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# Determination of rhodium by resonance light-scattering technique coupled with solid phase extraction using Rh(III) ion-imprinted polymers as sorbent

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ABSTRACT

A resonance light-scattering method (RLS) for the determination of Rh(III) was initially developed, based on the reaction among Rh(III), $WO_4^{2-}$ and ethylrhodamine B. The method possesses high sensitivity, but lacks selectivity. Therefore, a Rh(III) ion-imprinted polymer (IIP), prepared by precipitation polymerization using 2-(allylthio)nicotinic acid (ANA) as functional monomer, was used as sorbent to construct a ion-imprint based solid-phase extraction (IIP-SPE) method for separation of rhodium from complicated matrices prior to its determination by RLS. The experimental parameters affecting the extraction efficiency and selectivity of IIP-SPE were studied carefully. Under the optimal conditions, the IIP-SPE column with the enrichment factor (EF) of 10 could be used at least 20 times without decreasing its extraction recovery (above 90%) significantly. The calibration graph for the determination of rhodium by RLS coupled with IIP-SPE procedure was linear in the range of 0.06–1.5 ng mL$^{-1}$ with the detection limit of 0.024 ng mL$^{-1}$. There is no metal ions tested at the concentration below 10 ng mL$^{-1}$ interfered in the determination of 0.8 ng mL$^{-1}$ Rh(III). The proposed IIP-SPE–RLS method was successfully applied to the extraction and measurement of trace rhodium in catalyst, water and geochemical samples with the relative standard deviation (RSD) of less than 4.0% ($n=4$).

## 1. Introduction

The determination of rhodium has been studied by different techniques such as spectrophotometric methods [1], atomic absorption spectrometry [2], ICP-OES and ICP-MS [3] as well as resonance light-scattering technique (RLS) [4], a new spectral analysis technique characterized by high sensitivity, convenience in performance and simplicity in apparatus (usually common spectrofluorometer) [5,6]. Unfortunately, the direct determination of trace rhodium in complicated matrices by all these techniques is usually limited owing to the interferences caused by matrix elements. To overcome this problem, different separation procedures, such as liquid–liquid extraction [7], cloud point extraction [8,9], electrothermal vaporization [10], adsorption on microcrystalline naphthalene [11] and solid phase extraction (SPE) [12–15] have been used to isolate and preconcentrate rhodium from samples containing other metals. Among these separation procedures, solid phase extraction possesses several advantages as convenience, simplicity, cost and time saving [16]. However, classical sorbents used in SPE, liked ion-exchange resin, cellulose and silica gels functionalized or coated with different chelating group, often cause non-specific interactions that lead to the co-extraction of interfering compounds and prevent an easy and reliable quantification of the analyte. Recently, a new material called ion imprinted polymer (IIP) has attracted much attention as a highly selective sorbent for SPE in order to concentrate and clean-up samples prior to analysis [17–19].

Ion imprinted polymers are synthesized based on the idea of molecular imprinting technique but using a metal ion or its complex as template. As a result, IIPs possess imprinting sites of a complementary shape and functionality to the template. So far, several studies have been published with respect to the preparation of IIPs for metal ions in SPE [20–35]. Nearly in all of these studies, good selectivity was reported towards the analyte ion over the other ions.

The aim of this research is to prepare an effective Rh(III) ion-imprinted polymer for SPE of Rh(III) from complicated matrices prior to its determination by RLS. For this purpose, a ligand with N, S and O as donor atoms named 2-(allylthio)nicotinic acid (ANA), was selected for the first time as functional monomer to prepare Rh(III) ion-imprinted polymer in view to its mixed hard–soft donor character and versatile coordination behavior. The experimental parameters affecting the extraction efficiency and determination sensitivity of Rh(III) were carefully optimized. The analytical application and selectivity behavior of the RLS coupled

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with ion-imprinted based solid-phase extraction method (IIP-SPE–RLS) were also described and discussed.

## 2. Experimental

### 2.1. Apparatus and instrumentation

A F-4500 fluorescence spectrometer (Hitachi, Japan) equipped with an 150 W xenon lamp and an 1 cm quartz cell was used for the determination of Rh(III) by resonance light-scattering method (RLS). A HZ constant temperature bath oscillator (Jiangsu, China) and a Mars 5 microwave oven with a Teflon high-pressure microwave acid digestion bomb (CEM, USA) were used for the binding experiments and decomposition of the catalyst materials, respectively. The surface morphology was observed on a Hitachi S-520 field emission scanning electron microscopy (Tokyo, Japan). The BET nitrogen adsorption analysis was carried out by a NOVA 2000e surface area and pore size analyzer (Quantachrome Corp., USA). A ICP-1000 II inductively coupled plasma atomic emission spectrometer (Shimadzu, Japan) was used for the analysis of the mixture of platinum group metals.

