# Microextraction technique based on ionic liquid for preconcentration and determination of palladium in food additive, sea water, tea and biological samples

Meysam vaezzadeh, Farzaneh Shemirani *, Behrooz Majidi

*Department of Analytical Chemistry, Faculty of Chemistry, University College of Science, University of Tehran, Tehran, Iran*

## ARTICLE INFO

## ABSTRACT

Modified cold-induced aggregation microextraction (M-CIAME) is a fast and simple method for extraction and preconcentration of metal ions from samples with high salt content. Furthermore, this technique is much safer in comparison with the organic solvent extraction. The extraction of palladium (Pd) was performed in the presence of Michler thioketone (TMK) as the complexing agent. In this method, sodium hexafluorophosphate ($NaPF_6$) was added to the sample solution containing small amounts of 1-hexyl-3-methylimidazolium tetrafluoroborate $[Hmim][BF_4]$. Afterwards, the solution was placed in the ice bath and a cloudy solution was formed. After centrifuging, the extraction phase was settled. Under the optimum conditions, the limit of detection (LOD) was $0.2 \ ng \ mL^{-1}$. The relative standard deviation (RSD) was 1.7% for $40 \ ng \ mL^{-1}$ of palladium ($n = 5$).

## 1. Introduction

Noble metals, especially palladium (Pd) finds an extensive use in the electrical industry (Daniel et al., 2003). Some of palladium compounds have been reported as potential health risks to humans, causing asthma, allergy, rhino conjunctivitis and other serious health problems (Liang et al., 2009). Noble metals such as palladium in various forms are currently used as catalysts for a wide variety of hydrogenation, oxidation, isomerization, cyclization, dehydration.

Several techniques such as flame atomic absorption spectroscopy (FAAS) (Wu et al., 2004; Farhadi and Teimouri, 2005; Soylak and Tuzen, 2008), graphite furnace atomic absorption spectrometry (GFAAS) (Chwastowska et al., 2004; Godlewska Zyłkiewicz and Kozłowska, 2005; Jamali et al., 2007; Tsogas et al., 2008), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Fan et al., 2004; Shokoufi et al., 2007), neutron activation analysis (NAA) (Dai et al., 2001), inductively coupled plasma mass spectrometry (ICP-MS) (Fang et al., 2006; Lesniewska et al., 2006) and ultraviolet–visible spectrometry (UV–Vis) (Arab Chamjangali et al., 2005; Moawed, 2006; Niazi et al., 2008) been used for determination of palladium.

Unfortunately, the direct determination by all these techniques is restricted owing to interferences caused by environmental sample matrices. In environmental samples, the low concentration of palladium together with the high concentration of interfering matrix components often required a preconcentration/enrichment step combined with a matrix separation. Several methods have been described for the separation and determination of Pd(II), such as solid phase extraction (SPE) (Farhadi and Teimouri, 2005; Godlewska Zyłkiewicz and Kozłowska, 2005), liquid–liquid extraction (LLE) (Lokhande et al., 1998; Anthemidis et al., 2001), flow injection extraction (FIE) (Kovalev et al., 2000; Tang et al., 2004), cloud point extraction (CPE) (Shemirani et al., 2006; Tavakoli et al., 2008) and dispersive liquid–liquid microextraction (DLLME) (Shokoufi et al., 2007; Liang et al., 2009).

Room-temperature ionic liquids (RTILs) are being recently considered as replacement solvents in the sample preparation, due to their unique chemical and physical properties such as negligible vapor pressure, non-flammability, good extractability for various organic compounds and metal ions as neutral or charged complexes, as well as tunable viscosity and miscibility with water and organic solvents. Several reports of preconcentration methods based on ionic liquids (ILs) have been reported previously (Gharehbaghi et al., 2009; Baghdadi and Shemirani, 2009; Abdolmohammad-Zadeh and Sadeghi, 2009). Unfortunately, all of these preconcentration methods suffer from high content of salt and could not be efficient in extraction and preconcentration of analyte.

Baghdadi and Shemirani (2008) developed new method termed cold-induced aggregation microextraction (CIAME) based on using of ILs (Baghdadi and Shemirani, 2009). In modified cold-induced aggregation microextraction (M-CIAME), Triton X-114 was elimi-

* Corresponding author. Tel.: +98 21 61112481; fax: +98 21 66405141.
*E-mail address:* shemiran@khayam.ut.ac.ir (F. Shemirani).

nated, so extractant phase merely contains [Hmim][PF$_6$], which has high density, so it can easily settle up to 40% salt.

