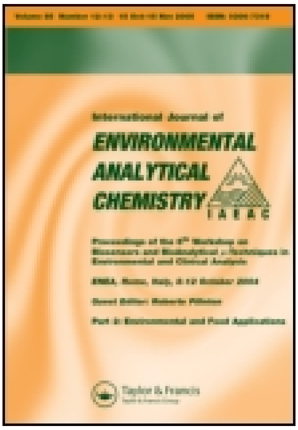

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Modified-cold induced aggregation microextraction based on ionic liquid and fibre optic-linear array detection spectrophotometric determination of palladium in saline solutions

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Modified-cold induced aggregation microextraction based on ionic liquid and fibre optic-linear array detection spectrophotometric determination of palladium in saline solutions

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In this research, a novel microextraction technique based on ionic liquids (ILs) termed in modified-cold induced aggregation microextraction (M-CIAME) was used for determination of palladium in saline solution. 1-(2-pyridylazo)-2-naphtol (PAN) was chosen as the complexing agent. Analysis was carried out using fibre optic-linear array detection spectrophotometric method which is suitable for analyte determination after microextraction. M-CIAME is based on phase separation phenomenon of ionic liquids in aqueous solutions. This method is simple and rapid for extraction and preconcentration of metal ions from water samples. It can be applied for the sample solutions containing much higher concentrations of salt, in comparison with CIAME (cold induced aggregation microextraction). Furthermore, this technique is much safer in comparison with other microextraction techniques in which organic solvent is used as the extraction solvent. Some effective parameters on extraction and complex formation such as amount of IL, salt effect, pH, concentration of the chelating agent and the other parameters were optimised. Under the optimum conditions, the limit of detection (LOD) and repeatability, expressed as relative standard deviation ($n = 5$) for $20\,\mathrm{ng\,mL^{-1}}$ of palladium were $0.4\,\mathrm{ng\,mL^{-1}}$ and 2.23%, respectively. The extraction percentage was 86%.

Keywords: modified-cold induced aggregation microextraction; ionic liquid; sample preparation; palladium; saline solutions; fibre optic-linear array detection spectrophotometry

1. Introduction

The platinum group metals are elements having the lowest abundance in the earth's crust. They have produced a very widespread technical application, and the three metals of the group, i.e. Pt, Pd and Rh, are mainly used in auto-catalysis, chemical, electrical, petroleum and pharmaceutical products [1]. Palladium has been applied in various ways as microcontactors in electronics, in jewellery and as a hard alloy in dentistry. Because of such applications palladium can be distributed and can cause damage to the environment, even at low concentrations. Possessing inherent toxicity, it has a tendency to accumulate in the food chain, as it has a low decomposition rate, and thus palladium is grouped within

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the category of environmental toxins [2]. Therefore, determination of trace amounts of palladium is important in industrial, environmental and geochemical samples.

Spectrophotometric methods are the most commonly used techniques and continue to enjoy wide popularity. The common availability of the instrumentation, the simplicity of procedures, the speed, precision and accuracy of the technique, make spectrophotometric methods attractive.

With recent advances in sensitive array detectors, fibre optic wave guides, high speed electronics and powerful software, many new generations of spectrometers have been developed. These new spectrometers use charged couple devices (CCDs) or photodiode arrays (PDAs) to replace the photomultipliers and photodiodes used in conventional spectrometers. Because of their unique combination of outstanding sensitivity, high speed, low noise, compactness, instantaneous capture of full spectra, low cost and robustness, these detectors have revolutionised spectroscopic detection [3–6].

Direct determination of trace amount of metals in seawater is difficult. This is because of the low concentration of trace amount of metals, strong interference from the sample matrix and high concentration of salt. Preconcentration methods could dissolve low concentration and interferences problems. There are a number of methods for preconcentration and separation of palladium, such as flow injection methods (FI) [7–9], hollow fibre microextraction [10], solid-phase microextraction (SPME) [11], cloud point extraction (CPE) [12–15] and dispersive liquid-liquid microextraction (DLLME) [16–18]. But these methods cannot be applied successfully in high concentrations of salt.

