

## Determination of Rhodium in Water Samples Using Ion Liquid Based on Ultrasonic Assisted Dispersive Liquid-Liquid Microextraction Coupled with Spectrophotometric Technique

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### Abstract

Ionic liquid based ultrasound-assisted dispersive liquid-liquid microextraction of trace levels of Rh<sup>3+</sup> ions from aqueous samples is illustrated, to investigate a rapid and reliable sample pretreatment to determine Rh<sup>3+</sup> ions spectrophotometrically. The Rh<sup>3+</sup> is converted into its complex with 5-(4-chlorophenylazo)-6-hydroxy-pyrimidine-2,4-dione (CPAHPD) as a complexing agent, and an ultrasonic bath is used with the ionic liquid, 1-octyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) imide at room temperature is applied to extract the analyte. The centrifuged rhodium complex is enhanced in the form of ionic liquid droplets and prior to its spectrophotometric analysis, 250  $\mu$ L ethanol is added to the ionic liquid-rich phase. Finally, the influence of various parameters on the recovery of Rh<sup>3+</sup> is examined and optimized. Under optimum conditions, the calibration graph is linear in the range of 10–260 ng mL<sup>-1</sup>, the detection limit is 3.2 ng mL<sup>-1</sup> (3Sb/m, n=7) and the relative standard deviation is  $\pm$  1.78 % (n=7, C = 150 ng mL<sup>-1</sup>). Comparison with other procedures, the proposed procedure reduces the danger of exposure to toxic solvents, applied for extraction in conventional extraction procedures, it also requires a shorter extraction time. The method is successfully validated by the analysis of real samples and compared statistically with FG-AAS method. The proposed method is successfully validated by the analysis different complex materials such as environmental water and alloy samples and compared statistically with ETAAS method.

### Keywords

Liquid-Liquid Dispersive Microextraction; Rhodium Determination; Ultrasonic Assisted Extraction; Green Separation; Environmental Analysis.

## 1. INTRODUCTION

At present there is growing demand of platinum group metals, the name platinum group metals include the six elements: Ruthenium, Rhodium, Platinum, Palladium, Osmium, and Iridium. In the past few decades these metals have found new applications outside the jewellery and decorative industries due to its excellent physical and chemical properties and are used extensively for electronic devices, catalysis in the chemical and petroleum refining industries, glass industries, pharmaceutical industries etc. Rhodium is one of the most expensive platinum group metal, a rare, silvery white, hard and chemically inert transition metal, and is indispensable for automotive catalytic converters. Rhodium compounds are encountered relatively rarely by most people. All rhodium compounds should be regarded as highly toxic and as carcinogenic. Compounds of rhodium stain the skin, eyes and respiratory tract (mouth, throat, and lungs) very strongly. The primary uses of rhodium are in alloys and as catalysts for industrial processes. Literature survey reveals that many extractants are used for

the separation of rhodium(III) but very few of them give quantitative results with positive merits. Hence low abundance, high price, low natural occurrence, and a wide range of applications, demand a novel method for separation and determination of rhodium. Normally, it is difficult for metals such as palladium, platinum, and rhodium to form complex with extractant at the room temperature, while at a high temperature the water-insoluble complex can form easily and rapidly. In 1969, Fujinaga et al. developed a method involving the extraction of the complex at high temperature followed by the solid liquid separation at room temperature. Gao has done much work on the solid-liquid extraction [1–4]. Literature survey reveals that various reagents [5–12] are available for the spectrophotometric determination of Rh<sup>3+</sup> ion.

Ionic liquids (ILs) have been accepted as the new green chemicals by both the academia and the chemical industries. Because of their unique characteristics [13], this new chemical group can

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reduce the use of hazardous and polluting organic solvents. Their volatility is negligible and this is the basic property which characterizes them as green solvents [14,15]. 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 [16,17]. Classical extraction methods require large amounts of high purity solvents, which may also result in environmental and safety problems because of volatilization [18] and different methods of microextraction such as cloud point developed in [19,20]. 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 [21,22] and metal ions [23]. 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 [24] and a third component 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) procedure, combined with spectrophotometry, is developed and its feasibility systematically investigated. Preconcentration and extraction of  $\text{Rh}^{3+}$  ions after complex formation was carried out using 5-(4'-chlorophenylazo)-6-hydroxy-pyrimidine-2,4dione (CPAHPD) and an ion liquid based on ultrasonic assisted dispersive liquid-liquid microextraction (IL-USA-DLLME). This was followed by spectrophotometric analysis. IL-USADLLME is a technique by which ultrasonic mass transfer between substances located in different phases is brought about or accelerated [25].

