use, on the one hand, and the toxicity of Pd(II) compounds to mammals, fish, and higher plants, on the other hand [4], the separation, concentration, and determination of palladium are of interest in environmental analysis.

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The complexity of matrix and low concentration levels of palladium in industrials ($\mu g\,g^{-1}$) and environmental samples ($ng\,g^{-1}$) make direct measurement of this metal difficult. Therefore, the application of highly sensitive techniques, such as ICP-MS [5–7] and GF AAS [8], coupled with a separation/preconcentration procedure is necessary.

Separation and preconcentration procedures have been developed for several matrices. For this purpose, systems based on liquid–liquid extraction [9–11], ion exchange [12–14], solid-sorbent extraction [15–18], electrochemical deposition [19], and micellar system [20] have been used.

The latter system has been used in different fields of analytical chemistry, mainly those focusing on separation and preconcentration based on cloud-point procedures [21].

The cloud point is the temperature above which aqueous solutions of non-ionic surfactants become turbid. Specifically, above the cloud point, the solution is separated into two phases: a rich phase containing a high surfactant concentration in a small volume, and a poor phase with a surfactant concentration close to the critical micelle concentration (cmc) [21]. Hydrophobic species (hydrophobic organic compounds or metal ions after reaction with suitable hydrophobic ligand) present in the sample are able to interact with the micelles, so they are concentrated in the small volume of the surfactant-rich phase [20].

Cloud-point extraction has several important advantages: low cost, safety, faster operation, and easier manipulation. In addition, there is no need to use large amounts of organic solvents, and there are less stringent requirements for separation and higher preconcentration factors. Cloud point extraction was later applied in extraction, preconcentration and speciation of trace metals in a variety of different samples [21–23].

In the present work, we have reported the results obtained in a study of the cloud point extraction and preconcentration of palladium, after the formation of a hydrophobic complex with Thio-Michler's ketone (TMK), 4,4′-bis(dimethylamino) thiobenzophenone. We have used octylphenoxypoly ethoxy ethanol (Triton X-114) as surfactant in this analysis. The proposed method is used to determine palladium in water samples.

2. Experimental

2.1 *Reagents and solutions*

All reagents used were of analytical grade. A stock solution of palladium ion was prepared by dissolving the appropriate amount of metallic Pd in aqua regia. Working solutions were prepared from the stock solution by serial dilutions with doubly distilled water.

Other reagents used were; the non-ionic surfactant Triton X-114 (Fluka chemie AG-Switzerland), chelating agent TMK, nitric acid, sodium hydroxide and ethanol (Merck-Darmstadt, Germany). A stock standard acetate buffer solution ($pH = 3.0$; $0.1\,mol\,L^{-1}$), was prepared by dissolving appropriate amounts of sodium acetate (Merck-Darmstadt) and hydrochloric acid (Merck-Darmstadt).

The pipettes and vessels used for trace analysis were kept in sulphochromic acid mixture for at least 1 h and subsequently washed four times with distilled water.

2.2 *Apparatus*

A model UV-2550 spectrophotometer (Shimadzu) with a 1.0 cm glass cell was used. A thermostated bath model (Stuart, Scientific) was maintained at the desired temperature experiments, and phase separation was assisted using a centrifuge (ECCO-5170). The pH of the solutions was controlled with a Metrohm pH-meter model 713.

2.3 *Recommended procedure*

For the cloud-point extraction, 50 mL of analytical solution containing palladium, 1.0 mL of 5% Triton X-114, 0.2 mL of 5×10^{-4} mol L^{-1} TMK in ethanol, and 1.0 mL of 5×10^{-2} mol L^{-1} buffer solution (pH = 3.0) was prepared. The mixture was kept for 10 min in the thermostatic bath at 50°C. Subsequently, separation of phases was accelerated by centrifugation for 5 min at 4000 rpm. The phases were cooled down in an ice bath to increase the viscosity of the surfactant rich phase. The bulk aqueous phase was easily decanted by simply inverting the tube. The surfactant rich phase in the tube was made up to 1.0 mL by adding methanol. The absorbance was measured at the wavelength of maximum absorbance of complex, 508 nm, for palladium(II).