The modified CIAME method is simple, rapid for extraction and preconcentration of metal ions and organic compounds from water samples. This method is robust against high medium salt content (about 40%). Additionally, in comparison with the organic solvent extraction, it is much safer since only small amounts of hexafluorophosphate (NaPF$_6$) and IL are used, which are being considered as "Green Solvents" for various separation processes.

We used modified cold-induced aggregation microextraction for determination of Pd(II) in sea water, tea, biological samples and food additive such as nitrate salt using spectrophotometric detection.

Nitrite and/or nitrate are usually added to processed meat products as their sodium or potassium salts to retain the red color and flavor of fresh meat and provide protection against microorganisms, such as Clostridium botulinum that can cause food poisoning (Thiago et al., 2007; Ferreira and Silva, 2008; Honikel, 2008).

## 2. Experimental

### 2.1. Apparatus

A lambda 25 UV–Vis spectrometer was purchased from Perkin–Elmer (Waltham, MA, USA) and used for recording the spectra and measuring the absorbance. A Universal 320R refrigerated centrifuge equipped with an awning out rotor (12-place, 5000 rpm, Cat. No. 1628A) and a Jeio Tech BW-05G water bath was obtained from Hettich (Kirchlengern, Germany).

### 2.2. Reagents and materials

All reagents used were of analytical grade. Michler thioketone (TMK), 1-propanol, acetone, ethanol, acetic acid, sodium acetate, 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF$_4$] and all salts used were obtained from Merck (Darmstadt, Germany). Sodium hexafluorophosphate (NaPF$_6$) purchased from ACROS (Geel, Belgium). A solution of $2 \times 10^{-4}$ mol L$^{-1}$ TMK was prepared by dissolving appropriate amount of this reagent in 1-propanol and was then kept far from light. The viscosity of ILs is high and their handling is a difficult, so working solution [Hmim][BF$_4$], 0.6 mg μL$^{-1}$ was prepared in acetone. A solution of 120 mg mL$^{-1}$ NaPF$_6$ was prepared by dissolving appropriate amount of NaPF$_6$ in doubly distilled water.

Pd(II) stock solution (1000 mg L$^{-1}$) was prepared by dissolution of the proper amount of PdCl$_2$ (Merck, Darmstadt, Germany) in 3:1, HCl/HNO$_3$ (V/V) according to the standard methods and then diluted with double distilled water (Marczenko, 1986). The working standard solutions were prepared by appropriate step by step dilution of the stock standard solutions. A buffer solution (pH 4, 4 mol L$^{-1}$) was prepared by mixing of 82 mL acetic acid (4 mol L$^{-1}$) and 18 mL of sodium acetate (4 mol L$^{-1}$).

### 2.3. Modified CIAME procedure

Ten milliliters of the sample or standard solution containing Pd(II), TMK ($5.2 \times 10^{-6}$ mol L$^{-1}$), acetate/acetic acid buffer (pH 4, 0.2 mol L$^{-1}$), 60 μL [Hmim][BF$_4$] (60 mg μL$^{-1}$) was transferred to a 10 mL screw-cap conical-bottom glass centrifuge tube and was kept in a thermo stated bath at 50 °C for 4 min. Then 1.2 mL NaPF$_6$ (120 mg mL$^{-1}$) was added to solution sample. After shaking, it was placed in an ice bath for 10 min and a cloudy solution was formed. Subsequently, the mixture was centrifuged for 5 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 100 μL of ethanol solution (85%) and transferred to 350 μL quartz cell. The absorbance of the complex was measured at 530 nm.

## 3. Results and discussion

### 3.1. Effect of pH

The effect of pH plays a significant role in the preconcentration studies. Separation of metal ions by modified CIAME involves the prior complex formation with sufficient hydrophobic, which could be extracted into small volume of the IL-phase. Extraction yield depends on the pH at which complex formation is carried out. The effect of pH upon the complex formation of the analyte was studied in the range of 2–8. The results illustrated in Fig. 1, reveal that the absorbance is nearly constant in the pH range of 3–5. Therefore, pH 4 was chosen for further extractions.

### 3.2. Effect of TMK

The solutions of TMK and its complexes are light sensitive, but 1-propanol solution of TMK can be kept for 40 days in a dark place at room temperature (Cheng et al., 1982), so TMK reagent was prepared in 1-propanol. The effect of the TMK on the absorbance is shown in Fig. 2. The absorbance increased by increasing the TMK concentration. A concentration of $5.2 \times 10^{-6}$ mol L$^{-1}$ was chosen as the optimum concentration.

