



Ionic liquid ultrasound assisted dispersive liquid–liquid microextraction method for preconcentration of trace amounts of rhodium prior to flame atomic absorption spectrometry determination

Elaheh Molaakbari^{a,b}, Ali Mostafavi^{a,*}, Daryoush Afzali^{c,d}

^a Chemistry Department, Shahid Bahonar University of Kerman, Kerman, Iran

^b Young Research Society, Shahid Bahonar University of Kerman, Kerman, Iran

^c Environment and Nanochemistry Department, Research Institute of Environmental Science, International Center for Science, High Technology & Environmental Science, Kerman, Iran

^d Mineral Industries Research Center, Shahid Bahonar University of Kerman, Kerman, Iran

ARTICLE INFO

Article history:

Received 27 April 2010

Received in revised form 28 August 2010

Accepted 21 September 2010

Available online 29 September 2010

Keywords:

Liquid–liquid dispersive microextraction

Room temperature ionic liquid

Green separation

Ultrasonic assisted extraction

Rhodium determination

ABSTRACT

In this article, we consider ionic liquid based ultrasound-assisted dispersive liquid–liquid microextraction of trace amounts of rhodium from aqueous samples and show that this is a fast and reliable sample pre-treatment for the determination of rhodium ions by flame atomic absorption spectrometry. The Rh(III) was transferred into its complex with 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol as a chelating agent, and an ultrasonic bath with the ionic liquid, 1-octyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide at room temperature was used to extract the analyte. The centrifuged rhodium complex was then enriched in the form of ionic liquid droplets and prior to its analysis by flame atomic absorption spectrometry, 300 μ L ethanol was added to the ionic liquid-rich phase. Finally, the influence of various parameters on the recovery of Rh(III) was optimized. Under optimum conditions, the calibration graph was linear in the range of 4.0–500.0 ng mL^{-1} , the detection limit was 0.37 ng mL^{-1} ($3S_b/m$, $n=7$) and the relative standard deviation was $\pm 1.63\%$ ($n=7$, $C=200 \text{ ng mL}^{-1}$). The results show that ionic liquid based ultrasound assisted dispersive liquid–liquid microextraction, combined with flame atomic absorption spectrometry, is a rapid, simple, sensitive and efficient analytical method for the separation and determination of trace amounts of Rh(III) ions with minimum organic solvent consumption.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Rhodium, together with platinum and palladium, plays a decisive role in the performance of exhaust systems, and is used worldwide to reduce the emission of gaseous pollutants by vehicles [1,2]. The monitoring of rhodium originating from the emission of the automotive catalytic [3] converter attrition into the environment is of paramount importance for the estimation of the future risk on human health and the ecosystem. However, the concentration of this element is still relatively low in environmental compartments and thus the analysis requires very sensitive and selective methods and control of interference effects [4]. Ionic liquids (ILs) have been accepted as the new green chemicals by both the academia and the chemical industries. Because of their unique characteristics [5], this new chemical group can reduce the use of hazardous and polluting organic solvents. Their volatility is neg-

ligible and this is the basic property which characterizes them as green solvents [6–8]. Recently the ultrasound-assisted extraction of trace elements from a variety of matrices, using both bath and probe ultrasonic processors, has emerged as an efficient approach for sample preparation in trace element analysis [9,10]. Several applications have been reported for the determination of rhodium [11–13], and ultrasonic baths, i.e., the most extended ultrasonic processors, have been used for metal extraction from fish and water samples [14–16]. Classical extraction methods require large amounts of high purity solvents, which may also result in environmental and safety problems because of volatilization [17] and different methods of microextraction such as cloud point developed in [18,19]. A microextraction technique, dispersive liquid–liquid microextraction (DLLME), developed in 2007, is a type of solvent microextraction (SME). DLLME has been widely used for the extraction, preconcentration and determination of organic compounds [20,21] and metal ions [22]. This method is simple, fast and inexpensive, but the amount of disperser solvent used is relatively high, so it is possible that recoveries decrease proportionately for less hydrophobic species [23] and a third component

* Corresponding author. Fax: +98 3413222033.

E-mail address: mostafavi.ali@gmail.com (A. Mostafavi).

is necessary, which usually decreases the partition coefficient of the analytes into the extractant solvent. In this work, a green separation and preconcentration of rhodium based ultrasound-assisted dispersive liquid–liquid microextraction (USA-DLLME) method, combined with flame atomic absorption spectroscopy, is developed and its feasibility systematically investigated. Preconcentration and extraction of Rh(III) ions with complexation was carried out using 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol (5-Br-PADAP), and an ion liquid based on ultrasonic assisted dispersive liquid–liquid microextraction (IL-USA-DLLME). This was followed by flame atomic absorption spectroscopy (FAAS). IL-USA-DLLME is a technique by which ultrasonic mass transfer between substances located in different phases is brought about or accelerated [24].