3. Results and discussion

3.1 *Effect of pH*

The CPE can be used for the preconcentration of metal ions after the formation of a sparingly water-soluble complex. The CPE efficiency depends on the hydrophobicity of the ligand and complex formed, the apparent equilibrium constants in the micellar medium, the kinetics of complex formation and the transference between the phases [21]. Since pH plays a unique role in metal-chelate formation and subsequent extraction, the pH of the sample solution was evaluated for its effect on the CPE preconcentration of Pd(II).

Figure 1 shows the influence of pH on the absorbance of the Pd(II) complex at 508 nm. As can be seen, in the range of 2.5–3.5 maximum absorbance was obtained. Hence, pH 3.0 was chosen as the working pH.

3.2 *Effect of TMK concentration*

The effect of concentration of TMK on analytical response is shown in figure 2. As can be seen for the palladium complex, the signal increases up to a known concentration of TMK, reaching a plateau, which is considered complete extraction. Above this concentration (1×10^{-6} mol L^{-1}), the extraction efficiency is not affected by the addition of ligand excess. A concentration of 2×10^{-6} mol L^{-1} was chosen as the optimum.

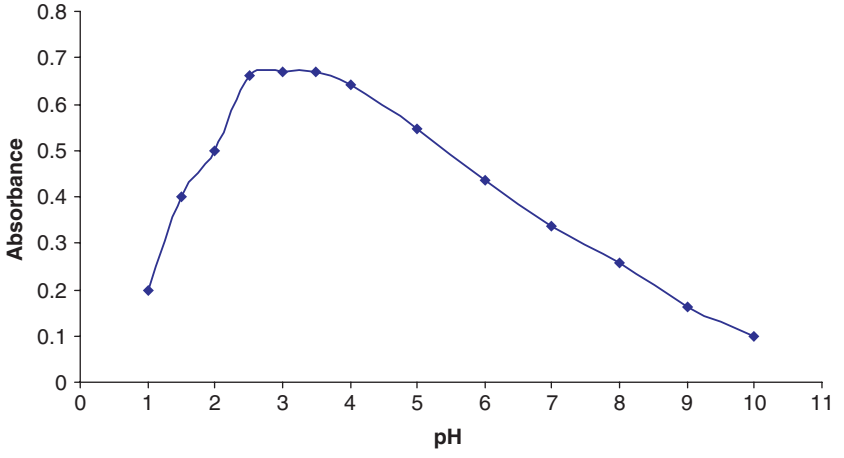

Figure 1. Effect of pH on the CPE-preconcentration performance: Pd(II) 20 ng mL^{-1}; Triton X-114 0.1% (w/v); TMK 2×10^{-6} mol L^{-1}.

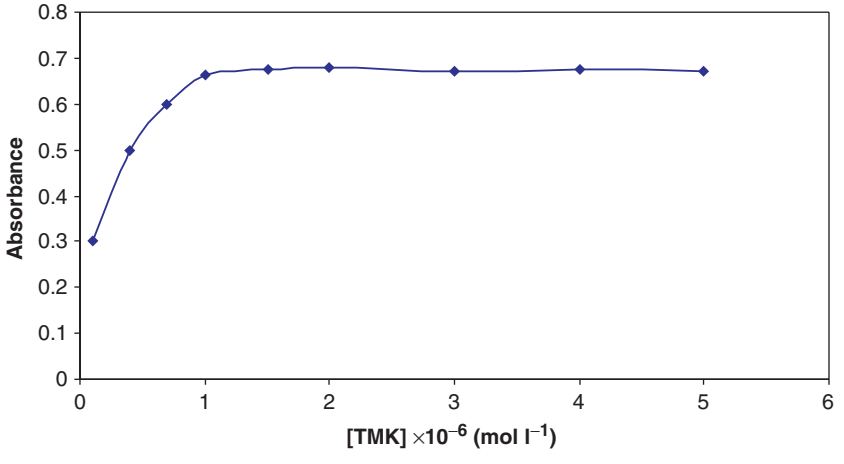

Figure 2. Effect of TMK concentration on the CPE-preconcentration performance: Pd(II) 20 ng mL^{-1}; buffer 1×10^{-3} mol L^{-1}; Triton X-114 0.1% (w/v).