### 3.3. Effect of NaPF$_6$ and [Hmim][BF$_4$]

Effect of NaPF$_6$ was investigated in the range of 0.4–1.6 mL (120 mg mL$^{-1}$) in the presence of 60 μL [Hmim][BF$_4$] (60 mg μL$^{-1}$) and the results are shown in Fig. 3. 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. Over 1 mL NaPF$_6$, absorbance is nearly constant. NaPF$_6$ (1.2 mL) was chosen for the subsequent experiments in order to have a robust extraction system against high medium salt content.

Influence of [Hmim][BF$_4$] was studied in the range of 30–120 μL (0.6 mg μL$^{-1}$) in the presence of 1.2 mL NaPF$_6$ (120 mg mL$^{-1}$). By increasing the amount of [Hmim][BF$_4$], absorbance decreased (Fig. 4) which is due to increase in the volume of the settled phase.
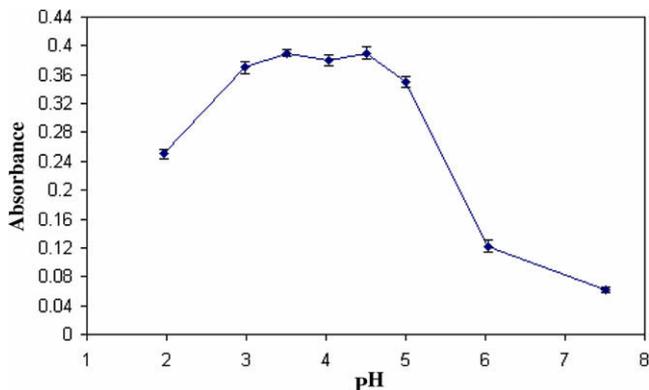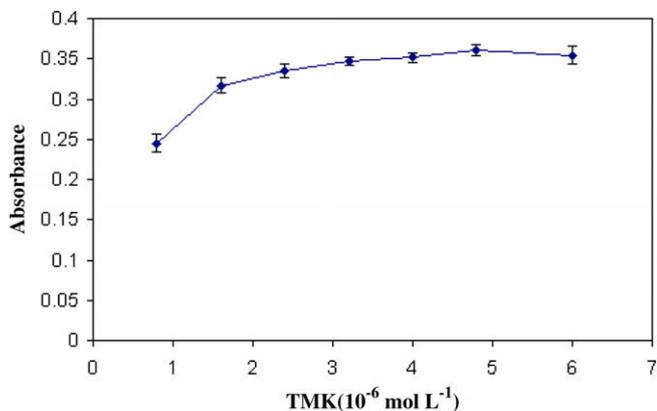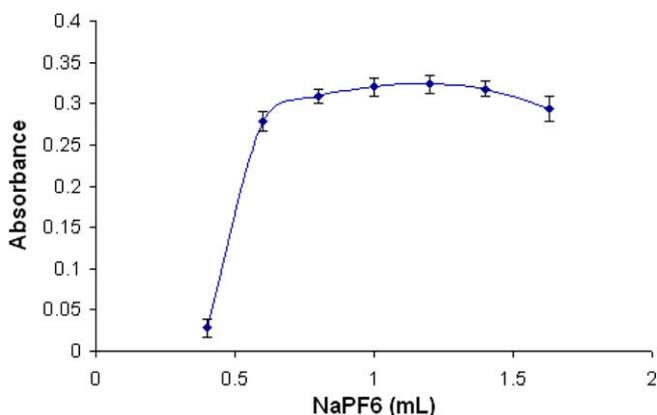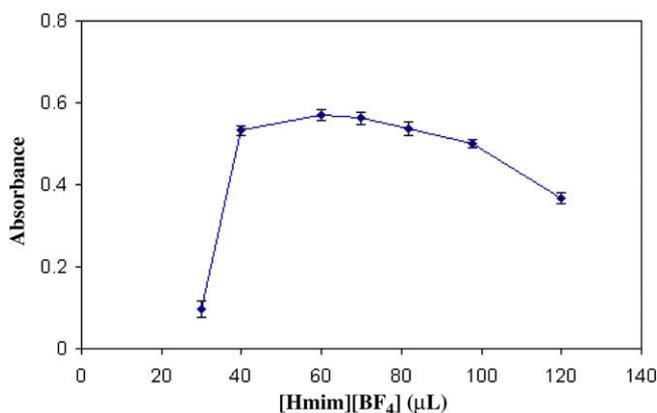


**Fig. 1.** Effect of pH on the absorbance of the complex. Conditions: palladium 20 ng mL$^{-1}$, TMK $7 \times 10^{-6}$ mol L$^{-1}$, [Hmim][BF$_4$] 70 μL of 0.6 mg μL$^{-1}$, NaPF$_6$ 1 mL of 120 mg mL$^{-1}$, diluting agent 100 μL.