2. Experimental

2.1. Instrumentation

A Varian model Spectra AA 220 (Murglave, Australia) atomic absorption spectrometer, equipped with deuterium background correction and rhodium hollow-cathode lamps as the radiation source, was used for absorbance measurements at a wavelength of 343.5 nm. All measurements were carried out in an air/acetylene flame. The instrumental parameters were adjusted according to the manufacturer's recommendations. The ionic liquid, 1-octyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [Omim][TF₂N], was homogenized using Sonorex ultrasonic baths (Bandelin, Germany) at 35 kHz for 2 min. A centrifuge (6-place, 2500 rpm) model IEC HN-S was used for phase separation and a water bath from Memmert (Buchenbach, Germany) was used. A digital pH meter 827 (Zofingen, Switzerland) equipped with a combined glass calomel electrode was used for the pH adjustment.

2.2. Reagents and sample solutions

All reagents used were of analytical grade. Distilled water was used throughout the experiment. 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol and all salts and materials used were obtained from Merck (Darmstadt, Germany). 1-octyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [Omim][TF₂N] were synthesized. Triton X-100 and Triton X-114 were purchased from Fluka (Busch, Switzerland). A stock solution of Rh(III) 1000.0 mg L⁻¹ was prepared by dissolving the appropriate amount of RhCl₃ in 1 mol L⁻¹ HCl and working standard solutions were obtained by appropriate stepwise dilution of the stock standard solutions. Platinum–iridium alloy was purchased from the Fine Wire Company (CA, USA). 12 mL Conical bottom centrifuge tubes were cleaned before use by soaking in 10% nitric acid solution for at least 24 h and then rinsing thoroughly with distilled water. A 0.01% mol L⁻¹ 5-Br-PADAP solution was prepared by dissolving the appropriate amount in ethanol. A buffer solution (pH 3.7) was prepared from 0.5 mol L⁻¹ acetic acid and 0.5 mol L⁻¹ sodium acetate.

2.3. RTIL synthesis

1-octyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [Omim][TF₂N] was synthesized as described in [25–27]. Briefly, [Omim][Cl] was prepared by adding equal amounts of 1-methylimidazole and 1-chlorooctane to a round-bottomed flask fitted with a reflux condenser and, after reacting for 72 h at 70 °C, was washed with ethylacetate. [Omim][TF₂N] was prepared by adding lithium bis (trifluoromethylsulfonyl) imide salt (1.1 equal 1-methylimidazole) to [Omim]Cl in water. After stirring for 3 h to remove chloride ions and protonic impurities, the prepared

RTIL was washed with deionized water, (the control of chloride ions was performed by an AgNO₃ test) and dried under vacuum at 70 °C for 24 h. Then a 0.6 mg μL⁻¹ RTILs solution was prepared with acetone were stored in the dark at 25–30 °C. (The amount of chloride ions was checked by an AgNO₃ test)

2.4. Extraction procedure

The 10.0 mL sample and standard solutions containing Rh(III) in the range of 4.0–500.0 ng mL⁻¹ and 5-Br-PADAP (1.7 × 10⁻⁵ mol L⁻¹) were adjusted to pH 3.7 by an acetate/acetic acid buffer in a 12 mL conical-bottom glass centrifuge tube and heated for 40 min at 95 °C to form the complex of rhodium, as reported in [28]. Complexation is usually necessary for the LPME of elements to facilitate the transfer of the target species to the organic phase. The chelating reagent, 5-Br-PADAP, played dual roles. It first forms complexes with the target Rh(III), thus promoting the LPME process and then facilitate this process. Since 5-Br-PADAP forms complexes with Rh(III), selective extraction of the later could be achieved. Then Triton X-114 (0.03% w/v), sodium nitrate (0.6%, w/v) and [Omim][TF₂N] (30 mg) were added and the tube was kept in an ultrasonic bath until a cloudy solution (resulting from the dispersion of the fine droplets of [Omim][TF₂N] by ultrasonic bath in the aqueous sample) was formed in the test tube (2 min), and the complex of Rh(III) ions extracted in the form of fine droplets of [Omim][TF₂N]. The mixture was then centrifuged at 2500 rpm for 4 min so that, the dispersed fine droplets of [Omim][TF₂N] by ultrasonic bath were sedimented at the bottom of the conical test tube. The bulk aqueous phase was removed simply by decanting the tubes. Now, the IL-phase was dissolved in 300 μL of 96% ethanol and the final solution was aspirated directly into the FAAS.

2.5. Sampling

2.5.1. Determination of metal ions in water sample

Water samples were collected from four regions in Kerman province, Iran (Kerman tap and well water, waste water of Copper factory, Sarcheshmeh and Zahra rose water Co., Bardsir). Before the analysis, the organic content of the water samples was oxidized in the presence of 1% H₂O₂ and then concentrated nitric acid was added. These water samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm to remove particulate matter. The pH of the filtered water samples were adjusted to approximately 3.7 using sodium acetate/acetic acid buffer solution.

2.5.2. Digestion of leaves of rose flower

Leaves of rose flower were purchased from Lalehzar of Bardsir in Kerman, Iran. Then, they were dried and sieved through a small mesh size. A 20.0 g leaves of rose flower was burned for 30 min and the charred material was transferred to furnace for 3 h at 600 °C. The residue was cooled, treated with 10 mL concentrated chloridric acid and evaporated by hot plates, so that all the metals changed to respective ions. The solid residue was dissolved in water, filtered and diluted. The volume of the filtrate was made up to 100.0 mL with distilled water in a calibrated flask. 10.0 mL from the dissolved solution of metals concentration was determined after suitable preconcentration using FAAS.