### 2.2. Reagents and materials

$Na_3RhCl_6$ was purchased from Kunming Institute of Precious Metals (Yunnan, China). 2-(allylthio)nicotinic acid (ANA) was purchased from Sigma Aldrich (USA). Ethylene glycol dimethacrylate (EGDMA) was purchased from Suzhou Anli Chemical Factory (Jiangsu, China) and distilled under vacuum to remove the stabilizers prior to use. Azobisisobutyronitrile (AIBN) was purchased from Shanghai Reagent Factory (Shanghai, China) and purified by recrystallization from ethanol before used.

The stock solution (1.0 mg $mL^{-1}$) of Rh(III), Ru(III), Pd(II), Ir(IV) and Pt(IV) were prepared by dissolving appropriate amount of $Na_3RhCl_6$, $RuCl_3$, $PdCl_2$, $Na_2IrCl_6$ and $Na_2PtCl_6$ (all of these compounds were obtained from Kunming Institute of Precious Metals, Yunnan, China) in 50 mL of 2.0 mol $L^{-1}$ HCl and then diluted to 100 mL with de-ionized water, respectively. The stock solution (1.0 mg $mL^{-1}$) of the other metal ions used in this work was prepared with their nitrate or chloride. The working standard solution was obtained by diluting the stock solution with de-ionized water. $1.0\times10^{-3}$ mol $L^{-1}$ ethylrhodamine B (Fluka, France) solution, $5.0\times10^{-4}$ mol $L^{-1}$ sodium tungstate (Shanghai Reagent Factory, Shanghai, China) solution, 20 g $L^{-1}$ poly(vinyl alcohol) (PVA, Sigma Aldrich, USA) solution and 6.0 mol $L^{-1}$ hydrochloric acid were prepared with de-ionized water and used for the determination of Rh(III) by RLS.

The reagents and solvents used without special illustration were of analytical reagent grade and used without further purification. De-ionized water was produced by a Millipore water system composed of Milli-RO 60 and Milli-Q SP.

### 2.3. Determination of Rh(III) by resonance light-scattering technique

Transferred an appropriate amount of sample or Rh(III) standard solution in a 25 mL volumetric flask. Added 2.0 mL of $Na_2WO_4$ solution ($5.0\times10^{-4}$ mol $L^{-1}$), 3.0 mL of 6.0 mol $L^{-1}$ HCl, 1.5 mL of 20 g $L^{-1}$ poly(vinyl alcohol) (PVA) and 2.5 mL of $1.0\times10^{-3}$ mol $L^{-1}$ ethylrhodamine B solution. Diluted to volume with water and mixed well. After the mixture was placed at room temperature for 10 min, resonance light-scattering spectra was obtained with the excitation and emission monochromators of the fluorimeter scanned synchronously (0.0 nm interval between excitation and emission wavelength) through the wavelength range of 300–700 nm. The light-scattering intensity was determined at the excitation and emission wavelength of 605 nm by keeping the slit width of the excitation and emission of the fluorimeter at 5 nm. The difference in the light-scattering intensity between the reaction system ($I$) and reagent blank ($I_0$), which prepared in a similar way to that of the reaction system described as above but without the addition of Rh(III), was calculated as $\Delta I = I - I_0$.

### 2.4. Preparation of Rh(III) ion-imprinted polymer

Rh(III) ion-imprinted polymer (IIP) was prepared by precipitation polymerization using $RhCl_6^{3-}$ as template, ANA as functional monomer, EGDMA as crosslinker, AIBN as initiator and methanol as porogen. The typical procedure for preparing IIP was as follows: After the mixture containing 0.1 mmol (0.0385 g) $Na_3RhCl_6$, the required amounts of ANA (see Table 1) and 20 mL of methanol in a glass ampoule was shaken at room temperature for 3 h to ensure the formation of the complete complex between template and functional monomer, the appropriate amounts of EGDMA listed in Table 1 and 15 mg of AIBN were added. The polymerization mixture in the ampoule was sparged by nitrogen for 10 min, and then sealed under vacuum. The polymerization reaction was allowed to proceed at 60 °C for 24 h in a constant temperature bath oscillator. The obtained particles were washed with MeOH/AcOH (5/5, v/v) by Soxhlet extraction until Rh(III) could no longer be detected in the recovered solution by RLS. The particles were then washed with methanol to remove the residual acetic acid and dried to constant weight under vacuum.

To evaluate the recognition properties of imprinted material, non-imprinted polymer (NIP) as a control polymer was also synthesized in the absence of $Na_3RhCl_6$ and treated with the same procedure as IIP.