**Fig. 2.** Effect of TMK on the absorbance of the complex. Conditions: palladium 20 ng mL$^{-1}$, pH 4, [Hmim][BF$_4$] 70 μL of 0.6 mg μL$^{-1}$, NaPF$_6$ 1 mL of 120 mg mL$^{-1}$, diluting agent 100 μL.



**Fig. 3.** Effect of NaPF$_6$ on the absorbance of the complex. Conditions: palladium 20 ng mL$^{-1}$, TMK 5.2 × 10$^{-6}$ mol L$^{-1}$, pH 4, [Hmim][BF$_4$] 70 μL of 0.6 mg μL$^{-1}$, diluting agent 100 μL.



**Fig. 4.** Effect of [Hmim][BF$_4$] on the absorbance of the complex. Conditions: palladium 20 ng mL$^{-1}$, TMK 5.2 × 10$^{-6}$ mol L$^{-1}$, pH 4, NaPF$_6$ 1.2 mL of 120 mg mL$^{-1}$, diluting agent 100 μL.

Sixty microliters of [Hmim][BF$_4$] was chosen for the subsequent experiments.

### 3.4. Effect of salt content

In the presence of high medium salt content, the solubility of ILs increases and phase separation does not occur. But, according to the common ion effect, solubility decreases in the presence of common ion. NaNO$_3$ was chosen in order to study the salt effect. Due to high solubility of NaNO$_3$, salt effect was studied up to 50% (w/v). As it is shown in Fig. 5, the excess of NaPF$_6$, phase separation occurred successfully.

### 3.5. Effect of temperature

Before shaking a solution containing IL, they were heated in the range of 20–50 °C. Since ILs are dissolved more easily at the temperatures above 30 °C, so the temperature 50 °C was chosen for heating step. However, very high temperature is unsuitable, since they could create are stability problems for chelates and chelating agent. After dissolving of IL, samples were cooled in the temperature range of 0–25 °C. When the temperature decreased, the absorbance increased due to decreasing IL solubility. Hence, a temperature of 0 °C was applied in all experiments by placing the centrifuge tubes in the ice bath for 10 min.

### 3.6. Effects of centrifuge conditions

The effect of centrifugation rate on the absorbance was studied in the range of 1000–8000 rpm. It was found that over 4000 rpm, IL-phase completely settled, so the rate of 5000 rpm was selected as the optimum point. At the optimum rate, absorbance was investigated as a function of centrifugation time. Five minutes was selected as optimum centrifugation time, because complete separation occurred at this time and no appreciable improvements were observed for longer times. However, the centrifugation time did not have considerable effect on the analytical characteristics of the modified CIAME method.

### 3.7. Selectivity of the method

Under the optimum conditions cited above and with 20 ng mL$^{-1}$ of palladium, a systematic study of the effect of foreign ions was undertaken. The results are summarized in Table 1. The tolerance limit of ions was fixed as the maximum amount causing an error not greater than 5% in the absorbance. As it is shown, most of the substances did not have any interference on the determination of palladium. Au(III), Cu(II) and Hg(II) interfered at 10 order concentration as palladium, that interference of these was eliminated in the presence of 2.0 × 10$^{-3}$ mol L$^{-1}$ thiourea.
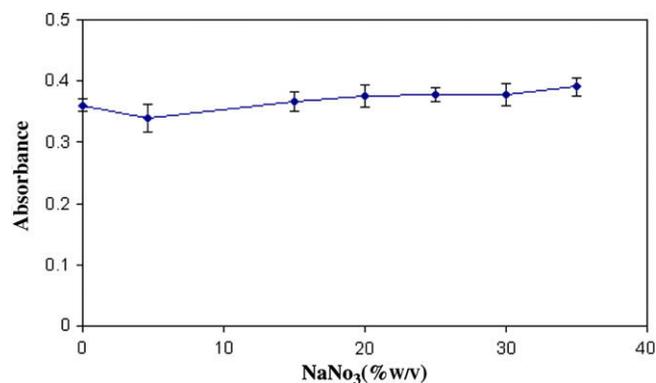


**Fig. 5.** Effect of NaNO$_3$ on the absorbance of the complex. Conditions: palladium 20 ng mL$^{-1}$, TMK 5.2 × 10$^{-6}$ mol L$^{-1}$, pH 4, [Hmim][BF$_4$] 60 μL of 0.6 mg μL$^{-1}$, NaPF$_6$ 1.2 mL of 120 mg mL$^{-1}$, diluting agent 100 μL.