3. Results and discussion

In order to reach optimum experimental conditions for quantitative extraction of rhodium ions via IL-USA-DLLME, the influence of different parameters such as concentration of NaNO₃ and 5-Br-PADAP, pH, ionic liquid amounts, centrifugation and sonication times, were investigated. In the IL-USA-DLLME/FAAS method,

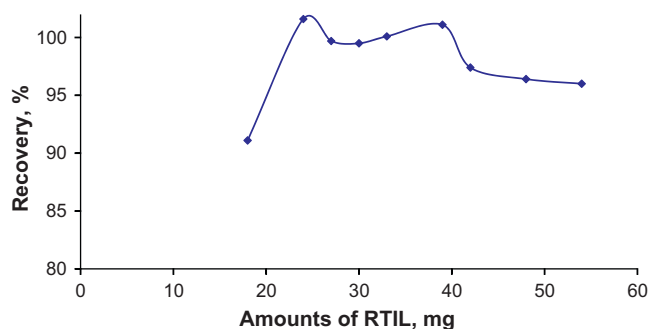


Fig. 1. Effect of amount of RTIL on the recovery of rhodium. Utilized conditions: Rhodium 20.0 ng mL^{-1} , pH 3.7, 5-Br-PADAP, 1.7×10^{-5} , NaNO_3 0.6% (w/v), Triton X-114 0.03% (w/v), and diluting agent $300 \mu\text{L}$ ethanol.

enrichment factor and percentage of extraction are calculated as follows:

$$\text{Percentage of extraction} = \frac{C_o V_o}{C_{\text{aq}} V_{\text{aq}}} \times 100 \quad (1)$$

$$\text{Enrichment factor} = \frac{C_o}{C_{\text{aq}}} \quad (2)$$

where V and C are the volume and concentration and the suffixes o and aq indicate organic and aqueous phases, respectively. C_o was calculated from the calibration graph of a standard solution of the relevant metal in ethanol.

3.1. Selection of ionic liquid

The solvent properties of ILs are mainly determined by the ability of the salt to act as a hydrogen bond donor and/or acceptor and the degree of localization of the charges on the anions [5,29]. Charge distribution on the anions, H-bonding ability, polarity and dispersive interactions are the main factors that influence the physical properties of ILs [30]. Imidazolium-based ILs are highly ordered hydrogen-bonded solvents and have a significant effect on chemical reactions and processes. Due to their immiscibility with water, ILs based on $[\text{TF}_2\text{N}]$ anions are preferred as solvents for forming biphasic systems. The green character of ILs has been usually related to their vapor pressure which is exceedingly small. Although, in general, ILs will not evaporate and thus will not cause air pollution, it does not mean that they will not harm the environment. TF_2N^- is much more stable in the presence of water and also has other advantages because of its hydrophobicity [5,31].

3.2. Effect of ionic liquid amount

The viscosity of ILs is high and handling is difficult, so working solutions ($[\text{Omim}][\text{TF}_2\text{N}]$, $(0.6 \text{ mg } \mu\text{L}^{-1})$) were prepared in acetone. The amount of $[\text{Omim}][\text{TF}_2\text{N}]$ IL used in this preconcentration procedure is a critical factor for obtaining high recovery of the analyte and, at the same time, obtaining a high volume ratio of the phases. Therefore the extraction system was carefully studied in order to define the lowest IL-phase mass necessary for achieving the highest preconcentration factor possible. The variation in the recovery as a function of the amount of IL, added to 10.0 mL sample, was investigated in the range of $18\text{--}54 \text{ mg}$. It was observed that the extraction efficiency of the proposed system was affected significantly by the IL amount. Fig. 1 shows that the efficiency of extraction reaches a maximum for an IL amount of 24 mg and no significant changes were observed on the extraction efficiency for higher IL amounts. Therefore, in order to achieve a good enrichment factor, low viscosity and relatively high hydrophobicity, 30 mg IL was chosen as optimum.

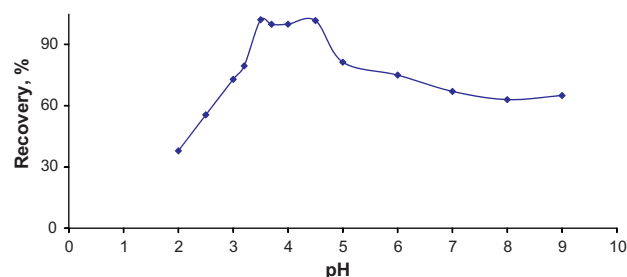


Fig. 2. Effect of pH on the recovery of rhodium. Conditions are same as in Fig. 1 except for pH.

3.3. Effect of PH

In the IL-USA-DLLME method, the pH of the sample solution is a very important factor which affects the formation of a complex with sufficient hydrophobicity and the subsequent extraction. The effect of pH on the complex formation was investigated in the pH range of $2\text{--}9$ while maintaining the other parameters constant. For the $\text{pH} < 3$ nitrogens of 5-BrPADAP are protonated and sites of bonding to Rh are limited, for the pH in the range $3.5\text{--}4.5$ hydroxyl group of 5-Br-PADAP is protonated and Rh bonded to amide nitrogens and complex was formed. The transformation of Rh(III) to Rh(OH)_3 is responsible for a decrease in the efficiency of Rh(III) separation and preconcentration at alkali pHs. The results (Fig. 2) reveal that the recovery is nearly constant in the pH range of $3.5\text{--}4.5$. Accordingly, a pH approximately of 3.7 was selected for further experiments.