## 2. EXPERIMENTAL

### 2.1. Instrumentation

An Orion research model 601 A/digital ionalyzer pH meter was used for checking the pH of solutions. ETAAS instrument (Perkin Elmer model Analyst 100, USA) was used. A Perkin-Elmer Lambda 12 UV/Vis spectrometer was used for recording absorbance spectra with 1.0-mm quartz cell. The ionic liquid, 1-octyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [Omim] [TF<sub>2</sub>N], was homo-genized using Sonorex ultrasonic baths (Bandelin, Germany) at 35 kHz for 2.0 min. A water bath with good temperature control and a centrifuge with 25-mL calibrated centrifuge tubes (Superior, Germany) were used to accelerate the phase separation process.

### 2.2. Reagents and sample solutions

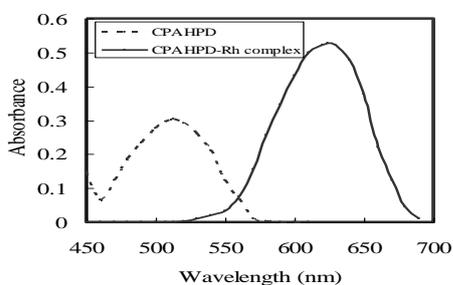
A standard stock solution of rhodium ( $1000.0 \mu\text{g mL}^{-1}$ ) was prepared by dissolving spectroscopically pure  $(\text{NH}_4)_2\text{RhCl}_5 \cdot \text{H}_2\text{O}$  (E-Merck, Darmstadt, Germany) in  $1.0 \text{ mol L}^{-1}$  HCl. Working solutions were prepared by appropriate dilution of the stock solution with water. [Omim][TF<sub>2</sub>N] were synthesized as described in [26,27]. Triton X-100 and Triton X-114 were purchased from Fluka (Busch, Switzerland). 25 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.

5-(4'-chlorophenylazo)-6-hydroxypyrimidine-2,4-dione (CPAHPD) used in the present investigation was prepared according to the procedure described previously [28]. An appropriate weight was dissolved in 100 mL of absolute ethanol ( $5 \times 10^{-3} \text{ mol L}^{-1}$ ). The solution was stable for more than two weeks. The solutions of different pH 2.75–11.63 acetate, phosphate, thiel and universal buffers were prepared as described early [29]. Acetonitrile solvent and potassium iodide salt were purchased from Merck.

### 2.4. Extraction procedure

The 20 mL sample and standard solutions containing  $\text{Rh}^{3+}$  ion in the range of 0.25–6.50  $\mu\text{g mL}^{-1}$  and 2.0 mL of CPAHPD ( $5 \times 10^{-3} \text{ mol L}^{-1}$ ) were adjusted to pH 4.5 by adding 3.0 mL of an acetate buffer in a 25 mL conical-bottom glass centrifuge tube and heated for 10 min at 90 °C to form the complex of rhodium. Complexation is usually necessary for the LPME of elements to facilitate the transfer of the target species to the organic phase. The complexing reagent, CPAHPD, played dual roles. It first forms complexes with the target  $\text{Rh}^{3+}$ , thus promoting the LPME process and then facilitates this process. Since CPAHPD forms complexes with  $\text{Rh}^{3+}$ , selective extraction of the later could be achieved. Then 1.0 mL Triton X-100 (0.05% w/v), 1.0 mL sodium nitrate (1.0%, w/v) and [Omim][TF<sub>2</sub>N] (60 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][TF<sub>2</sub>N] by ultrasonic bath in the aqueous sample) was formed in the test tube (2.0 min), and the complex of  $\text{Rh}^{3+}$  ions extracted in the form of fine droplets of [Omim][TF<sub>2</sub>N]. The mixture was then centrifuged at 3800 rpm for 3.0 min so that, the dispersed fine droplets of [Omim][TF<sub>2</sub>N] 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 250  $\mu\text{L}$  of 95 % ethanol and the final

solution was transferred into a 1.0-mm quartz cell. The absorbance of the solution was measured at 624 nm. The blank solution was submitted to the same procedure without  $\text{Rh}^{3+}$  ions [Fig. 1].