### 2.5. Binding experiments

To evaluate the binding affinity of IIPs towards Rh(III), 10.0 mg of dry polymers (IIPs or NIPs) were mixed with 10 mL of 10.0 mg $L^{-1}$ Rh(III) standard solution with pH 6.0 adjusted by using diluted NaOH or HCl. The mixture was oscillated in a constant temperature bath oscillator at 25 °C for 5 h, and then filtered from a 0.45 μm pore size membrane filter. The concentration of Rh(III) in filtrate was determined quantitatively by RLS. The binging capacity ($Q$, mg $g^{-1}$), which is defined as mg of substrate (Rh(III)) bound per 1 g polymers, was calculated by subtracting the amount of substrate in filtrate from that in the initial solution. The imprinting factor ($IF$) is defined as the ratio

**Table 1**
The polymerization conditions and binding properties of the polymers prepared by precipitation polymerization.

| Polymers | Polymerization conditions[a] | | Binding properties[b] | | |
|---|---|---|---|---|---|
| | ANA added (mmol) | EGDMA added (mmol) | $Q_{IIP}$ (mg $g^{-1}$) | $Q_{NIP}$ (mg $g^{-1}$) | $Q_{IIP}/Q_{NIP}$ |
| IIP1/NIP1 | 0.1 | 3.0 | 4.42 | 3.75 | 1.18 |
| IIP2/NIP2 | 0.2 | 3.0 | 5.11 | 4.02 | 1.27 |
| IIP3/NIP3 | 0.4 | 3.0 | 5.92 | 4.16 | 1.42 |
| IIP4/NIP4 | 0.6 | 3.0 | 6.50 | 4.27 | 1.52 |
| IIP5/NIP5 | 0.8 | 3.0 | 6.77 | 5.01 | 1.35 |
| IIP6/NIP6 | 0.6 | 1.0 | 4.28 | 3.57 | 1.20 |
| IIP7/NIP7 | 0.6 | 2.0 | 5.68 | 4.12 | 1.38 |
| IIP8/NIP8 | 0.6 | 4.0 | 6.98 | 4.36 | 1.60 |
| IIP9/NIP9 | 0.6 | 5.0 | 5.52 | 3.60 | 1.53 |

[a] All of the IIPs are prepared with $RhCl_6^{3-}$(0.1 mmol) as template, methanol (20 mL) as porogen and AIBN (15 mg) as initiator. All of the NIPs are synthesized according to the same procedure for IIPs but omitting the addition of $RhCl_6^{3-}$.

[b] The binding properties are determined by adding 10.0 mg polymer to 10 mL of 10.0 μg $mL^{-1}$ Rh(III) standard solution (pH 6.0) for 5 h.

of the binding capacity of IIPs ($Q_{IIP}$) with respect to that of NIPs ($Q_{NIP}$).

### *2.6. Ion imprint based solid-phase extraction (IIP-SPE) experiments*

A 200 mg sample of IIPs was dry-packed in a glassy column with an i.d. of 5 mm. The column was conditioned by passing 3 mL of 1.0 mol $L^{-1}$ HCl and next 3 mL of water at a flow rate of 1.0 mL $min^{-1}$. Extraction experiments involved three steps, i.e. loading, washing and eluting. For loading, Rh(III) standard solution or sample solution was adjusted to pH 6.0 with diluted NaOH or HCl and passed through the column at a flow rate of 0.5 mL $min^{-1}$. After loading, the column was washed with 2 mL of aqueous solution with pH 5.0 adjusted by diluted NaOH or HCl at a flow rate of 2.0 mL $min^{-1}$, and then eluted with 2 mL of 3.0 mol $L^{-1}$ HCl at a flow rate of 0.5 mL $min^{-1}$.

### *2.7. Preparation of the sample solution*

#### *2.7.1. Preparation of the catalyst sample solutions*

After the catalyst materials were ground to pass through a 200 mesh size sieve to facilitate sample dissolution, 10.0 mg of samples was weighed accurately into a Teflon high-pressure microwave acid digestion bomb and 3.0 mL of concentrated nitric acid, 2.0 mL of hydrochloric acid and 5.0 mL of 30% hydrogen peroxide were added. The bomb was sealed tightly and then positioned on the carousel of the microwave oven. The system was operated at 600 W and 350 psi with a heating program as 120 °C (5 min, hold 2 min), 180 °C (6 min, hold 10 min). The digest was evaporated to near dryness. The residue was dissolved with 5 mL of 2.0 mol $L^{-1}$ HCl and then diluted to 100 mL with de-ionized water.