Recent research activities are being focused on the development of efficient, economical and miniaturised sample preparation methods in high concentrations of salt [19,20].

In these methods, room-temperature ionic liquids (RTILs) are being considered as replacement solvents in sample preparation, because of their unique chemical and physical properties such as negligible vapour pressure, non-flammability, good extractability for various organic compounds and metal ions as a neutral or charged complexes, as well as tunable viscosity and miscibility with water and organic solvents.

In CIAME (cold induced aggregation microextraction), a very small amount of 1-hexyl-3-methylimidazolium hexafluorophosphate [Hmim][PF_6] and 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [Hmim][Tf_2N] were dissolved in a sample solution containing Triton X-114. In the M-CIAME (modified-cold induced aggregation microextraction), sodium hexafluorophosphate ($NaPF_6$) was used in order to decrease solubility of IL-phase in saline solutions. The solubility of IL decreases according to common ion effect, so phase separation can occur successfully and the volume of settled phase is constant up to 40% of medium salt concentration. In this method, $NaPF_6$ was added to the sample solution (50°C) containing a very small amount of 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF_4]). Afterwards, the solution was cooled in an ice bath and a cloudy solution was formed. After centrifuging, the fine droplets of extractant phase were settled to the bottom of the conical-bottom glass centrifuge tube. M-CIAME can be applied for sample solutions containing much higher concentrations of salt, in comparison with CIAME.

M-CIAME is robust against high concentration of salt (up to 40%). In this work, M-CIAME was applied for determination of Pd (II) in seawater, using 1-(2-pyridylazo)-2-naphtol (PAN) as a complexing agent. The effects of various experimental parameters on the extraction were investigated.

2. Experimental

2.1 *Reagents*

All reagents used were of analytical grade, 1-(2-pyridylazo)-2-naphtol (PAN), acetone, 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF_4] and all salts used were obtained from Merck (Darmstadt, Germany), except sodium hexafluorophosphate ($NaPF_6$) which was purchased from ACROS (Geel, Belgium).

The stock standard solutions of palladium at a concentration of $1000\,mg\,L^{-1}$ were prepared by dissolving 0.4166 g of $PdCl_2$ (Merck) in 10 mL of hydrochloric acid (10 %w/w) and diluted to 250 mL in a standard flask. The working standard solutions were obtained by appropriate dilution of the stock standard solution. A solution of $2 \times 10^{-3}\,mol\,L^{-1}$ PAN was prepared by dissolving an appropriate amount of this reagent in acetone. A solution of $120\,mg\,mL^{-1}$ $NaPF_6$ was prepared by dissolving an appropriate amount of $NaPF_6$ in doubly distilled water. The viscosity of ILs is high and their handling is difficult, so a working solution [Hmim][BF_4], $0.6\,mg\,\mu L^{-1}$ was prepared in acetone.

2.2 *Apparatus*

Fibre optic-linear array detection UV–vis spectrophotometry, Avantes (Eerbeek, The Netherlands) Model 2048, equipped with 50 µLquartz cylindrical micro cell (Hellma, Mullheim, Germany), was used for recording the spectra and measuring the absorbance. A Universal 320R refrigerated centrifuge equipped with a swing out rotor (12-place, 5000 rpm, Cat. No. 1628A) was obtained from Hettich (Kirchlengern, Germany). The pH-meter model 692 from Metrohm (Herisau, Switzerland) with combined glass electrode was used for the pH measurements.