**Table 1**
Effects of the foreign ions on the recovery of 20 ng mL$^{-1}$ of Pd from the aqueous solutions.

| Ions | Ion/Pd ratio (w/w) | Recovery (%) |
|---|---|---|
| Li$^+$ | 1000 | 100.7 |
| Na$^+$ | 1000 | 97.8 |
| Pb(II) | 1000 | 103.2 |
| Cd(II) | 1000 | 96.3 |
| Al(III) | 1000 | 104.5 |
| Ba(II) | 1000 | 102.6 |
| Ca(II) | 1000 | 103.1 |
| Co(II) | 1000 | 95.2 |
| Zn(II) | 1000 | 95.6 |
| Mg(II) | 1000 | 104.2 |
| Ni(II) | 1000 | 104.5 |
| Cr(III) | 1000 | 95.8 |
| Mn(II) | 1000 | 104.7 |
| Cr(VI) | 1000 | 96.2 |
| Bi(III) | 500 | 103.6 |
| Fe(III) | 100 | 99.1 |
| Hg(II) | 10 | 95.1[a] |
| Cu(II) | 10 | 96.6[a] |
| Au(III) | 10 | 98.2[a] |
| I$^-$ | 10 | 46.4 |
| Cl$^-$ | 500 | 98.8 |
| PO$_4^{3-}$ | 500 | 96.6 |
| SO$_4^{2-}$ | 1000 | 98.9 |

[a] Au(III), Hg(II) and Cu(II) masked with $2.0 \times 10^{-3}$ mol L$^{-1}$ thiourea.

### 3.8. Figures of merit

Calibration graph was obtained using 10 mL of the standard solution of Pd ion buffered at pH 4 and containing 60 μL [Hmim][BF$_4$] (0.6 mg μL$^{-1}$) at optimal conditions. The obtained results showed that the calibration curve was linear in the concentration range of 0.6–100 ng mL$^{-1}$ Pd.

Analytical characteristics of the proposed method are presented in Table 2. The relative standard deviation (RSD) resulted from the analysis of five replicates of the 10 mL solution containing 40 ng mL$^{-1}$ Pd was 1.7%. The detection limit (calculated as the concentration equivalent to three times of the standard deviation of the blank divided into the slope of the calibration curve after preconcentration) was 0.2 ng mL$^{-1}$. Enhancement factor (97) was obtained from the slope ratio of the calibration curve after and before preconcentration.

### 3.9. Analysis of real samples

The modified CIAME was applied for the determination of palladium in blood, tea, sea water and sodium nitrate food grade (Table 3). The samples were spiked to assess the matrix effect.

**Table 2**
Analytical characteristics of modified CLAME method.

| Parameter | Pd with preconcentration |
|---|---|
| %RSD ($n = 5$)[a] | 1.7 (40 ng mL$^{-1}$) |
| Regression equation | $A = 0.0191\,C + 0.1336$ |
| Correlation coefficient ($R^2$) | 0.984 |
| Limit of detection (ng mL$^{-1}$)[b] | 0.2 |
| Limit of detection (ng g$^{-1}$)[c] | 0.67 |
| Enhancement factor[d] | 97 |

[a] Values in parentheses are the Pd concentration (ng mL$^{-1}$) for which the RSD was obtained.
[b] Determined as 3 Sb/m (where Sb and m are the standard deviation of the blank signal and the slope of the calibration graph, respectively).
[c] LOD of analyte in the solid sample. Calculated as: LOD of analyte in the sample solution × dilution factor (the ratio of volume of sample solution and weight of solid sample dissolved in it). The much solid sample is used; the lower LOD can be obtained.
[d] Calculated as the slope ratio of the calibration graph obtained with and without preconcentration.

Approximately, 2 mL of the whole blood samples were added in a 100 mL volumetric flask; 3 mL of HNO$_3$ 2 mol L$^{-1}$ solution was added, followed by the addition of 1 mL of hydrogen peroxide. The flask was manually shaken to promote oxidation of the sample and then taken to volume by addition of distilled–deionized water.