#### *2.7.2. Preparation of the geology sample solutions*

10.00 g of the geochemical reference sample (GBW07293) was weighed accurately into a porcelain crucible and then heated in a muffle furnace at 650 °C for 2 h. After the residue was cooled, it was dissolved by heating gently in 30 mL of aqua regia, and then filtered. The filtrate was evaporated gently to dryness and the residue was dissolved in 10 mL of concentrated hydrochloric acid. After the solution was evaporated to half its volume, it was cooled to room temperature and then diluted to 25 mL in a calibrated flask with de-ionized water.

## 3. Results and discussion

### *3.1. Optimization of the conditions for determination of Rh(III) by RLS*

Fig. 1 shows the resonance light-scattering spectra of the reagent blank (line 1) and reaction system of Rh(III)-$WO_4^{2-}$-ethylrhodamine B (line 2) in the presence of 0.72 mol $L^{-1}$ hydrochloric acid and 1.2 g $L^{-1}$ PVA. Intense light scattering signal is observed at 581nm and 605 nm for the reagent blank and reaction systems, respectively. Therefore, a RLS method for the determination of trace amounts of Rh(III) is developed based on the reaction among rhodium(III), tungstate and ethylrhodamine B.

The reaction among Rh(III), $WO_4^{2-}$ and ethylrhodamine B is easy to carry out in acidic media. Among sulfuric acid, nitric acid, phosphoric acid, perchloric acid and hydrochloric acid, the highest and most constant RLS signal is obtained with 0.25–1.0 mol $L^{-1}$ of hydrochloric acid. The use of 0.72 mol $L^{-1}$ hydrochloric acid was recommended.

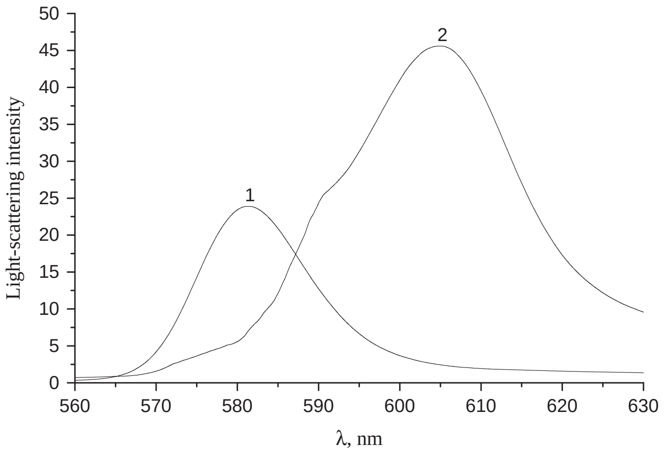

**Fig. 1.** Resonance light-scattering spectra of reagent blank (1) and ion-association complex of Rh(III)-$WO_4^{2-}$-ethylrhodamine B (2) in the presence of 0.72 mol $L^{-1}$ hydrochloric acid and 1.2 g $L^{-1}$ PVA. The concentration Rh(III), $Na_2WO_4$ and ethylrhodamine B are 1.0 ng $mL^{-1}$, $4.0 \times 10^{-5}$ mol $L^{-1}$ and $1.0 \times 10^{-4}$ mol $L^{-1}$, respectively.

The concentration of $Na_2WO_4$ and ethylrhodamine B varied in the range of $(0.1–1.0) \times 10^{-4}$ mol $L^{-1}$ and $(0.2–2.0) \times 10^{-4}$ mol $L^{-1}$ produced notable effect on the light scattering intensity of the reaction system. The highest analytical signals of the reaction system are observed in concentration range of $(3.0–6.0) \times 10^{-5}$ mol $L^{-1}$ for $Na_2WO_4$ and $(0.6–1.6) \times 10^{-4}$ mol $L^{-1}$ for ethylrhodamine B, and any concentration outside these range produces a decrease in the light scattering intensity. The use of $4.0 \times 10^{-5}$ mol $L^{-1}$ $Na_2WO_4$ and $1.0 \times 10^{-4}$ mol $L^{-1}$ ethylrhodamine B were recommended, respectively.

The ion-association complexes formed among Rh(III), $WO_4^{2-}$ and ethylrhodamine B can precipitate out of aqueous solution in the absence of an enhancing agent because of its hydrophobicity. Enhancing agents such as arabic gum, OP, PVA, Triton X-100, Tween-80, PVA+OP and PVA+arabic gum were tested. The results show that their effects on the sensitivity and stability of the ion-association reaction are different. When PVA is added, the maximum difference in the light scattering intensity between the ion-association system and the reagent blank is obtained. The optimum concentration range of PVA is 0.8–2.0 g $L^{-1}$. Hence 1.2 g $L^{-1}$ PVA was used in this work.