2.3 *Procedure*

An amount of 10 mL of the sample or standard solution containing Pd(II), PAN ($10 \times 10^{-6}\,mol\,L^{-1}$) and [Hmim][$BF_4$] (30 mg) was transferred to a 15 mL screw-cap conical-bottom glass centrifuge tube. After adjusting pH to 2.5 and warming the solution to 50°C, an amount of 1.4 mL $NaPF_6$ solution ($120\,mg\,mL^{-1}$) was added to the sample solution. The obtained solution was cooled in an ice bath and a cloudy solution was formed. Then, the mixture was centrifuged for 6 min at 5000 rpm. As a result, the fine droplets of IL settled at the bottom of the centrifuge tube. Bulk aqueous phase was removed simply by inverting the tubes. Afterwards, IL-phase was dissolved in 60 µL acetone and transferred to a 50 µL cylindrical micro-cell. Absorbance of the complex was measured at 665 nm by FO-LADS (Figure 1).

3. Results and discussion

3.1 *Selection of ionic liquid and ion-pairing agent*

ILs are composed of unsymmetrically substituted nitrogen-containing cations (e.g. imidazole, pyrrolidine, pyridine,...) with inorganic anions (e.g. Cl^-, BF_4^-, PF_6^-, $(CF_3SO_2)_2N^-$,...). Due to the fact that the range of available anion and cation combinations could provide up to 10^{18} different room temperature ILs, it may be difficult to select the desired IL and ion-pairing agent. However, for the selection of the ionic

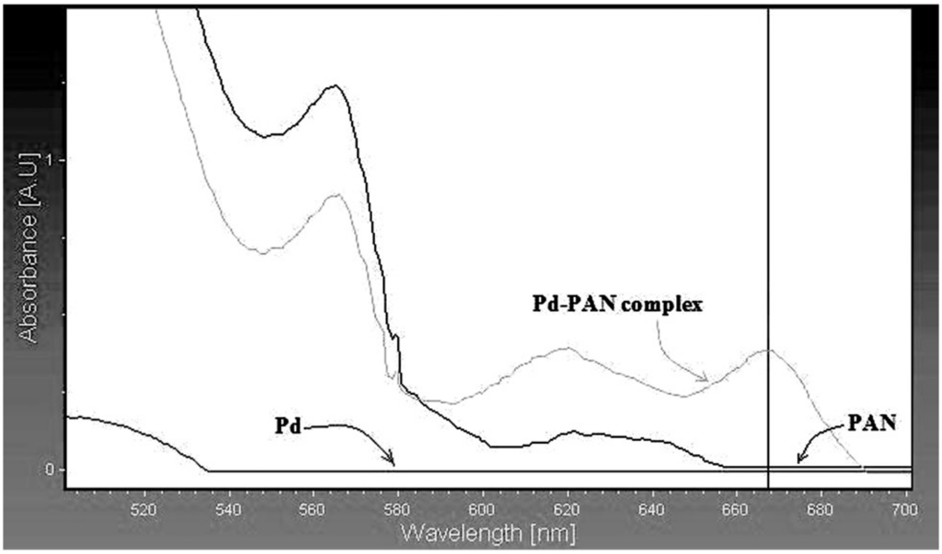

Figure 1. Pd, PAN, Pd-PAN complex spectra. Utilised conditions: palladium 20 ng mL^{-1}, PAN 10×10^{-6} mol L^{-1}, [Hmim][BF$_4$] 30 mg, NaPF$_6$ 156 mg, dissolving agent 60 µL.

liquids, some properties must be considered. The ILs should be water-miscible, liquid, inexpensive, have a higher density than water, and form a water immiscible IL with very low solubility as a result of reaction between water-miscible IL and ion-pairing agent. Also, the ion-pairing agent must have no interference in the extraction system.

According to the above-mentioned considerations, 1-hexyl-3-methylimidazolium tetrafluoroborate and sodium hexafluorophosphate were selected as hydrophilic IL and ion-pairing agent, respectively.

3.2 *Selection of the dissolving agent*

The dissolving agent must dissolve the IL and complex completely. Acetone and ethanol were examined in this work. In the presence of ethanol, IL-phase could not be dissolved completely. So, the solution was turbid; but in the presence of acetone, the sample was clear and maximum absorbance was acquired. Therefore, acetone was chosen as the dissolving agent.