**Fig. 1:** Absorption spectra of  $4 \times 10^{-4}$  mol  $\text{L}^{-1}$  CPAHPD and its complex with  $150 \text{ ng mL}^{-1}$  of  $\text{Rh}^{3+}$  ( ) under the optimum conditions used for IL-USA-DLLME

## 2.5. Sampling

### 2.5.1. Determination of $\text{Rh}^{3+}$ ions in water sample

Water samples were collected from four regions in Khalubia province, Egypt (Khalub tap and well water, waste water of Shoubra, Benha river Nile water and Al-Oboor ground water). Before the analysis, the organic content of the water samples was oxidized in the presence of 1.0%  $\text{H}_2\text{O}_2$  and then concentrated nitric acid was added. Water samples were spiked with known amounts of rhodium standards (50, 100, and  $150 \text{ ng mL}^{-1}$ ) and allowed to stand over night. The  $[\text{Rh}^{3+}]$  of rhodium in spiked water samples was determined. These water samples were filtered through a cellulose membrane filter (Millipore) of pore size  $0.45 \mu\text{m}$  to remove particulate matter. The pH of the filtered water samples were adjusted to approximately 4.5 using sodium acetate/acetic acid buffer solution.

## 3. RESULT AND DISCUSSION

In order to reach best experimental conditions for quantitative extraction of  $\text{Rh}^{3+}$  ions via, the influence of various parameters such as concentration of  $\text{NaNO}_3$ , the amount of CPAHPD, pH, ionic liquid amounts, centrifugation and sonication times, were studied. In the IL-USA-DLLME/spectral method, enrichment factor and percentage of extraction are calculated as follows:

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

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

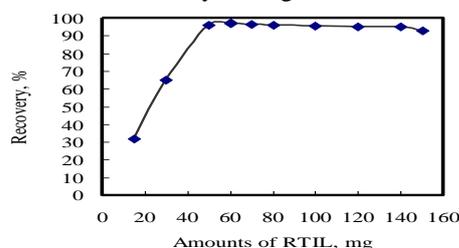
where V and C are the volume and concentration and the suffixes o and aq indicate organic and aqueous phases, respectively.  $C_o$  was calculated from the calibration graph of a standard solution of the relevant  $\text{Rh}^{3+}$  in ethanol.

### 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 [13,30]. Charge distribution on the anions, H-bonding ability, polarity and dispersive interactions are the main factors that influence the physical properties of ILs [31]. Imidazolium-based ILs is 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 is 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.  $\text{TF}_2\text{N}^-$  is much more stable in the presence of water and also has other advantages because of its hydrophobicity [13,32].

### 3.2. Effect of ionic liquid amount

The viscosity of ILs is high and handling is difficult, so working solutions ( $[\text{Omim}][\text{TF}_2\text{N}]$ ,  $(1.0 \text{ mg L}^{-1})$ ) 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 25 mL sample, was investigated in the range of 15–150 mg. It was observed that the extraction efficiency of the proposed system was affected significantly by the IL amount. Fig. 2 shows that the efficiency of extraction reaches a maximum for an IL amount of 50 mg and no significant changes were observed on the extraction efficiency for higher IL amounts.

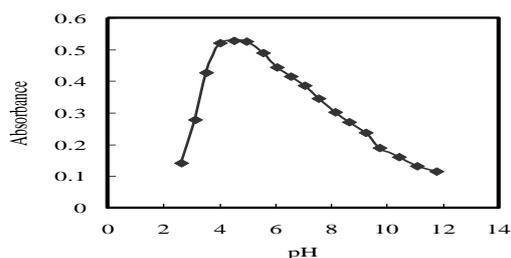


**Fig. 2.** Effect of amount of RTIL on the recovery of rhodium. Utilized conditions: Rhodium  $150 \text{ ng mL}^{-1}$ , pH 4.5, CPAHPD,  $4 \times 10^{-4}$  M,  $\text{NaNO}_3$  0.04% (w/v), Triton X-114 0.002% (w/v), and diluting agent  $250 \mu\text{L}$  ethanol.