Rh(III) can react with tungstate and ethylrhodamine B to form a ion-association complex in 5 min at room temperature (10–30 °C). The ion-association complex is stable at room temperature and the light scattering intensity can remain constant for at least 24 h at room temperature.

Under the optimum working conditions reported above, the calibration graphs for the determination of Rh(III) by RLS are linear in the concentration range of 0.060–1.25 ng $mL^{-1}$ with a regression equation of $\Delta I = 4.58 + 40.71c$ ($r = 0.9994$), here $\Delta I$ is the difference in the light-scattering intensity between the reaction system and reagent blank, $c$ is the concentration of Rh(III) expressed as ng $mL^{-1}$, and $r$ is the correlation coefficient. Moreover, the applicability of RLS for determination of Rh(III) in the complicated samples was investigated by evaluating the interference of foreign ions. The tolerable limit of the foreign ions, which is taken as the maximum concentration of these ions causing an error below 5% in the determination, is summarized in Table 2. As can be seen, most of selected cations at the concentration lower than 8 ng $mL^{-1}$ do not influence the determination of 0.8 ng $mL^{-1}$ Rh(III), but the platinum group metals especially for Pd(II) and Ir(IV) produce significant effect on the determination. These results indicate that the accurate results of rhodium determination in complicated samples may be obtained only after the effective separation of analyte from interfering matrix.

### 3.2. Preparation of Rh(III) ion-imprinted polymer

In order to obtain an effective sorbent for SPE of Rh(III), a chelating agent with sulfur and nitrogen in its molecular structures as coordination atoms named 2-(allylthio)nicotinic acid (ANA) was selected as functional monomers for the preparation of Rh(III) ion-imprinted polymers based on the Lewis theory of acids and bases (HSAB theory). It is hoped that thus imprinted material can then be used to selectively separate and enrich Rh(III) from samples with complicated matrix.

The quantity of MIP or IIP recognition sites is a direct function of both the extent of the monomer–template interactions present in the pre-polymerization and the degree of cross-linking in the polymerization. In order to optimize the ratio of template ($RhCl_6^{3-}$) to functional monomer (ANA) and the degree of cross-linking for the preparation of Rh(III) ion-imprinted polymers, a series of imprinted polymers were prepared with different combinations of functional monomer and cross-linker. All polymers were analyzed for binding of Rh(III) in equilibrium binding experiments. The results listed in Table 1 point out that the composition of imprinting system produces remarkably influence on the property of resulting imprinted polymer. Among the polymers prepared using ANA as a functional monomer, the polymer (IIP8) prepared with the ratio of Rh(III), ANA and EGDMA as 1:6:40 shows the highest binding affinity to Rh(III) (binding capacity: 6.98 mg $g^{-1}$, imprinting efficiency: 1.60), and the other IIPs prepared with more or less functional monomers and cross-linkers possess relatively weak binding of Rh(III).

### 3.3. Characterization of Rh(III) ion-imprinted polymer

The surface morphology of IIP8 and its control polymer (NIP8) was assessed by SEM. The respective micrographs are shown in Fig. 2. It can be seen that the surface of IIP8 exhibits a more porous and rough structure than NIP8. This porousness and roughness of the surface of ion-imprinted polymer should be considered as a factor providing in the surface area [34]. The surface area, pore volume and average pore radius of the polymers were determined by BET nitrogen adsorption analysis after the sample was heated at 150 °C under high vacuum for 30 min to be 9.28 $m^2\,g^{-1}$, 0.0285 $cm^3\,g^{-1}$ and 127.3 Å for IIP8, which are higher than that of NIP8 (i.e. 7.51 $m^2\,g^{-1}$, 0.0211 $cm^3\,g^{-1}$ and 116.8 Å, respectively), confirming that the pore properties of IIP8 are enhanced by the imprinting process.

**Table 2**
Tolerable amount of each foreign ion in determination of 0.8 ng $mL^{-1}$ Rh(III) by RLS and IIP-SPE–RLS method.

| Foreign ions | Tolerable amount ($ng\ mL^{-1}$) | | Foreign ions | Tolerable amount ($ng\ mL^{-1}$) | |
|---|---|---|---|---|---|
| | RLS | IIP-SPE–RLS | | RLS | IIP-SPE–RLS |
| $Mg^{2+}$, $Ca^{2+}$ | ≥ 100 | ≥ 100 | Mo(VI) | 8 | ≥ 100 |
| $Zn^{2+}$, $Co^{2+}$, Cr(VI) | 60 | ≥ 100 | $Cu^{2+}$, Au(III) | 8 | 60 |
| $Pb^{2+}$ | 40 | ≥ 100 | Os(IV) | 4 | 60 |
| V(V), Se(IV) | 30 | ≥ 100 | Pt(IV) | 3.5 | 40 |
| $Hg^{2+}$, $Ag^{+}$ | 30 | 60 | Ru(III) | 2 | 20 |
| $Cd^{2+}$, $Al^{3+}$, $Sn^{2+}$ | 20 | ≥ 100 | Ir(IV) | 1 | 15 |
| $Fe^{3+}$, $Ni^{2+}$ | 10 | 60 | Pd(II) | 0.8 | 10 |