3.3 *Effect of Triton X-114 concentration*

Triton X-114 was chosen for the formation of the surfactant-rich phase because of its commercial availability in a high-purified homogeneous form, low toxicological properties, lack of electro-active groups in its molecule, and cost. In addition, its low cloud-point temperature and high density of surfactant-rich phase facilitate phase separation by centrifugation.

The variation in the analytical signal upon surfactant concentration was examined with the following range: $C_{\text{Triton X-114}}$ 0.02–0.3% (w/v). The results showed that the absorbance of the solutions increased by increasing the Triton X-114 concentration up to 0.05% (w/v) (figure 3). At a concentration of less than 0.05%, the extraction

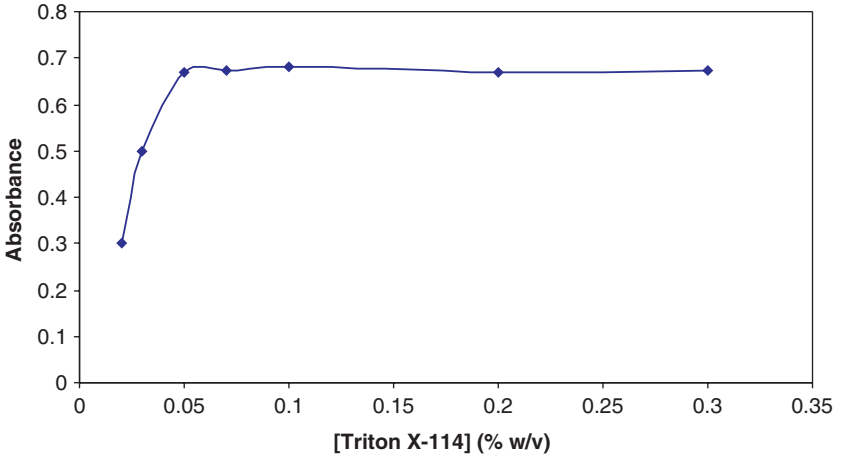

Figure 3. Effect of Triton X-114 concentration on the CPE-preconcentration performance: Pd(II) 20 ng mL^{-1}; buffer 1×10^{-3} mol L^{-1}; TMK 2×10^{-6} mol L^{-1}.

efficiency of complex is low, probably because of the inadequacy of the assemblies to trap the hydrophobic complex quantitatively. Therefore, 0.1% (w/v) Triton X-114 was used in the proposed method.

3.4 *Effect of buffer concentration and ionic strength*

The influence of buffer amount was assessed in which the other experimental variables remained constant. The results showed that above 5×10^{-4} mol L^{-1} buffer solution, no obvious variation took place in the extraction yield. Thus, 1×10^{-3} mol L^{-1} buffer solution was chosen as the optimal.

The effect of ionic strength on the extraction of palladium was investigated. The results showed that increasing the ionic strength enhances phase separation through salting-out phenomena, but ionic strength has a negligible effect on the performance of CPE up to 0.5 mol L^{-1}. This is in agreement with the results reported in the literature, which demonstrate that an increase in the ionic strength in a micelle-mediated system does not seriously alter the extraction efficiency of the analyte [24, 25].

3.5 *Effect of equilibration temperature and time*

The equilibration temperature and time have a significant effect on the extraction efficiency and sensitivity [21, 23]. The decrease in temperature during the centrifugation/phase separation step is the main experimental difficulty that causes the loss of extraction efficiency. To avoid this problem, we must choose the optimum temperature to be sufficiently higher than the cloud-point temperature. Also, very high temperatures are not suitable, since they could create stability problems for chelates and the chelating agent. Therefore, this parameter was studied within the range of 25–70°C. It was found that a temperature of 50°C was adequate.

Table 1. Analytical figures of proposed method.

Parameter	Analytical feature
Linear range ($ng\,mL^{-1}$)	2–50
Limit of detection ($ng\,mL^{-1}$) ($n=10$)	0.47
Repeatability (RSD[a],%) ($n=10$)	1.3
Enrichment factor[b]	50

[a] Pd(II) concentration was $20\,ng\,mL^{-1}$ for which the RSD was obtained.
[b] Enrichment factor is the ratio of aqueous phase to that of the final volume of the surfactant-rich phase.