Therefore, in order to achieve a good enrichment factor, low viscosity and relatively high hydrophobicity, 60 mg IL was chosen as optimum.

### 3.3. Effect of pH

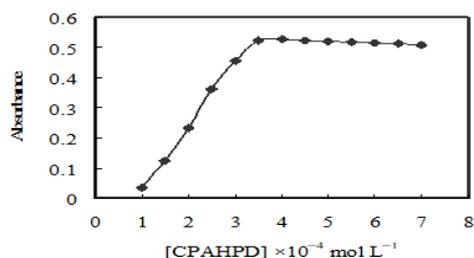
In the IL-USA-DLLME method, the pH of the sample solution is a very important factor which affects the formation of a complex with sufficient hydrophobicity and the subsequent extraction. The effect of pH on the complex formation was investigated in the pH range of 2.63–11.75, while maintaining the other parameters constant. For the pH < 3 nitrogens of CPAHPD are protonated and sites of bonding to Rh<sup>3+</sup> are limited, for the pH in the range 4.0–5.0 hydroxyl group of CPAHPD is protonated and Rh<sup>3+</sup> bonded to azo nitrogen and complex was formed. The transformation of Rh<sup>3+</sup> to Rh(OH)<sub>3</sub> is responsible for a decrease in the efficiency of Rh<sup>3+</sup> separation and preconcentration at alkali pHs. The results (Fig. 3) reveal that the recovery is nearly constant in the pH range of 4.0–5.0. Accordingly, a pH approximately of 4.5 was chosen for further experiments.



**Fig. 3.** Effect of pH on the recovery of rhodium. Utilized conditions: Rhodium 150 ng ml<sup>-1</sup>, CPAHPD, 4×10<sup>-4</sup>M, NaNO<sub>3</sub> 0.04%(w/v), Triton X-114 0.002%(w/v) and diluting agent 250 μL ethanol.

### 3.4. Effect of CPAHPD concentration

The influence of the CPAHPD concentration on the IL-USADLLME extraction efficiency of Rh<sup>3+</sup> ion was evaluated in the concentration range of 0.5–7.0×10<sup>-4</sup> mol L<sup>-1</sup>. The results (Fig. 4) show that the absorbance of the formed complex increases with increase of CPAHPD concentration upto 3.5 × 10<sup>-4</sup> mol L<sup>-1</sup>, and then stays constant. Therefore, a concentration of 4 × 10<sup>-4</sup> mol L<sup>-1</sup> CPAHPD was selected.



**Fig. 4.** Effect of CPAHPD concentration on the recovery of rhodium. Rhodium 150 ng ml<sup>-1</sup>, pH 4.5, NaNO<sub>3</sub> 0.04%(w/v), Triton X-114 0.002%(w/v) and diluting agent 250 μL ethanol.

### 3.5. Effect of salt concentration

Previous research shows that by increasing the salt concentration in single drop microextraction (SDME), DLLME [33,34] and hollow fiber liquid phase microextraction (HF-LPME) [35,26], the volume of extractant phase changes due to a salting in or salting out effect [37]. However, it is an interesting property of ILs that in the presence of a high content of salt, the solubility of [Oimim][TF<sub>2</sub>N] does not vary and, because of the high density of ILs, the fine droplets of extractant phase can settle even in the saturated solutions [38,39], 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 [37]. It is therefore expected that the volume of the extraction phase will not be significantly influenced by increasing salt content. NaNO<sub>3</sub> was chosen in order to study the salt effect in the range of 0.0–1.0% (w/v). Recovery of Rh<sup>3+</sup> slightly increased upto 0.04% (w/v) as a result of salting out effect and then did not vary from 0.05% to 1.0% (w/v). Hence the IL-USA-DLLME method can be employed for the separation and preconcentration of Rh<sup>3+</sup> ion from salty samples with a concentration of upto 1.0% (w/v). A concentration of 0.04% (w/v) NaNO<sub>3</sub> 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 [40]. 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-100 and Triton X-114) were investigated and compared. In the presence of Triton X-114, recovery decreased while, using Triton X-100, recovery increased, and so, Triton X-100 was selected as the anti-sticking agent. A concentration of 0.002% (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-USADLLME procedure, the interface between the extraction solvent and the bulk aqueous sample was enormously enlarged by forming a cloudy

solution [26]. 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 1.0–5.0 min and it was seen that sonication for at least 2.0 min was necessary to form a complete cloudy solution. Hence 2.0 min was selected for the dispersive procedure.