3.4. Effect of 5-Br-PADAP concentration

The influence of the 5-Br-PADAP concentration on the IL-USA-DLLME extraction efficiency of Rh(III) ion was evaluated in the concentration range of $0.3\text{--}2.3 \times 10^{-5} \text{ mol L}^{-1}$. The results (Fig. 3) show that the signal of Rh(III) increases with increase of 5-Br-PADAP concentration upto $1.7 \times 10^{-5} \text{ mol L}^{-1}$, and then stays constant. Therefore, a concentration of $1.7 \times 10^{-5} \text{ mol L}^{-1}$ 5-Br-PADAP was chosen.

3.5. Effect of salt concentration

Previous research shows that by increasing the salt concentration in single drop microextraction (SDME), DLLME [32,33] and hollow fiber liquid phase microextraction (HF-LPME) [34,35], the volume of extractant phase changes due to a salting in or salting out effect [36]. However, it is an interesting property of ILs that in the presence of a high content of salt, the solubility of $[\text{Omim}][\text{TF}_2\text{N}]$ does not vary and, because of the high density of ILs, the fine droplets of extractant phase can settle even in the saturated

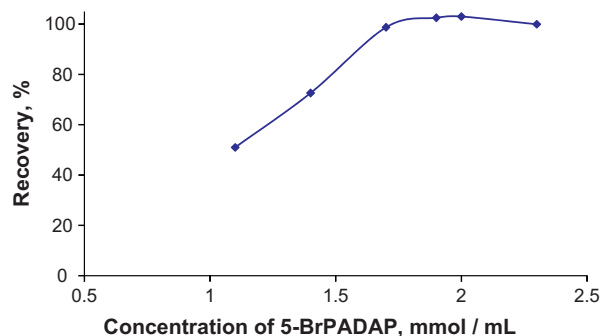


Fig. 3. Effect of 5-Br-PADAP concentration on the recovery of rhodium. Conditions are same as in Fig. 1 except for concentration of 5-Br-PADAP.

Table 1
Effect of foreign ions on the recovery of rhodium ion^a.

Diverse ion	Tolerance limit (μg)	Recovery (%)
Fe ³⁺	20	102.8
Au ³⁺	20	99.3
Cr ³⁺	25	98.3
Co ²⁺	30	96.5
Ni ²⁺	30	97.4
Ir ³⁺	50	98.5
Cu ²⁺	50	100.4
Bi ³⁺	100	97.2
Ag ⁺	130	96.2
Hg ²⁺	150	96.8
Al ³⁺	150	98.1
Zn ²⁺	350	103.6
Cd ²⁺	370	97.6
Pb ²⁺	1000	101.1
Ca ²⁺	2000	101.4
SO ₄ ²⁻	500	95.7
CH ₃ COO ⁻	1000	101.5
SCN ⁻	2000	99.2
CO ₃ ²⁻	2000	97.5
EDTA	30	98.6

^a For masking interferences of these ions, EDTA was used.

^a Initial samples contained 2.0 μg Rh(III) and different amounts of diverse ions in 10 mL water.

solutions [37,38], hence avoiding the adsorption of analytes on the surface of sample containers. Also, due to the very low solubility in water of hydrophobic ILs, residual salinity from the matrix is negligible [36]. It is therefore expected that in our method the volume of the extraction phase will not be significantly influenced by increasing salt content. NaNO₃ was chosen in order to study the salt effect in the range of 0–9% (w/v). Recovery of rhodium slightly increased upto 0.4% (w/v) as a result of salting out effect and then did not vary from 0.6% to 9% (w/v). Hence the IL-USA-DLLME method can be employed for the separation and preconcentration of Rh(III) ion from salty samples with a concentration of upto 9% (w/v). A concentration of 0.6% (w/v) NaNO₃ was selected for subsequent experiments for increasing recovery.

3.6. Type and volume of anti-sticking agent

It was observed that after centrifugation, some of the IL-phase sticks to the wall of the centrifuge tube. In order to overcome this problem, non-ionic surfactants were added to the sample solutions [39]. In the presence of non-ionic surfactants, molecules of the surfactant surrounded the fine droplets of IL, during phase separation. Hence, interactions of IL with the wall of the centrifuge tube decreased and consequently, the IL-phase did not stick to the wall of the centrifuge tube. The effects of two non-ionic surfactants (Triton X-114 and Triton X-100) were investigated and compared. In the presence of Triton X-100, recovery decreased while, using Triton X-114, recovery increased, and so, Triton X-114 was selected as the anti-sticking agent. A concentration of 0.03% (w/v) was chosen as the optimum concentration in the IL-USA-DLLME method.