3.3 *Effect of pH*

Separation of metal ions by M-CIAME involves prior complex formation with sufficient hydrophobicity to be extracted into the small volume of the IL-phase. The pH plays a unique role on metal-chelate formation and subsequent extraction. The effect of pH on the complex formation and extraction of palladium from water samples was studied in the range of 1.0–6.0 using HCl and NaOH. The results illustrated in Figure 2 reveal that the absorbance was slightly reduced by increasing pH. In order to prevent the formation of hydroxide of other metal ions presented in real samples at high pH values, pH 2.5 was chosen for the subsequent experiments.

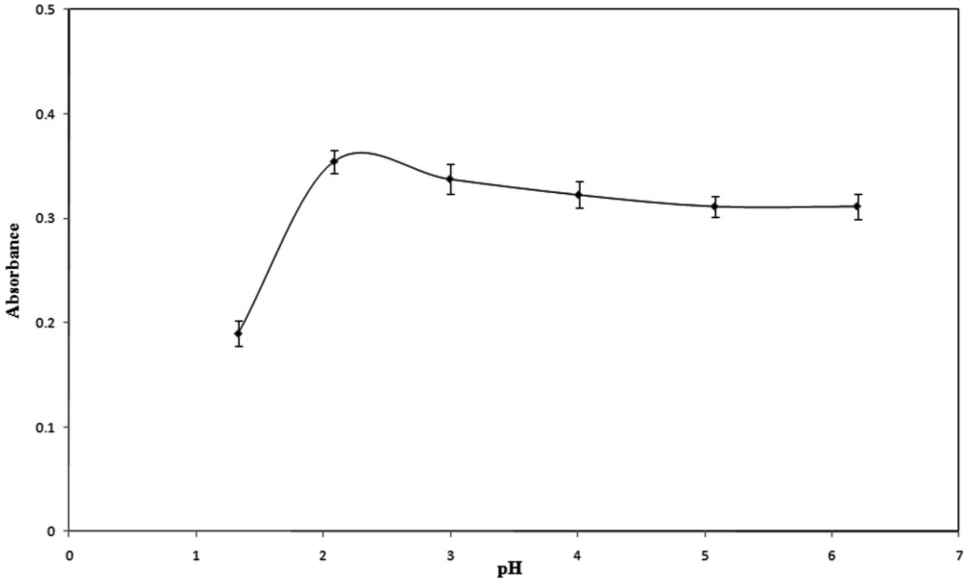

Figure 2. Effect of pH on the absorbance of Pd-PAN complex. Utilised conditions: palladium $20\,ng\,mL^{-1}$, PAN $10 \times 10^{-6}\,mol\,L^{-1}$, [Hmim][$BF_4$] 30 mg, $NaPF_6$ 156 mg, dissolving agent 60 μL.

3.4 *Effect of PAN concentration*

Complexation and extraction time are important factors in most preconcentration procedures. Since complex formation of palladium with PAN (complexing agent) is fast, the time of complex formation is short. Effect of PAN concentration on the absorbance was shown in Figure 3. We investigated PAN concentration in the range of $0–16 \times 10^{-6}\,mol\,L^{-1}$. The absorbance increased with increasing PAN concentration. Maximum absorbance was obtained at a concentration of $10 \times 10^{-6}\,mol\,L^{-1}$ of the ligand and after that, absorbance approximately stays constant. So concentration of $10 \times 10^{-6}\,mol\,L^{-1}\,mol\,L^{-1}$ was chosen as optimum value.

3.5 *Effect of ion-pairing agent and IL*

The effect of $NaPF_6$ was investigated in the range of 84–228 mg in the presence of 30 mg [Hmim][BF_4]. The results illustrated in Figure 4 reveal that according to common ion effect, by increasing the amount of $NaPF_6$ the solubility of [Hmim][PF_6] decreased, so extraction recovery and absorbance increased. Therefore, 168 mg $NaPF_6$ was chosen for the subsequent experiments.