### 3.8. Effect of centrifugation time

Also centrifugation time is an important parameter that influences the separation of ionic liquid from the water phase. A centrifugation time in the range of 1–7.0 min at the rate of 3800 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, 3.0 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 complexing agent and their subsequent co-extraction with  $\text{Rh}^{3+}$  was evaluated. A given species was considered to interfere if it resulted in a  $\pm 5.0\%$  variation of the absorbance, the results are shown in Table 1. Most of cations and anions examined, did not

interfere with the microextraction and determination of  $\text{Rh}^{3+}$ . However, some of the species tested, such as  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  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  $\text{Rh}^{3+}$  in different water samples.

**Table 1.** Effect of foreign ions on the recovery of  $\text{Rh}^{3+}$  ion<sup>a</sup>.

Diverse ion	Tolerance limit ( $\mu\text{g}$ )	Recovery (%)
Acetate, phosphate cetrate	2000	101.5
$\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{K}^+$	1500	101.4
$\text{SO}_4^{2-}, \text{Cl}^-, \text{ClO}_4^-, \text{NO}_3^-$	1200	95.7
$\text{Li}^+, \text{Tl}^+, \text{Ag}^+, \text{SCN}^-$	1000	96.2
$\text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{Bi}^{3+}$	750	102.8
$\text{Ir}^{3+}, \text{La}^{3+}, \text{Y}^{3+}, \text{Sm}^{3+}$ ,	500	98.5
$\text{Ni}^{2+}, \text{Pd}^{2+}$	300	97.4
$\text{Cd}^{2+}, \text{Mn}^{2+}$	200	101.1
$\text{Zn}^{2+}, \text{Pb}^{2+}$ ,	150	103.6
EDTA	100	98.6
$\text{Au}^{3+}, \text{Sc}^{3+}, \text{Ru}^{3+}$	75	99.3
$\text{Cu}^{2+}$ *	50	100.4
$\text{Co}^{2+}$ *	30	96.5

<sup>a</sup> Initial samples contained  $150 \text{ ng mL}^{-1} \text{ Rh}^{3+}$  and different amounts of diverse ions in 25 mL water.

<sup>b</sup> For masking interferences of these ions, EDTA was used.

### 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 were determined to evaluate method performance (Table 2).

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

Parameters	IL-USA-DLLME method	Before IL-USA-DLLME
Amount of ethanol	250 $\mu\text{L}$	--
pH	4.5	4.5
Optimum [CPAHPD]	$4 \times 10^{-4}$	$4 \times 10^{-4}$
Reaction time (min)	10	25
Stirring time (min)	5.0	----
$\lambda_{(\text{nm})}$	624	611
Beer's range ( $\text{ng mL}^{-1}$ )	10 - 260	7500-350000
Ringbom range ( $\text{ng mL}^{-1}$ )	25 - 235	10000-325000
Molar absorptivity ( $\text{L mol}^{-1} \text{ cm}^{-1}$ )	$3.61 \times 10^5$	$1.21 \times 10^3$
Sandell sensitivity ( $\text{ng cm}^{-2}$ )	0.0285	8.5
Regression equation		
Slope ( $\mu\text{g mL}^{-1}$ )	3.51	0.0067
Intercept	0.006	-0.03
Correlation coefficient ( $r$ )	0.9992	0.9975
RSD <sup>a</sup> (%)	1.78	2.66
Detection limits ( $\text{ng mL}^{-1}$ )	3.2	2200
Quantification limits ( $\text{ng mL}^{-1}$ )	9.8	7000
enhancement factor	67.53	--