3.7. Effect of sonication time

The high viscosity of extraction solvent decelerates the mass transfer of the analyte from the aqueous solution. In the IL-USA-DLLME procedure, the interface between the extraction solvent and the bulk aqueous sample was enormously enlarged by forming a cloudy solution [24]. Consequently dispersion is the key step to determining whether extraction is successfully carried out or not. Hence, sonication time plays an important role in this new procedure. Time will make the extracting solvent disperse more in the aqueous solution and result in an excellent cloudy solution. The effect of sonication time was evaluated in the range of 1–5 min

Table 2
Determination of rhodium in the real and spiked samples.

Sample	Spiked (ng mL^{-1})	Found ^a (ng mL^{-1})	Recovery (%)
Tap water (Kerman)	0.0	N.D. ^b	–
	8.0	7.8 \pm 0.1	97.5
	80.0	76.0 \pm 0.7	95.0
Well water (Kerman)	0.0	N.D.	–
	8.0	7.6 \pm 0.1	95.0
	80.0	77.0 \pm 0.5	96.2
Wastewater (Copper factory, Sarchashmeh, Rafsanjan)	0.0	N.D.	–
	8.0	7.7 \pm 0.4	96.2
	80.0	76.1 \pm 0.6	95.1
Rose water (Zahra factory, Bardsir)	0.0	N.D.	–
	8.0	8.0 \pm 0.0	100.7
	80.0	81.2 \pm 0.7	101.5
Rose flower bud (Lalehzar, Bardsir)	0.0	N.D.	–
	8.0	7.6 \pm 0.5	95.8
	80.0	76.8 \pm 0.5	96.0
Rose flower (Lalehzar, Bardsir)	0.0	N.D.	–
	8.0	7.8 \pm 0.1	97.8
	80.0	81.7 \pm 1.1	102.1

Conditions and instrumental settings were the same as in Fig. 1.

^a Mean \pm standard deviation ($n=3$).

^b N.D.: Not detected.

and it was seen that sonication for at least 2 min was necessary to form a complete cloudy solution. Hence 2 min was chosen for the dispersive procedure.

3.8. Effect of centrifugation time

Centrifugation time is also an important parameter that influences the separation of ionic liquid from the water phase. A centrifugation time in the range of 1–10 min at the rate of 2500 rpm was investigated. A very short centrifugation time can not insure satisfactory phase separation, and a longer centrifugation time causes the ionic liquid to again dissolve in water phase. Therefore, 4 min was chosen as optimum.

3.9. Effect of coexisting ion

In order to demonstrate the selectivity of the developed microextraction method for the determination of rhodium, the effect of common coexistence in water samples was investigated and the potential interference in the IL-USA-DLLME method due to the competition of other metal ions for the chelating agent and their subsequent co-extraction with Rh(III) was evaluated. A given species was considered to interfere if it resulted in a $\pm 5\%$ variation

Table 3
Determination of rhodium in a platinum–iridium alloy.

Composition (%)	Certified value (%)	Found ^a (%)	Recovery (%)
Pt, 55; Ir, 28; Cu, 3.0; Fe, 3.5; Pd, 3.5	Rh, 7.0	6.65 \pm 0.06	95.0

^a Mean \pm standard deviation ($n=3$).

Table 4
Comparison of our method with other methods for preconcentration and determination of rhodium.

Determination technique	Preconcentration method	Enrichment factor	Detection limit (ng mL ⁻¹)	RSD (%)	Linear range (ng mL ⁻¹)	Ref.
LI-TLS ^a /ETAAS ^b	CPE ^c	450	0.06	–	0.5–50	[40]
(ICP-AES) ^d	ETV ^e	–	0.8	2.4	–	[41]
ETAAS	Mg–W cell-electrodeposition	–	13	4.1	–	[42]
ETAAS	IEM ^f	20	0.3	1.8	0.9–50	[43]
DPP ^g	SPE ^h	–	60	0.72	250–7500	[44]
FIA-FAAS	SPE	–	3	–	–	[45]
FAAS	IL-USA-DLLME	29.1	0.37	1.63	4.0–500	This work

^a LI-TLS: Laser induced-thermal lens spectrometry.

^b ETAAS: Electrothermal atomic absorption spectrometry

^c CPE: Cloud point extraction.

^d ICP-AES: Inductively coupled plasma atomic emission spectrometry

^e ETV: Electrothermal vaporization

^f IEM: Ion exchange microcolumn.

^g DPP: Differential pulse polarography.

^h SPE: Solid phase extraction.

of the FAAS signal, the results are shown in Table 1. Most of cations and anions examined, did not interference with the microextraction and determination of Rh(III). However, some of the species tested, such as Cu²⁺ and Co²⁺ did interfere. Such interferences were eliminated in the presence of a proper masking agent, such as EDTA. The results indicate that the method is applicable to the analysis of Rh(III) in different water samples.