After 10 mg of dry tea (dried at 110 °C) was placed in a 50 mL beaker, 7 mL of concentration of nitric acid was added, and the beaker was covered with glass watch and content were heat on a hot plate (150 °C for 15 min). The sample was then cooled, 3 mL of Hydrogen peroxide was added and the mixer was heated again at 200 °C until the solution became clear (about 1 h). The glass watch was removed and the acid evaporated to dryness at 150 °C. The white residue was completely dissolved in 5 mL of 1 mol L$^{-1}$ nitric acid and the solution was transferred to a 100 mL volumetric flask. The solution was then neutralized with proper NaOH solution. The resulting solution was diluted to the mark, and the recommended procedure was followed. The results are given in Table 3.

### 3.10. Comparison of modified CIAME with other methods

Determination of palladium in the water samples by modified cold-induced aggregation microextraction and spectrophotometric detection was compared with other methods and the results are shown in Table 4. As it can be seen, the LOD of modified CIAME spectrophotometry using only 10 mL of sample is better than that of other methods and this method is robust against high medium salt content (about 40%). The RSD of the proposed method is very low; all these results indicate that modified CIAME is a reproducible, simple and low cost technique that can be used for the preconcentration of metal ions like palladium from water solution.

## 4. Conclusions

Some advantages of modified CIAME in comparison with similar extraction systems using organic solvents are: robust against high medium salt content (up to 40%), experimental convenience, low cost, easy and safe methodology for preconcentration and separation of trace elements (for example, palladium) in aqueous solutions.

In this method, a very low limit of detection and good precisions (low %RSD) was obtained for Palladium. To conclude this work, it is important to point out that the new class of solvents called "Room-temperature ionic liquid" has really unique properties. They were called 'green solvents' because they have a very low vapor pressure that minimizes the release of chemical in the atmosphere when they are used as a solvent. If the sample amount required for detection system is a little, high enhancement factor can be obtained.

In comparison with CPE, background is too little in the case of saline solutions, because of very low solubility of water in the ionic liquids (ILs). Also, owing to high viscosity of ILs removing the bulk aqueous phase is easier .This method is more suitable for extraction of heat susceptible species in comparison with CPE. Therefore, Modified CIAME is a powerful sample preparation technique for brines and salt products used in food and pharmacological industries (e.g., sodium nitrate and sodium citrate).

### Conflict of Interest

The authors declare that there are no conflicts of interest.

**Table 3**
Determination of Pd(II) in blood, tea, sodium nitrate food grade and sea water.

| Sample | Added | Founded Pd(II) mean ± SD[a] | Recovery (%) | GFAAS | ICP-OES |
|---|---|---|---|---|---|
| Blood | – | 28.1 ± 2.1 | 100.5 | – | 27.3 ± 1.84 |
| | 20 | 48.2 ± 1.8 (ng mL$^{-1}$) | | | 47.4 ± 1.1 |
| Indian black tea (seylon) | – | 34 ± 1.3 | 103 | – | 33 ± 1.6 |
| | 20 | 54.6 ± 1.4 (ng g$^{-1}$) | | | 55 ± 0.9 |
| Sodium nitrite | – | 19.9 ± 1.7 | 104.5 | 19.8 ± 2.1 | – |
| | 40 | 61.7 ± 1.4 (ng g$^{-1}$) | | 61.4 ± 1.6 | |
| Sea water[b] | – | No detect | 103.2 | – | No detect |
| | 50 | 51.6 ± 1.4 (ng mL$^{-1}$) | | | 51.4 ± 1.2 |

[a] Standard deviation ($n = 3$).
[b] Caspian sea water, Iran.

**Table 4**
Comparison of modified CIAME with other methods for determination of palladium.

| Method | LOD (ng mL$^{-1}$) | RSD (%) | Sample volume (ml) | Medium salt content (%) | Reference |
|---|---|---|---|---|---|
| SPE-FAAS | 1.2 | 1.7 | 50 | – | Tokalıo et al. (2004) |
| SPE-FAAS | 3.9 | 1.7 | 6 | – | Wu et al. (2004) |
| SPE-ICP-AES | 0.2 | 3.2 | 10 | 10.1[c] | Jamali et al. (2007) |
| CPE-ICP-OES[a] | 0.3 | 3.8 | 10 | 5.8[d] | Tavakoli et al. (2008) |
| FO-LADS-DLLME[b] | 0.25 | <4 | 10 | – | Liang et al. (2009) |
| FIA-SPE-FAAS | 1.0 | 2.4 | 8 | – | Praveen et al. (2006) |
| SPE-HPLC | 1.4 | 2.8 | 10 | - | Hu et al. (2005) |
| M-CIAME spectrophotometry | 0.2 | 1.7 | 10 | Up to 40[e] | Our study |

[a] Cloud point extraction – inductively coupled plasma-optical emission spectrometry.
[b] Fiber optic-linear array detection spectrophotometry and dispersive liquid–liquid microextraction.
[c] KNO$_3$.
[d] NaCl.
[e] NaNO$_3$.