**Table 3.** Recovery of rhodium from spiked water samples using the proposed method.

Sample	Proposed method (concentration added)					
	50 ng mL <sup>-1</sup>		100 ng mL <sup>-1</sup>		150 ng mL <sup>-1</sup>	
	Found	Recovery (%) <sup>a</sup>	Found	Recovery (%) <sup>a</sup>	Found	Recovery (%) <sup>a</sup>
Tap water-I <sup>b</sup>	49.4	98.80 ± 0.37	100.8	100.80 ± 0.28	151.7	101.13 ± 0.43
<i>t</i> - and <i>f</i> -test	0.87 and 1.98		0.76 and 1.83		1.06 and 2.27	
	ETAAS method (concentration added) [46]					
	50.9	101.80 ± 0.88	98.2	98.20 ± 0.78	148.3	98.87 ± 0.96
River water-I <sup>c</sup>	50.6	101.20 ± 0.67	99.2	99.20 ± 0.48	149.0	99.33 ± 0.63
<i>t</i> - and <i>f</i> -test	0.67 and 1.49		1.12 and 2.43		0.81 and 1.77	
	ETAAS method (concentration added) [46]					
	48.6	97.20 ± 0.81	102.4	102.40 ± 0.56	152.5	101.67 ± 0.80
Sea water- I <sup>d</sup>	50.8	101.60 ± 0.53	97.9	97.90 ± 0.92	153.2	102.13 ± 0.47
<i>t</i> - and <i>f</i> -test	1.17 and 2.58		0.95 and 2.09		0.82 and 2.16	
	ETAAS method (concentration added) [46]					
	51.0	102.00 ± 0.88	100.9	100.90 ± 0.74	148.8	99.20 ± 0.97
Well water- I <sup>b</sup>	51.4	102.80	98.2	98.20	153.6	102.40
<i>t</i> - and <i>f</i> -test	0.91 and 2.05		0.79 and 1.92		0.73 and 1.88	
	ETAAS method (concentration added) [46]					
	48.9	97.80	102.8	102.80	147.2	98.13
Wastewater-I <sup>e</sup>	50.8	101.50	98.7	100.25	152.5	100.33
<i>t</i> - and <i>f</i> -test	1.22 and 2.67		1.11 and 2.44		1.08 and 2.36	
	ETAAS method (concentration added) [46]					
	48.5	101.00	102.6	99.25	14.7	99.33

<sup>a</sup> Mean ± S.D. (n = 6); <sup>b</sup> Collected from Khalub, Benha, Egypt.; <sup>c</sup> Collected from Benha, Egypt.; <sup>d</sup> Collected from Shobra, Egypt.; <sup>e</sup> Collected from Alexandria, Egypt

The calibration curve was obtained after the standard series were subjected to the IL-USA-DLLME and then determined spectrophotometrically. Linearity was obtained with rhodium concentration in the range of 10–260 ng mL<sup>-1</sup>, for 25 mL of solution. The linear regression equation is  $A = 3.51 C - 0.004$  (where A is the absorbance and C is the concentration of Rh<sup>3+</sup> μg mL<sup>-1</sup>) in the final solution with a correlation coefficient of 0.9992. The enrichment factor, calculated by Eq. (2), was 67.53 and the limit of detection and the limit of quantification were determined by  $3S_b/m$  and  $10S_b/m$  respectively. The standard deviation of the blank,  $S_b$  was equal to  $2.3 \times 10^{-4}$  (for ten repetitions) and the slope of the calibration curve after extraction,  $m = 3.51$  ng mL<sup>-1</sup>. The detection limit was found to be 3.2 ng mL<sup>-1</sup>. The relative standard deviation (RSD) for seven replicates of 150 ng mL<sup>-1</sup> of Rh<sup>3+</sup> was ± 1.78%.

### 3.11. Validity of the method

For evaluating the accuracy of the IL-USA-DLLME method on rhodium, it was applied to

determine Rh<sup>3+</sup> in water and 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 four different water samples are presented in Table 3. Recovery, using spiked samples, shows the capability of our method for the determination of Rh<sup>3+</sup>. In fact, the recovery values calculated for added standard solutions were always higher than 98.5%, thus confirming the accuracy of the procedure and its independence from matrix effects.

The performance of the proposed method was assessed by calculation of the *t*-value (for accuracy) and *F*-test (for precision) [41] compared with ETAAS method. The mean values were obtained in a Student's *t*- and *F*-tests at 95% confidence limits for five degrees of freedom. The results showed that the calculated values (Table

3) did not exceed the theoretical values. A wider range of determination, higher accuracy, more stability and less time consuming, shows the advantage of the proposed method over other method.