The effect of [Hmim][BF_4] was studied in the range of 12–120 mg in the presence of 168 mg of $NaPF_6$. By increasing [Hmim][BF_4], the absorbance decreased due to an increase in the volume of the settled phase (Figure 5). In another way, we can use the corrected absorbance by determining the total volume after adding 60 μL of acetone by a microsyring; therefore, no decrease in absorbance values appears after 30 mg IL. Thus, 30 mg [Hmim][BF_4] was chosen for the subsequent experiments.

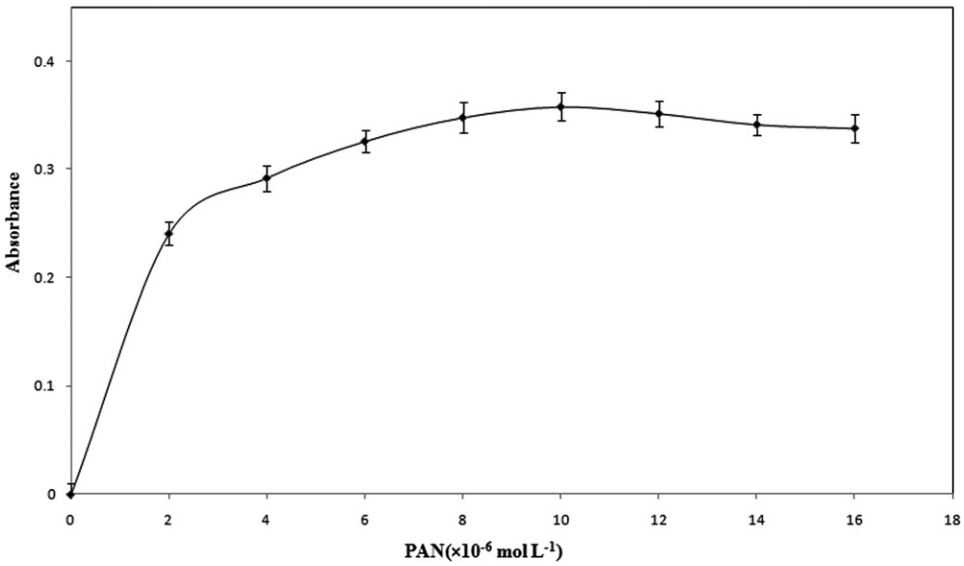

Figure 3. Effect of PAN on the absorbance of Pd-PAN complex. Utilised conditions: palladium $20\,ng\,mL^{-1}$, $pH = 2.5$, [Hmim][BF_4] 30 mg, $NaPF_6$ 156 mg, dissolving agent 60 µL.