3.10. Analytical performance

The analytical characteristics of the IL-USA-DLLME method, including quantification, reproducibility, limit of detection, correlation coefficient, enrichment factor, linear range, calibration graph and precision were determined to evaluate method performance. The calibration curve was obtained after the standard series were subjected to the IL-USA-DLLME and then determined by flame atomic absorption spectrometry. Linearity was obtained with rhodium concentration in the range of 4.0–500.0 ng mL⁻¹, for 10.0 mL of solution. The linear regression equation is $A = 1.9167C + 0.002$ (where A is the absorbance and C is the concentration of Rh(III) ($\mu\text{g mL}^{-1}$) in the final solution with a correlation coefficient of 0.9988. The enrichment factor, calculated by Eq. (2), was 29.3 and the limit of detection and quantification were determined by $3S_b/m$ and $10S_b/m$ respectively. The standard deviation of the blank, S_b was equal to 2.3×10^{-4} and the slope of the calibration curve after extraction, $m = 1.8737 \text{ ng mL}^{-1}$. The detection limit ($n = 7$) was found to be 0.37 ng mL^{-1} . The relative standard deviation (RSD) for seven replicates of 200 ng mL^{-1} of Rh (III) was $\pm 1.63\%$.

3.11. Validity of the method

For evaluating the accuracy of the IL-USA-DLLME method on rhodium, it was applied to determine Rh(III) in various samples with different concentration and in platinum–iridium alloy.

3.11.1. Analysis of water samples

The optimized method was used for the determination of Rh in well, tap and wastewater samples. Reliability was checked by spiking experiments and independent analysis. The results of this study for three different water samples are presented in Table 2. Recovery, using spiked samples, shows the capability of our method for the determination of Rh (III). In fact, the recovery values calculated for added standard solutions were always higher than 95%, thus confirming the accuracy of the procedure and its independence from matrix effects.

3.11.2. Analysis of a platinum–iridium alloy

In order to test the applicability of the proposed method for the analysis of real samples, a platinum–iridium alloy was analyzed. Seven mL of aqua regia was added to 5.0 mg of the alloy with known composition and the solution was evaporated. Then five milliliters of concentrated hydrochloric acid was added and the solution was warmed, transferred to a 100.0 mL volumetric flask, and made up to mark with distilled water. An aliquot of this solution was taken and rhodium was determined by the general procedure. Three determinations were made. The results (Table 3) indicate the effectiveness and accuracy of the IL-USA-DLLME method.

3.12. Comparison of IL-USA-DLLME with other methods

A comparison of IL-USA-DLLME combined with FAAS with other techniques for separation and determination of Rh(III) is given in Table 4. In comparison with the other reported methods [40–45], the IL-USA-DLLME/FAAS shows a comparatively low detection limit (0.37 ng mL^{-1}), a high enrichment factor (29.3) and better dynamic range (4.0–500.0) for Rh(III) in a short extraction time (2 min). In fact, the IL-USA-DLLME has higher enrichment factor and lower detection limit (0.37 ng mL^{-1}) than all the other methods except LI-TLS/CPE/ETAAS [40]. This could be the result of the determination system. Also, because our method has low toxicity we may say that it is green. The relative standard deviation (1.63%) is also better than that obtained using FAAS determination alone. Moreover, since this method uses only 300 μL ethanol, it is free of volatile organic compounds. All these results indicate that IL-USA-DLLME is a reproducible, rapid, environmentally friendly and simple technique that can be used for preconcentration of metal ions like rhodium from water and alloy samples.

4. Conclusion

It is well known that ultrasound is a powerful aid in the acceleration of various steps in the process of separation and extraction such as homogenizing, emulsion forming, and mass transferring between immiscible phases. Ultrasound-assisted LLE and emulsification extraction have been successfully used as alternatives to LLE, and can attain extraction equilibrium in a short time. Hence an ultrasonic bath was used to accelerate the formation of a cloudy dispersive extraction mixture in the short time of 2 min. The sample preparation time and the consumption of volatile organic solvents were minimized using the IL-USA-DLLME technique, which does not use volatile organic compounds, is solvent-free and has no need of a dispersive solvent compared with the conventional DLLME. The use of 1-octyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide as an extraction solvent, removes the need of an ice bath

for the creation of a cloudy solution. The Rh(III) complex showed excellent performance in IL-USA-DLLME. This method is safe, rapid, simple, and reproducible. It is applicable to the qualitative and quantitative analysis of Rh and uses small volumes of sample and μ -scale size of [Omim][TF₂N]. The high enrichment factor along with easy operation is another advantage. Also, the method has a low detection limit that is comparable with, or better than in other methodologies developed for Rh species determination (Table 4), and has a good calibration range with a reduced amount of sample. Therefore, the method is of interest, especially for routine analytical work. The solution is cooled during centrifuging, fine droplets of extractant phase are continuously formed and analytes extracted are transferred to the bottom of the centrifuge tube the method can be operated continuously, and may be automated. Of course, individual projects require testing the capability of this property.

Acknowledgment

This paper is dedicated to the memory of the founder of Kerman University, Mr. Alireza Afzalipour, on the occasion of the centenary of his birth.