### 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 mL volumetric flask, and made up to mark with distilled water. An aliquot of was taken and rhodium was determined by the general procedure described early. Six determinations were made. The results (Table 4) indicate the effectiveness and accuracy of the IL-USA-DLLME method.

**Table 4.** Determination of rhodium in a platinum–iridium alloy.

Composition (%)	Certified value (%)	Found <sup>a</sup> (%)		T-test <sup>b</sup>	F-value <sup>c</sup>
		PM	ETAAS [46]		
Pt, 55; Ir, 28; Cu, 3.0; Fe, 3.5; Pd, 3.5	Rh, 7.0	6.83 ± 0.06	6.75 ± 0.10	1.42	3.27

<sup>a</sup> Mean ± standard deviation (n = 6).

<sup>b</sup> Tabulated t-value for five degrees of freedom at P (0.95) is 2.57;

<sup>c</sup> Tabulated F-value at P (0.95) is 5.05.

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

A comparison of IL-USA-DLLME combined with spectrophotometry with other techniques for separation and determination of Rh<sup>3+</sup> is given in Table 5 and 6. In comparison with the other

reported methods [42–52], the IL-USA-DLLME/ spectrophotometry shows a comparatively low detection limit (3.2 ng mL<sup>-1</sup>), a high enrichment factor (67.53) and better dynamic range (10–260) for Rh<sup>3+</sup> in a short extraction time (2.0 min). In fact, the IL-USA-DLLME has higher enrichment factor and lower detection limit than all the other methods except LITLS/ CPE/ETAAS [42]. 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 (1.78%) is also better than that obtained using spectrophotometric determination alone. Moreover, since this method uses only 250 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.

Table 6 compares the proposed method with those was reported previously for the determination of rhodium after preconcentration procedure. It shows that the proposed method has a low detection limit compared with previous studies and it allows the determination of ng mL<sup>-1</sup> levels of rhodium. Also, TLS requires low volume of the remained phase after CPE (20 µL) for determination of analyte in comparison with the other similar determination methods such as FAAS, spectrophotometry or ICP-AES that they require about 500–5000 µL of the remained phase after preconcentration methods, So the remained phase was dissolved by low volume of solvent in the proposed method. The proposed method has a high enhancement factor in compare to the other similar methods because of high volume ratio (sample volume to the remained phase volume after CPE).

**Table 5.** Comparison of our method with other methods for preconcentration and determination of rhodium.

Determination technique	Preconcentration method	Enrichment factor	Detection limit, ng mL <sup>-1</sup>	RSD (%)	Linear range (ng mL <sup>-1</sup> )	Ref.
LI-TLS <sup>a</sup> /ETAAS <sup>b</sup>	CPE <sup>c</sup>	450	0.06	–	0.5–50	[42]
DPP <sup>d</sup>	SPE <sup>e</sup>	–	60	0.72	250–7500	[43]
(ICP-AES) <sup>f</sup>	ETV <sup>g</sup>	–	0.8	2.4	–	[44]
FIA-FAAS	SPE	–	3	–	–	[45]
ETAAS	ETAAS Mg–W cell-electrodeposition	–	13	4.1	–	[46]
ETAAS	IEM <sup>h</sup>	20	0.3	1.8	0.9–50	[47]
FAAS	IL-USA-DLLME	29.1	0.37	1.63	4.0–500	[48]
Spectrophotometry	IL-USA-DLLME	–	3.2	1.78	10–260	Thiswork

<sup>a</sup> LI-TLS: Laser induced-thermal lens spectrometry; <sup>b</sup> ETAAS: Electrothermal atomic absorption spectrometry; <sup>c</sup> CPE: Cloud point extraction; <sup>d</sup> DPP: Differential pulse polarography; <sup>e</sup> SPE: Solid phase extraction; <sup>f</sup> ICP-AES: Inductively coupled plasma atomic emission spectrometry; <sup>g</sup> ETV: Electrothermal vaporization; <sup>h</sup> IEM: Ion exchange microcolumn.

**Table 6.** Comparison of preconcentration-determination methods for rhodium reported in the literature with the proposed method.