### 3.4. Optimization of IIP-SPE conditions

For the purpose of developing a selective and accurate ion-imprint based SPE method for separation of Rh(III), IIP8 was used as sorbent. Numerous parameters, like the effect of pH, volume and flow rate of sample and eluent were optimized. As it can be noticed, the washing step is not considered in the preliminary experiments.

Since sample pH is considered to be one of the important analytical factors in solid-phase extraction of metal ion [14], the influence of the sample pH on the extraction of Rh(III) from 2 mL of Rh(III) standard solution (50 ng $mL^{-1}$) was studied at pH range from 1.0 to 9.0. The extraction curve of Rh(III) as a function of the sample pH is shown in Fig. 3A. It is clear that the percent extraction of Rh(III) takes its maximum value in the pH range of 5.5–6.5, and any pH outside this range produces a decrease in the sorption of Rh(III). In strongly acidic media, the preconcentration of Rh(III) is hindered because of the protonation of the active sites in the sorbent. Again, the decrease in percent extraction of pHs greater than 6.5 is due to the competition between rebinding by formation of the complexes of Rh(III) with ANA anchored to the polymer particles with the formation of hydroxide of Rh(III). To obtain the maximum extraction efficiency, the sample solution was adjusted to pH 6.0 with diluted HCl or NaOH. The effect of the flow rate of the sample solution on the retention of Rh(III) was studied in the range of 0.1–2.0 mL $min^{-1}$ at the optimal pH, because the flow rate is also an important parameter for the time controls of the adsorption of the column procedure [34]. The results reveal that Rh(III) can be adsorbed quantitatively by IIPs up to the flow rate of 0.8 mL $min^{-1}$. The percent extraction of Rh(III) reduced to below 95% at the sample flow rate above 0.8 mL $min^{-1}$ and further decreased to less than 90% when the sample flow rate surpassed 1.0 mL $min^{-1}$. This decrease in adsorption of Rh(III) with increasing flow rate seems due to the decrease in the contact time of Rh(III) with the sorbent. A sample flow rate of 0.5 mL $min^{-1}$ was therefore chosen in the subsequent works.

Elution of Rh(III) was studied by using 2 mL of HCl with different concentration. Fig. 3B shows the effect of HCl concentration on the recovery of Rh(III) at the flow rate of 1.0 mL $min^{-1}$. It can be seen that