## Acknowledgment

## References

Abdolmohammad-Zadeh, H., Sadeghi, G.H., 2009. A novel microextraction technique based on 1-hexylpyridinium hexafluorophosphate ionic liquid for the preconcentration of zinc in water and milk samples. J. Anal. Chim. Acta 649, 211–217.

Anthemidis, A.N., Themelis, D.G., Stratis, J.A., 2001. Stopped-flow injection liquid–liquid extraction spectrophotometric determination of palladium in airborne particulate matter and automobile catalysts. Talanta 54, 37–43.

Arab Chamjangali, M., Bagherian, G., Azizi, G., 2005. Simultaneous determination of cobalt, nickel and palladium in micellar media using partial least square regression and direct orthogonal signal correction. J. Spectrochim. Acta A 62, 189–196.

Baghdadi, M., Shemirani, F., 2008. Cold-induced aggregation microextraction: a novel sample preparation technique based on ionic liquids. Anal. Chim. Acta 613, 56–63.

Baghdadi, M., Shemirani, F., 2009. In situ solvent formation microextraction based on ionic liquids: a novel sample preparation technique for determination of inorganic species in saline solutions. Anal. Chim. Acta 634, 186–191.

Cheng, K.L., Ueno, K., Imamura, T., 1982. Handbook of Organic Analytical Reagents, first ed. CRC Press, Boca Raton, FL. p. 425.

Chwastowska, J., Skwara, W., Sterlinska, E., Pszonicki, L., 2004. Determination of platinum and palladium in environmental samples by graphite furnace atomic absorption spectrometry after separation on dithizone sorbent. Talanta 64, 224–229.

Dai, X., Koeberl, C., Froschl, H., 2001. Determination of platinum group elements in impact breccias using neutron activation analysis and ultrasonic nebulization inductively coupled plasma mass spectrometry after anion exchange preconcentration. Anal. Chim. Acta 436, 79–85.

Daniel, S., Gladis, J.M., Rao, T.P., 2003. Synthesis of imprinted polymer material with palladium ion nanopores and its analytical application. Anal. Chim. Acta 488, 173–182.

Fan, Z., Jiang, Z., Yang, F., Hu, B., 2004. Determination of platinum, palladium and rhodium in biological and environmental samples by low temperature electrothermal vaporization inductively coupled plasma atomic emission spectrometry with diethyldithiocarbamate as chemical modifier. Anal. Chim. Acta 510, 45–51.

Fang, J., Liu, L., Yan, X., 2006. Minimization of mass interferences in quadrupole inductively coupled plasma mass spectrometric (ICP-MS) determination of palladium using a flow injection on-line displacement solid-phase extraction protocol. J. Spectrochim. Acta B 61, 864–869.

Farhadi, K., Teimouri, G., 2005. Flame atomic absorption determination of palladium in solutions after preconcentration using octadecyl silica membrane disks modified by thioridazine HCl. Talanta 65, 925–929.

Ferreira, I.M.P.L.V.O., Silva, S., 2008. Quantification of residual nitrite and nitrate in ham by reverse-phase high performance liquid chromatography/diode array detector. Talanta 74, 1598–1602.

Gharehbaghi, M., Shemirani, F., Davudabadi Farahani, M., 2009. Cold-induced aggregation microextraction based on ionic liquids and fiber optic-linear array detection spectrophotometry of cobalt in water samples. J. Hazard. Mater. 165, 1049–1055.

Godlewska Zyłkiewicz, B., Kozłowska, M., 2005. Solid phase extraction using immobilized yeast Saccharomyces cerevisiae for determination of palladium in road dust. Anal. Chim. Acta 539, 61–67.

Honikel, K.O., 2008. The use and control of nitrate and nitrite for the processing of meat products. J. Meat Sci. 78, 68–76.

Hu, Q., Yang, X., Huang, Z., Chen, J., Yang, G., 2005. Simultaneous determination of palladium, platinum, rhodium and gold by on-line solid phase extraction and high performance liquid chromatography with 5-(2-hydroxy-5-nitrophenylazo) thiorhodanine as pre-column derivatization regents. J. Chromatogr. A 1094, 77–82.