It was desirable to use a short equilibration time and the lowest possible equilibration temperature, which compromise completion of extraction and efficient separation of phases. The dependence of absorbance upon equilibration time was studied within the range of 2–30 min. A time of 10 min was chosen as the optimal time.

3.6 *Effect of centrifugation time*

A centrifugation time of 5 min at 4000 rpm was selected as the optimum, since complete separation occurred at this time, and no considerable improvement was observed for longer periods of time.

3.7 *Figures of merit*

Table 1 summarizes the analytical characteristics of the optimized method, including linear range, limit of detection, repeatability, and enrichment factor. The limit of detection, 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 $0.47\,ng\,mL^{-1}$. Since the amount of Pd(II) in 50 mL of sample solution is measured after preconcentration by CPE in the final volume of 1.0 mL, the enrichment factor is 50. In our work, surfactant had no significant enhancement effect on absorbance of complex, and the enhancement factor was equal to the enrichment factor.

The relative standard deviation (RSD) for 10 replicate measurements of $20\,ng\,mL^{-1}$ Pd(II) was 1.3%.

3.8 *Interference effects*

The effect of different cations on the determination of $20\,ng\,mL^{-1}$ palladium ion by the proposed method was studied. An ion was considered to be interfering when it caused a variation greater than ±5% in the absorption of the sample.

The results (table 2) indicate that the Pd(II) recoveries are almost quantitative in the presence of interfering cations. This is in agreement with the results reported in the literature, in which TMK is highly selective for palladium at $pH = 3 \pm 0.2$ [26], and interferences by foreign cations only affect the TMK concentration; therefore, any loss of reagents could be avoided by increasing the TMK concentration.

Table 2. Effect of foreign ions on the preconcentration and determination of palladium.

Ion	Ion/Pd(II) (w/w)	Recovery (%)
Li^+	1000	99
K^+	1000	100.5
Na^+	1000	100
Co^{2+}	500	101.5
Cd^{2+}	500	99
Ag^+	500	98.5
Cu^{2+}	500	100
Al^{3+}	500	99
Fe^{2+}	500	99.5
Sr^{2+}	500	98
Fe^{3+}	500	98
Cr^{3+}	500	101
Ni^{2+}	400	99
Bi^{3+}	50	98
Hg^{2+}	5	98.5

Table 3. Recovery of 1.0 μg of Pd(II) added to 50 mL water samples.

Sample	Pd(II) found (μg)	Recovery (%)	% RSD
Sample 1[a]	0.97	97	1.4
Sample 2[b]	0.98	98	1.2
Seawater	0.97	97	1.3
Tap water	0.99	99	1.1
Spring water	0.98	98	1.3

[a] (Cu^{2+}, Co^{2+}, Cd^{2+}, Fe^{3+}, Ag^+, Cr^{3+}, 500 μg of each cation) K^+ and Li^+, 1.0 mg of each.
[b] (Cu^{2+}, Co^{2+}, Cd^{2+}, Fe^{3+}, Ag^+, Cr^{3+}, 250 μg of each cation) K^+ and Li^+, 0.5 mg of each.

3.9 *Application to samples*

In order to assess the applicability of the proposed method to real samples with different matrices containing varying amounts of a variety of diverse ions, this method was applied to the separation and recovery of palladium ions from two different synthetic samples and also for the determination of palladium in three water samples. The results of three replicate analyses of each sample are presented in table 3. As can be seen in all cases, the palladium recovery is approximately quantitative. Thus, the proposed method can be applied to environmental and/or other samples having Pd levels higher than the detection limit of the method.

4. Conclusion

In this work, the use of micellar system as an alternative to other techniques of separation and preconcentration offers several advantages, including low cost, good safety, and high capacity for preconcentration of palladium with a high recovery and very good extraction efficiency.

The results of this work demonstrate the possibility of using the TMK–Triton X-114 system for the preconcentration of Pd(II) as a prior step to determination at the $ng\,mL^{-1}$ level in water samples. The separation occurred efficiently, resulting in a good enrichment factor and low LOD.

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