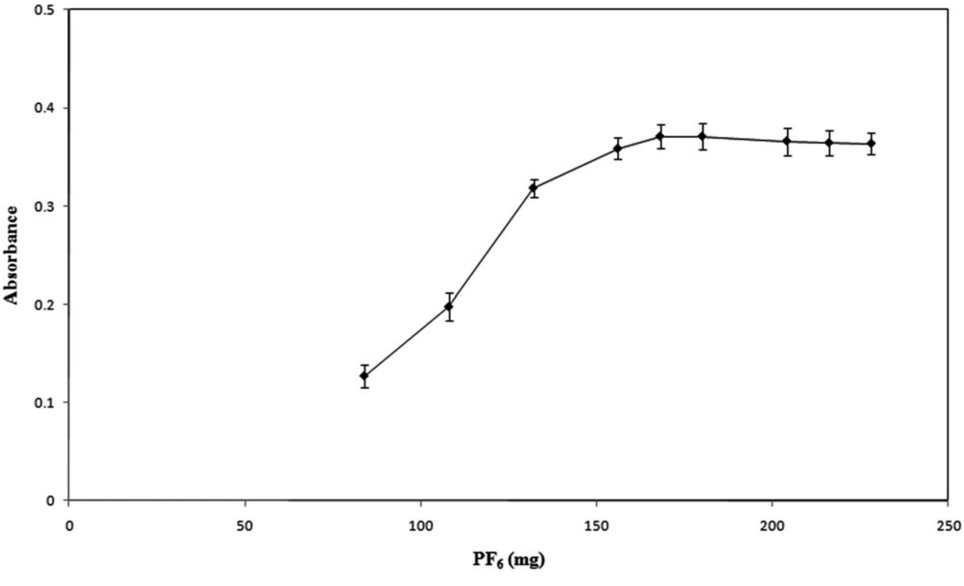

Figure 4. Effect of ion-pairing agent on the absorbance of Pd-PAN. Utilised conditions: palladium $20\,ng\,mL^{-1}$, PAN $10 \times 10^{-6}\,mol\,L^{-1}$, $pH = 2.5$, [Hmim][BF_4] 30 mg, dissolving agent 60 µL.

3.6 *Effect of salt content*

$NaNO_3$ was chosen in order to study the salt effect. Due to the high solubility of $NaNO_3$, the salt effect can be studied up to 40% (w/v). As shown in Figure 6, in the excess of

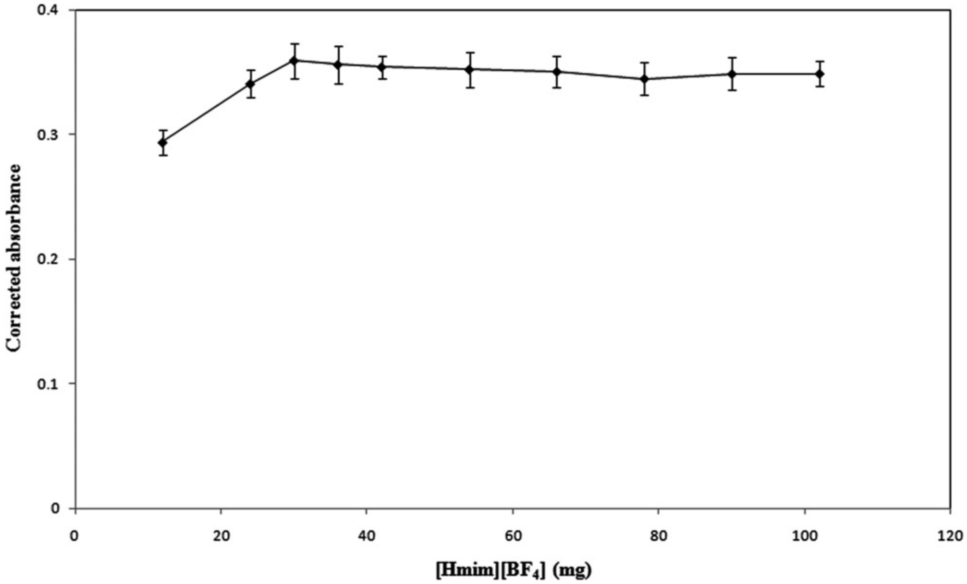

Figure 5. Effect of IL on the absorbance of Pd-PAN. Utilised conditions: palladium 20 ng mL^{-1}, PAN 10×10^{-6} mol L^{-1}, pH = 2.5, $NaPF_6$ 168 mg, dissolving agent 60 µL.