Jamali, M.R., Assadi, Y., Shemirani, F., Salavati-Niasari, M., 2007. Application of thiophene-2-carbaldehyde-modified mesoporous silica as a new sorbent for separation and preconcentration of palladium prior to inductively coupled plasma atomic emission spectrometric determination. Talanta 71, 1524–1529.

Kovalev, I.A., Bogacheva, L.V., Tsysin, G.I., Formanovsky, A.A., Zolotov, Y.A., 2000. FIA-FAAS system including on-line solid phase extraction for the determination of palladium, platinum and rhodium in alloys and ores. Talanta 52, 39–50.

Lesniewska, B.A., Godlewska, Z.B., Ruszczynska, A., Bulska, E., Hulanicki, A., 2006. Elimination of interferences in determination of platinum and palladium in environmental samples by inductively coupled plasma mass spectrometry. Anal. Chim. Acta 564, 236–242.

Liang, P., Zhao, E., Li, F., 2009. Dispersie liquid–liquid microextraction preconcentration of palladium in water samples and determination by graphite furnace atomic absorption spectrometry. Talanta 77, 1854–1857.

Lokhande, T.N., Anuse, M.A., Chavan, M.B., 1998. Liquid–liquid extraction of palladium(II) with N-n-octylaniline from hydrochloric acid media. Talanta 46, 163–169.

Marczenko, Z., 1986. Separation and Spectrophotometric Determination of Elements, first ed. E. Horwood Halsted Press, New York. p. 318.

Moawed, E.A., 2006. Preparation of novel ion exchange polyurethane foam and its application for separation and determination of palladium in environmental samples. Anal. Chim. Acta 580, 263–270.

Niazi, A., Azizi, A., Ramezani, M., 2008. Simultaneous spectrophotometric determination of mercury and palladium with Thio-Michler's Ketone using partial least squares regression and orthogonal signal correction. J. Spectrochim. Acta A 71, 1172–1177.

Praveen, R.S., Daniel, S., Prasada, R.T., Sampath, S., Sreenivasa, R.K., 2006. Flow injection on-line solid phase extractive preconcentration of palladium(II) in dust and rock samples using exfoliated graphite packed microcolumns and determination by flame atomic absorption spectrometry. Talanta 70, 437–443.

Shemirani, F., Rahnama, R.K., Jamali, M.R., Assadi, Y., Milani Hosseini, M.R., 2006. Cloud-point extraction, preconcentration, and spectrophotometric determination of palladium in water samples. Int. J. Environ. Anal. Chem. 86, 1105–1112.

Shokoufi, N., Shemirani, F., Assadi, Y., 2007. Fiber optic-linear array detection spectrophotometry in combination with dispersive liquid–liquid microextraction for simultaneous preconcentration and determination of palladium and cobalt. Anal. Chim. Acta 597, 349–356.

Soylak, M., Tuzen, M., 2008. Coprecipitation of gold(III), palladium(II) and lead(II) for their flame atomic absorption spectrometric determinations. J. Hazard. Mater. 152, 656–661.

Tang, B., Zhang, H., Wang, Y., 2004. Flow injection kinetic spectrofluorimetric determination of trace amounts of palladium. Anal. Chim. Acta 511, 17–23.

Tavakoli, L., Yamini, Y., Ebrahimzadeh, H., Nezhadali, A., Shariati, S., Nourmohammadiand, F., 2008. Development of cloud point extraction for simultaneous extraction and determination of gold and palladium using ICP-OES. J. Hazard. Mater. 152, 737–743.

Thiago, R.L.C.P., Juliana, L.C., Mauro, B., 2007. Determination of nitrate in mineral water and sausage samples by using a renewable in situ copper modified electrode. Talanta 71, 186–191.

Tokalıo, G.S., Oymak, T., Kartal, S., 2004. Determination of palladium in various samples by atomic absorption spectrometry after preconcentration with dimethylglyoxime on silica gel. Anal. Chim. Acta 511, 255–260.

Tsogas, G.Z., Giokas, D.L., Vlessidis, A.G., Evmiridis, N.P., 2008. On the re-assessment of the optimum conditions for the determination of platinum, palladium and rhodium in environmental samples by electrothermal atomic absorption spectrometry and microwave digestion. Talanta 76, 635–641.

Wu, X.Z., Liu, P., Pu, Q.S., Sun, Q.Y., Su, Z.X., 2004. Preparation of dendrimer-like polyamidoamine immobilized silica gel and its application to online preconcentration and separation palladium prior to FAAS determination. Talanta 62, 918–923.