References

- [1] L. Swarczfter, F. Eduardo Mendes, E.L. La Rovere, Enhancing the effects of the Brazilian program to reduce atmospheric pollutant emissions from vehicles, *Transport. Res. D. Tr. E* 10 (2005) 153–160.
- [2] C. Colombo, A.J. Monhemius, J.A. Plant, Platinum, palladium and rhodium release from vehicle exhaust catalysts and road dust exposed to simulated lung fluids, *Ecotoxicol. Environ. Saf.* 71 (2008) 722–730.
- [3] S. Tagliafeti, R.A. Kijppel, A. Baiker, Influence of rhodium- and ceria-promotion of automotive palladium catalyst on its catalytic behavior under steady-state and dynamic operation, *Appl. Catal. B. Environ.* 15 (1998) 159–177.
- [4] C.B. Ojeda, F.S. Rojas, Determination of rhodium: since the origins until today Spectrophotometric methods, *Talanta* 67 (2005) 1–19.
- [5] T. Welton, Room temperature ionic liquids: solvents for synthesis and catalysis, *Chem. Rev.* 99 (1999) 2071–2084.
- [6] C. Chiappe, D. Pieraccini, Review commentary: ionic liquids: solvent properties and organic reactivity, *J. Phys. Org. Chem.* 18 (2005) 275–297.
- [7] S. Keskin, D.K. Talay, U. Akman, O. Hortaçsu, A review of ionic liquids towards supercritical fluid applications, *J. Supercrit. Fluids* 43 (2007) 150–180.
- [8] H. Zhao, S. Xia, P. Ma, Review: use of ionic liquids as green solvents for extractions, *J. Chem. Technol. Biotechnol.* 80 (2005) 1089–1096.
- [9] K. Ashley, R.N. Andrews, L. Cavazos, M. Demange, Ultrasonic extraction as a sample preparation technique for elemental analysis by atomic spectrometry, *J. Anal. At. Spectrom.* 16 (2001) 1147–1153.
- [10] D.S. Junior, F.J. Krug, M.D.G. Pereira, M. Korn, Currents on ultrasound-assisted extraction for sample preparation and spectroscopic analytes determination, *Appl. Spectrosc. Rev.* 41 (2006) 305–321.
- [11] C.B. Ojeda, F.S. Rojas, Determination of rhodium: since the origins until today; Atomic absorption spectrometry, *Talanta* 68 (2006) 1407–1420.
- [12] C.B. Ojeda, F.S. Rojas, Determination of rhodium: since the origins until today ICP-OES and ICP-MS, *Talanta* 71 (2007) 1–12.
- [13] S. Ghaseminezhad, D. Afzali, M.A. Taher, Flame atomic absorption spectrometry for the determination of trace amount of rhodium after separation and preconcentration on to modified multiwalled carbon nanotubes as a new solid sorbent, *Talanta* 80 (2009) 168–172.
- [14] H.E. Azouzi, M.L. Cervera, M.L. Guardia, Multielemental analysis of mussels samples by atomic absorption spectrometry after room temperature sonication, *J. Anal. At. Spectrom.* 13 (1998) 533–538.
- [15] N. Manutsewee, W. Aeungmaitrepirom, P. Varanusupakul, A. Imyim, Determination of Cd, Cu and Zn in fish and mussel by AAS after ultrasound assisted acid leaching extraction, *Food Chem.* 101 (2007) 817–824.
- [16] M.H. Entezari, A.A. Shamel, Phase-transfer catalysis and ultrasonic waves I Cannizzaro reaction, *Ultrason. Sonochem.* 7 (2000) 169–172.
- [17] A. Heintz, Recent developments in thermodynamics and thermophysics of non-aqueous mixtures containing ionic liquids, *J. Chem. Thermodyn.* 37 (2005) 259–252.
- [18] M. Ghaedi, Pyrimidine-2-thiol as selective and sensitive ligand for preconcentration and determination of Pb²⁺, *Chem. Anal.* 51 (2006) 593–602.
- [19] M. Ghaedi, A. Shokrollahi, A.H. Kianfar, A.S. Mirsadeghi, A. Pourfarokhi, M. Soy-lak, The determination of some heavy metals in food samples by flame atomic absorption spectrometry after their separation-preconcentration on bis salicyl aldehyde, 1,3 propan diimine (BSPDI) loaded on activated carbon, *J. Hazard. Mater.* 154 (2008) 128–134.
- [20] E. Zhao, W. Zhao, L. Han, S. Jiang, Z. Zhou, Application of dispersive liquid-liquid microextraction for the analysis of organophosphorus pesticides in water-melon and cucumber, *J. Chromatogr. A* 1175 (2007) 137–140.
- [21] M.A. Farajzadeh, M. Bahram, J.A. Jonsson, Dispersive liquid-liquid microextraction followed by high-performance liquid chromatography-diode array detection as an efficient and sensitive technique for determination of antioxidants, *Anal. Chim. Acta* 591 (2007) 69–79.
- [22] A. Bidari, E.Z. Jahromi, Y. Assadi, M.R.M. Hosseini, Monitoring of selenium in water samples using dispersive liquid-liquid microextraction followed by iridium-modified tube graphite furnace atomic absorption spectrometry, *Microchem. J.* 87 (2007) 6–12.
- [23] M. Gharehbaghi, F. Shemirani, M.D. Farahani, Cold-induced aggregation microextraction based on ionic liquids and fiber optic-linear array detection spectrophotometry of cobalt in water samples, *J. Hazard. Mater.* 165 (2009) 1049–1055.