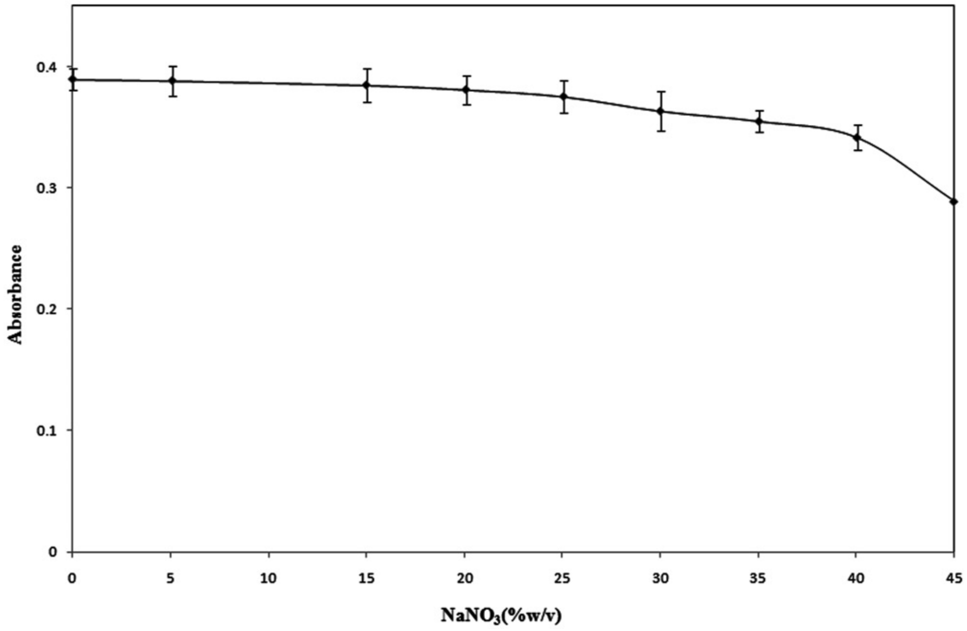

Figure 6. Effect of $NaNO_3$ on the absorbance of Pd-PAN. Utilised conditions: palladium 20 ng mL^{-1}, PAN 10×10^{-6} mol L^{-1}, pH = 2.5, [Hmim][BF_4] 30 mg, $NaPF_6$ 168 mg, dissolving agent 60 µL.

Table 1. Effect of foreign ions on the recovery of palladium (20 ng mL^{-1}).

Ion	Ion/Pd (II) mass ratio	Recovery (%)
Al^{3+}	1000	103.4
K^{+}	1000	96.1
Na^{+}	1000	98.7
Mn^{2+}	1000	104.8
Ni^{2+}	1000	99.4
Cd^{2+}	1000	101.6
Mg^{2+}	1000	104.1
Cr^{3+}	1000	104.2
Ca^{2+}	1000	103.5
Pb^{2+}	1000	98
Hg^{2+}	1000	101.7
Fe^{3+}	500	96.2
Cu^{2+}	10	90.1
Co^{+2}	5	123.2
NO_3^-	1000	95.6
Cl^-	1000	96.7
SO_4^{2-}	500	98
PO_4^{3-}	500	95.1

$NaPF_6$, phase separation occurred successfully up to 40% $NaNO_3$. At higher salt concentrations, the density of solution became higher than that of IL; consequently the extractant phase did not settle.

3.7 *Interferences*

The effect of foreign ions in the natural water samples on the recovery of palladium was studied by spiking appropriate amounts of the relative ions to the solutions containing 20 ng mL^{-1} of palladium and they were treated according to the recommended procedure. An ion was considered as interfering when it caused a variation in the absorbance of the sample greater than 5%. As can be seen in Table 1, most of the cations and anions did not interfere with the extraction and determination of palladium. However, Co^{2+} interfered with the determination of palladium. This interference was eliminated in the presence of a proper masking agent. In the presence of 1.6×10^{-4} M EDTA as a masking agent, no interference was observed for Co^{+2} up to 10 times relative to Pd^{+2} concentration. Thus, quantitative extraction of palladium was possible.

3.8 *Figures of merit*

Table 2 summarises the analytical characteristics of the optimised method, including limit of detection, reproducibility and enhancement factor. The limit of detection (LOD = 0.4 ng mL^{-1}) was calculated as $3S_b/m$ (S_b: standard deviation of the blank signals; m: slope of calibration curve after preconcentration). A good correlation coefficient ($r = 0.9964$) was obtained and the relative standard deviation (RSD) for five replicate measurements of 20 ng mL^{-1} Pd (II) was 2.23%. The calibration curve was

Table 2. Analytical characteristics of the method.