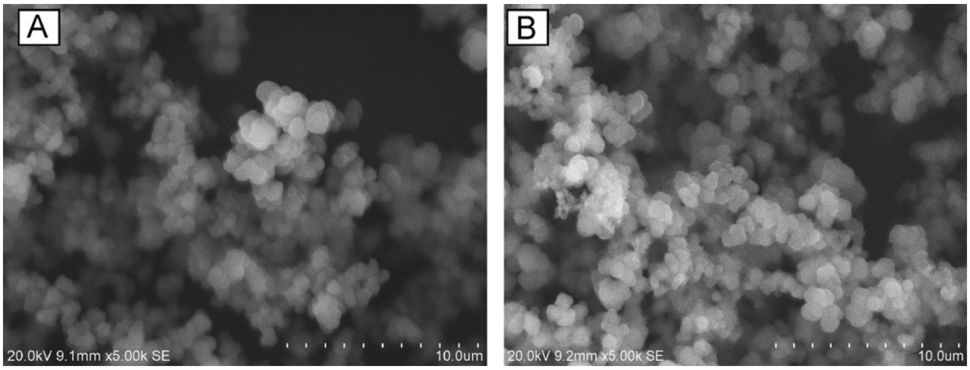

**Fig. 2.** SEM photographs of NIP (A) and IIP (B).

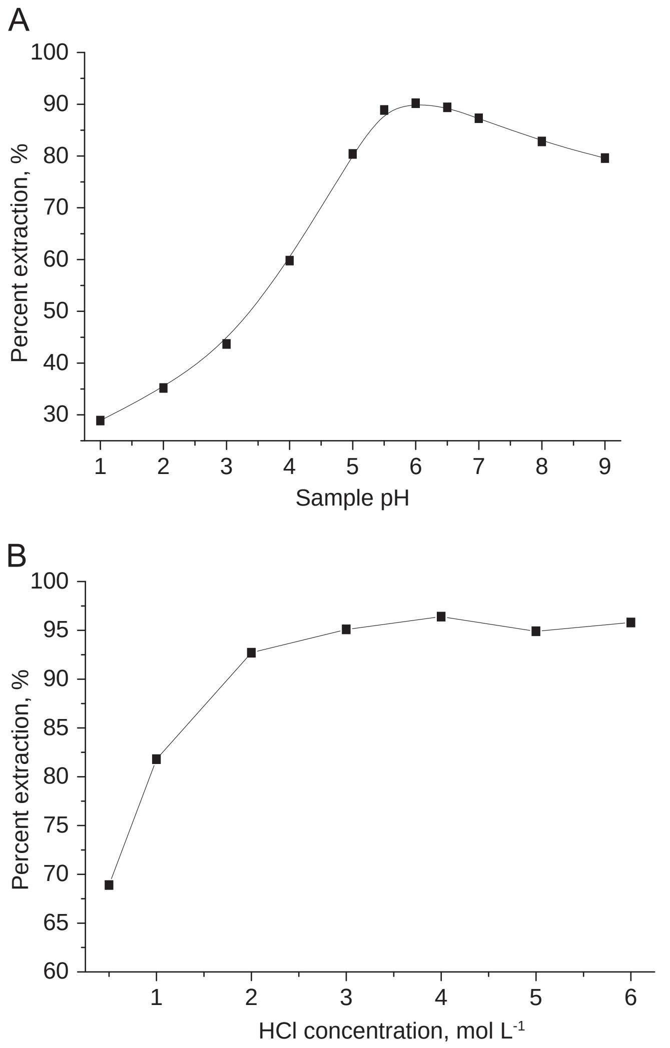

**Fig. 3.** The extraction curve of Rh(III) as a function of the sample pH (A) and HCl concentration in eluent (B). The IIP-SPE conditions for (A): Loading, 2 mL of sample solution containing 100 ng of Rh(III) at a flow rate of 1.0 mL min$^{-1}$; Eluting, 2 mL of 3 mol L$^{-1}$ HCl at a flow rate of 1.0 mL min$^{-1}$. The IIP-SPE conditions for (B): Loading, 2 mL sample solution containing 100 ng of Rh(III) at pH 6.0 and a flow rate of 0.5 mL min$^{-1}$; Eluting, 2 mL of HCl solution with different concentration at a flow rate of 1.0 mL min$^{-1}$.

the percent extraction of Rh(III) reaches its maximum and remains almost constant when HCl concentration is above 2.0 mol L$^{-1}$. The effect of the eluent volume (0.5–2.0 mL) and its flow rate (0.1–2.0 mL min$^{-1}$) were also investigated. The results indicate that Rh(III) can be eluted quantitatively with 1.5 mL of 3.0 mol L$^{-1}$ HCl solution at the flow rate below 1.0 mL min$^{-1}$. Hence, the elution process was carried out with 2.0 mL of 3.0 mol L$^{-1}$ HCl solution at the flow rate of 0.5 mL min$^{-1}$.

Under the conditions selected for loading and eluting, the selectivity of IIP sorbents was investigated by competitive adsorption of Rh(III) with other platinum group metals ions from their mixture. These ions have similar ionic radius and notable effect on the determination of Rh(III) by RLS method (see Table 2 for details). As illustrated in Fig. 4A, when 2 mL of sample solution containing 100 ng of each of Rh(III), Ru(III), Pd(II), Ir(III) and Pt(IV) ions is loaded onto the column, about 21.2–40.1% of the interfering ions are retained on the polymers by non-specific interactions. Therefore, a washing step was introduced prior to the eluting step to remove the non-specifically retained matrices from IIPs.

A set of experiments was carried out to determine the optimum pH, volume and flow rate of washing solvent by loading 2 mL of sample solution containing 100 ng of each of Rh(III), Ru(III), Pd(II), Ir(III) and Pt(IV) on SPE column. The concentration of the platinum group metals ions washed from the column was determined by ICP-OES method with the incident power of 1.2 kW, flow rate for cooling gas, auxiliary gas and carrier gas of 15 L min$^{-1}$, 0.8 L min$^{-1}$ and 0.2 L min$^{-1}$, observation height of 15 mm and determination wavelength for Pt, Pd, Rh, Ir and Ru as 299.797, 340.458, 343.489, 224.268 and 267.876 nm, respectively. The desorption efficiency is defined as the percentage of the amount of metal ions washed from the column to that in the initial sample solution. The results obtained were compiled in Table 3. It is evident from these results that a volume of 2 mL of aqueous solution with pH 5.0 at a flow rate of 2.0 mL min$^{-1}$, which shows low desorption efficiency for Rh(III) (5.3%), can remove effectively the residual non-specific interactions with the desorption efficiency for the other platinum group metals ions as above 70%.