- [24] S. Li, S. Cai, W. Hu, H. Chen, H. Liu, Ionic liquid-based ultrasound-assisted dispersive liquid-liquid microextraction combined with electrothermal atomic absorption spectrometry for a sensitive determination of cadmium in water samples, *Spectrochim. Acta B* 64 (2009) 666–671.
- [25] B.R. Hyun, S.V. Dzyuba, R.A. Bartsch, E.L. Quitevis, Intermolecular dynamics of room-temperature ionic liquids: femtosecond optical Kerr effect measurements on 1-alkyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimides, *J. Phys. Chem. A* 106 (2002) 7579–7585.
- [26] S.V. Dzyuba, R.A. Bartsch, Influence of structural variations in 1-alkyl (aralkyl)-3-methylimidazolium hexafluorophosphates and bis(trifluoromethylsulfonyl) imides on physical properties of the ionic liquids, *Chem. Phys. Chem.* 3 (2002) 161–166.
- [27] G.T. Wei, Z. Yang, C.J. Chen, Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions, *Anal. Chim. Acta* 488 (2003) 183–192.
- [28] J.R. Stokley, W.D. Jacobs, Simultaneous spectrophotometric determination of rhodium and iridium with 1-(2-pyridylazo)-2-naphthol, *Anal. Chem.* 35 (1963) 149.
- [29] J. Dupont, C.S. Consorti, J. Spencer, Room-temperature molten salts: neoteric green solvents for chemical reactions and processes, *J. Braz. Chem. Soc.* 11 (2000) 337–344.
- [30] F. Mutelet, V. Butet, J.N. Jaubert, Application of inverse gas chromatography and regular solution theory for characterization of ionic liquids, *Ind. Eng. Chem. Res.* 44 (2005) 4120–4127.
- [31] S.N.V.K. Aki, J.F. Brennecke, A. Samanta, How polar are room temperature ionic liquids, *Chem. Commun.* 5 (2001) 413–414.
- [32] P. Liang, J. Xu, Q. Li, Application of dispersive liquid-liquid microextraction and high-performance liquid chromatography for the determination of three phthalate esters in water samples, *Anal. Chim. Acta* 609 (2008) 53–58.
- [33] M.T. Naseri, P. Hemmatkhan, M.R. Milani Hosseini, Y. Assadi, Combination of dispersive liquid-liquid microextraction with flame atomic absorption spectrometry using microsample introduction for determination of lead in water samples, *Anal. Chim. Acta* 610 (2008) 135–141.
- [34] D.K. Dubej, D. Pardasani, A.K. Gupta, M. Palit, P.K. Kanaujia, V. Tak, Hollow fiber-mediated liquid-phase microextraction of chemical warfare agents from water, *J. Chromatogr. A* 1107 (2006) 29–35.
- [35] J.F. Peng, J.F. Liu, X.L. Hu, G.B. Jiang, Direct determination of chlorophenols in environmental water samples by hollow fiber supported ionic liquid membrane extraction coupled with high-performance liquid chromatography, *J. Chromatogr. A* 1139 (2007) 165–170.
- [36] M. Baghdadi, F. Shemirani, 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 (2009) 186–191.
- [37] C. Jungnickel, J. Luczak, J. Ranke, J.F. Fernandez, A. Muller, J. Thoming, Micelle formation of imidazolium ionic liquids in aqueous solution, *Colloids Surf. A* 316 (2008) 278–284.
- [38] B. Dong, X. Zhao, L. Zheng, J. Zhang, N. Li, T. Inoue, Aggregation behavior of long-chain imidazolium ionic liquids in aqueous solution: micellization and characterization of micelle microenvironment, *Colloids Surf. A* 317 (2008) 666–672.
- [39] M. Baghdadi, F. Shemirani, Cold-induced aggregation microextraction: a novel sample preparation technique based on ionic liquids, *Anal. Chim. Acta* 613 (2008) 56–63.
- [40] N. Shokoufi, F. Shemirani, Laser induced-thermal lens spectrometry after cloud point extraction for the determination of trace amounts of rhodium, *Talanta* 73 (2007) 662–667.
- [41] Z. Fan, Z. Jiang, F. Yang, B. Hu, 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 (2004) 45–51.
- [42] S. Kaneco, J. Ogawa, K. Ohta, S. Itoh, T. Mizuno, Determination of rhodium in waters by Mg–W cell-electrodeposition and electrothermal atomic absorption spectrometry, *Talanta* 46 (1998) 139–143.
- [43] F.S. Rojas, C.B. Ojeda, J.M.C. Pavon, On-line preconcentration of rhodium on an anion-exchange resin loaded with 1,5-bis(2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide and its determination in environmental samples, *Talanta* 64 (2004) 230–236.
- [44] R.K. Dubej, A. Bhalotra, M.K. Gupta, B.K. Puri, Differential pulse polarographic determination of rhodium (III) and ruthenium (III) in synthetic samples after preconcentration of their quinolin-8-olate complexes onto microcrystalline naphthalene, *Microchem. J.* 58 (1998) 117–126.
- [45] I.A. Kovalev, L.V. Bogacheva, G.I. Tsytsin, A.A. Formanovsky, Y.A. Zolotov, FIA-FAAS system including on-line solid phase extraction for the determination of palladium, platinum and rhodium in alloys and ores, *Talanta* 52 (2000) 39–50.