Parameter	Analytical feature
Slope	0.021
Intercept	0.02008
Linear range (ng mL^{-1})	5–100
Correlation coefficient (r)	0.9964
RSD (%) ($n=5$)[a]	2.23
LOD (ng mL^{-1})[b]	0.4
Enhancement factor[c]	164

[a] Value in parenthesis is the number of determination for which the RSD was obtained (palladium concentration: 20 ng mL^{-1}).
[b] Determined as 3 S_b/m (where S_b and m are the standard deviation of the blank signal and the slope of the calibration graph, respectively).
[c] Calculated as the slope ratio of the calibration graph obtained with and without preconcentration.

Table 3. Determination of Pd (II) in seawater samples and relative recoveries of spiked samples.

Sample	Concentration of Pd (II) mean ± S.D[a] (ppb)	Added Pd (II) (ppb)	Found Pd (II) mean ± S.D[a] (ppb)	Recovery (%)
Seawater[b]	n.d[c]	20	19.3 ± 3.4	96.5
Sodium nitrate	62.1 ± 2.4(ng g^{-1})	20	84.9 ± 5.3	103.4

[a] Standard deviation ($n=5$).
[b] Caspian sea water, Iran.
[c] Not detected.

linear from 5 to 100 ng mL^{-1}. Enhancement factor (EF = 164) was obtained from the slope ratio of calibration curve after and before preconcentration.

3.9 *Analysis of real samples*

In order to establish the validity of the proposed procedure, the method has been applied to the determination of Pd in geological standard reference materials (GBW07291 peridotite). The determined value (56 ± 7 ngg^{-1}, $n=5$) was in agreement with the certified value (60 ± 9 ng g^{-1}).

M-CIAME was applied for the determination of palladium in seawater samples and sodium nitrate (Table 3). The palladium was spiked to assess the matrix effect. The relative recovery of palladium from seawater samples and sodium nitrate at spiking level of 20 ng mL^{-1} were 96.5% and 103.4%, respectively, showing no matrix interferences.

3.10 *Comparison of M-CIAME with other methods*

Determination of palladium in water samples by M-CIAME and spectrophotometric detection was compared with other methods [21–25] and the results are shown in Table 4.

Table 4. Comparison of M-CIAME with other methods for determination of palladium in water samples.

Determination technique	Preconcentration method	Sample volume (mL)	Enhancement factor	LOD (ng mL^{-1})	Medium salt concentration (%)	Reference
ICP-MS	HF-LPME	2.5	24	7.9 ng L^{-1}	–	10
ICP-AES	CPE	100	20.2	0.3	5.85[d]	13
Spectrophotometry	CPE	50	50	0.47	–	15
ETAAS	DLLME	5	156	2.4 ng L^{-1}	–	17
FO-LADS	DLLME	10	162	0.25	–	18
FAAS	SPE	8	80	1	–	21
ETAAS	SPE	5	8.7	2	–	22
ETAAS	FI-MC[a]	5	70[b]	0.4	–	23
ICP-AES	SPE	10	20	0.45	–	24
ICP-AES	SPE	100	100	0.2	10.11[c]	25
FO-LADS	M-CIAME	10	164	0.4	$\leq$40[e]	This work

[a] Micro Column.

[b] Ratio of the initial volume to the final volume.

[c] KNO_3.

[d] NaCl.

[e] $NaNO_3$.

In comparison with other reported methods, M-CIAME gave low LOD (0.4 ng mL^{-1}) and high enhancement factor (164). Furthermore, this method is powerful against high medium salt concentration.

4. Conclusion

Determination of trace amounts of palladium is important in industrial, environmental, geochemical samples and saline solutions. We developed a novel microextraction technique based on ionic liquids (ILs) termed in modified-cold induced aggregation microextraction (M-CIAME) for determination of palladium in saline solutions. M-CIAME is simple, rapid, safe and robust against very high content of salt (up to 40%). Therefore, M-CIAME is a powerful sample preparation technique for brines and salt products used in food and pharmacological industries (e.g. sodium chloride, sodium nitrate, etc.).

Acknowledgement

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