Determination technique	Preconc. method	Sample volume (mL)	Solvent volume ( $\mu\text{L}$ )	EF <sup>a</sup>	LDR <sup>b</sup> ng mL <sup>-1</sup>	LOD <sup>c</sup> ng mL <sup>-1</sup>	Ref.
FIA-FAAS	SPE	50	–	–	–	8.0	[45]
ETAAS	IEM <sup>d</sup>	2.4	40	20	0.9–50	0.3	[50]
FAAS	CPE	100	300	50	0.16–1.5	0.052	[49]
LI-TLS	CPE	10	20	450	0.5–50	0.06	[42]
Spectrophotometry	SLS <sup>e</sup>	250	5000	40	30–2500	14.4	[50]
Spectrophotometry	LLE	–	–	–	440–4400	–	[51]
Spectrophotometry	CPE	250	500	500	0.5–75	0.15	[52]
Spectrophotometry	IL-USA-DLLME	25	250	67.53	10–260	3.2	Present work

<sup>a</sup> Enhancement factor; <sup>b</sup> Linear dynamic range; <sup>c</sup> Limit of detection; <sup>d</sup> Ion exchange microcolumn; <sup>e</sup> Solid liquid separation.

#### 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 2.0 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<sup>3+</sup> 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  $\mu$ -scale size of [Omim][TF<sub>2</sub>N]. 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 5), 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. The results indicated that ionic liquid based ultrasound assisted dispersive liquid–liquid microextraction, combined with spectro-

photometry, is a fast, simple, sensitive, selective, and efficient analytical procedure to separate and determine ultra trace amounts of Rh<sup>3+</sup> ions with minimum solvent consumption and may be safely applied to its determination in different complex materials such as environmental water and alloy samples.

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## تعیین رودیوم در نمونه‌های آبی با استفاده از مایع یونی به روش میکرواستخراج مایع-مایع پخشی کمک‌شده با آلتراسونیک و کوپل‌شده با تکنیک اسپکتروفتومتری

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### چکیده

روش میکرواستخراج مایع-مایع پخشی کمک‌شده با آلتراسونیک بر اساس مایع یونی برای تعیین مقادیر ناچیز یون‌های  $Rh^{3+}$  از محلول‌های آبی بکار گرفته شد تا یک روش آماده‌سازی سریع و معتبر برای تعیین یون‌های  $Rh^{3+}$  به روش اسپکتروفتومتری ارائه گردد. یون‌های  $Rh^{3+}$  با استفاده از واکنشگر کمپلکس‌دهنده ۵- (۴-کلروفنیل آزو)-۶-هیدروکسی-پیریمیدین-۲ و ۴ دی ان (CPAHPD) و با استفاده از یک حمام آلتراسونیک با مایع یونی ۱-کتیل-۳-متیل ایمیدازولیوم بیس (تری فلورورومتیل-سولفونیل) امید برای استخراج آنالیت در دمای اتاق مورد استفاده قرار گرفتند. ۲۵۰ میکرولیتر اتانول به فاز غنی از مایع یونی، بعد از سانتریفیوژ کمپلکس رودیم اضافه شده تا تشکیل قطرات مایع یونی را قبل از آنالیز اسپکتروفتومتری بهبود بخشد. در آخر تاثیر پارامترهای مختلف بر روی بازیابی یونی  $Rh^{3+}$  بررسی و بهینه گردید. تحت شرایط بهینه، منحنی کالیبراسیون در محدوده ۲۶۰-۱۰ نانوگرم بر میلی لیتر خطی بوده و حد تشخیص ۳٫۲ نانوگرم بر میلی لیتر با انحراف استاندارد نسبی  $\pm ۱٫۷۸\%$  بدست آمد. مقایسه‌ی این روش با سایر روش‌ها، خطر تماس با حلال‌های سمی را کاهش داده ضمن اینکه نیاز به یک زمان استخراج کوتاه‌تری را لازم دارد. این روش بطور موفقیت آمیزی برای آنالیز نمونه‌های حقیقی بکار گرفته و با روش GF-AAS مقایسه گردید. روش پیشنهادی بطور موفقیت آمیزی برای آنالیز و با روش ETAAS مقایسه گردید.

### واژه‌های کلیدی

میکرواستخراج مایع-مایع پخشی؛ تعیین رودیوم؛ استخراج کمک‌شده با آلتراسونیک؛ جداسازی سبز؛ تجزیه محیطی.