Based on the results obtained as above, the IIP-SPE procedure involved three steps, i.e. loading, washing and eluting, was recommended in this research. And a volume of 2 mL of sample containing 100 ng of each of Rh(III), Ru(III), Pd(II), Ir(III) and Pt(IV) was analyzed by this procedure. The percent extraction of all the platinum group metals ions is shown in Fig. 4B. Comparison of the data listed in Fig. 4B with that in Fig. 4A reveals a significant

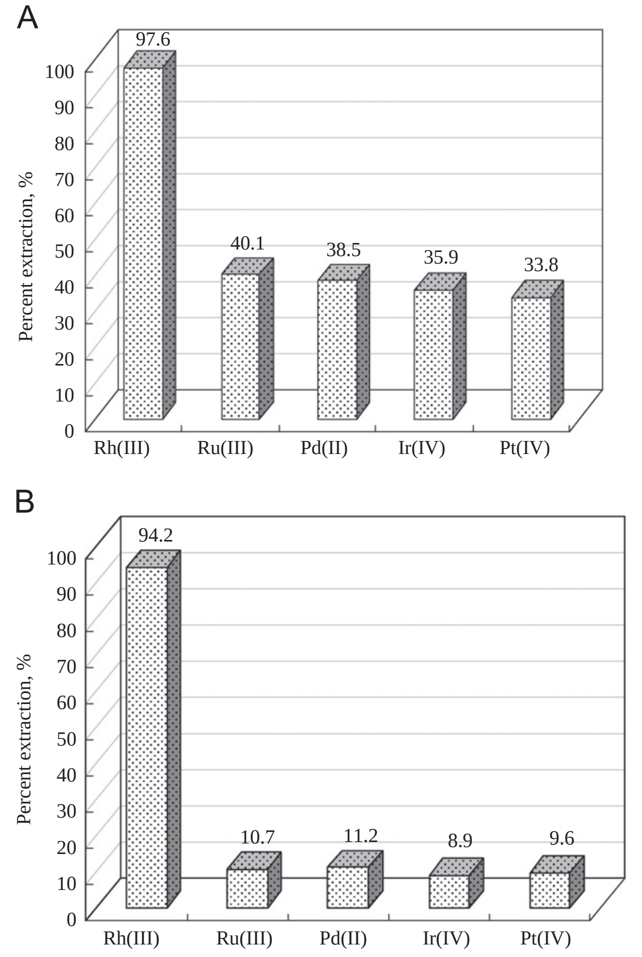

**Fig. 4.** The percent extraction of the platinum group metals ions without (A) and with (B) a washing step. IIP-SPE procedure for (B): Loading, 2 mL of sample solution containing 100 ng of each of Rh(III), Ru(III), Pd(II), Ir(III) and Pt(IV) with pH 6.0 at a flow rate of 0.5 mL min$^{-1}$; Washing, 2 mL of aqueous solution with pH 5.0 at a flow rate of 2.0 mL min$^{-1}$; Eluting, 2 mL of 3 mol L$^{-1}$ HCl at a flow rate of 0.5 mL min$^{-1}$. The IIP-SPE procedure for (A) is the same as that for (B) but omitting the step of washing.

increase in the selectivity of the IIP-SPE procedure through a washing step.

### 3.5. *Enrichment factor, adsorption capacity and sorbent stability*

In order to study the enrichment factor (EF), the ability of polymers to preconcentrate Rh(III) (100 ng) from large volumes of sample solution (10–50 mL) was tested. It is found that the IIP-SPE procedure may be applied for the preconcentration of trace amounts of Rh(III) from volumes up to 20 mL with the percent extraction of above 90%. Therefore, enrichment factor (EF) is calculated as 10 because the eluent volume is 2.0 mL.

The adsorption capacity was examined by the method recommended by Maquieira et al. [36]. 10 mL aliquots of a series of Rh(III) solution with different concentrations (10–250 mg $L^{-1}$) were adjusted to pH 6.0, then loaded, washed and eluted. The recovery of Rh(III) at each concentration level was determined and the experiment was completed when the recovery decreased to 90%. On this basis the maximum sorbent capacity of the polymers for Rh(III) is 14.5 mg $g^{-1}$.

**Table 3**
Effects of various parameters of washing on the desorption efficiency (%) of platinum group metals ions.

| Parameters | Rh(III) | Ru(III) | Pd(II) | Ir(IV) | Pt(IV) |
|---|---|---|---|---|---|
| pH of washing solvent | | | | | |
| 1.0 | 32.8 | 89.7 | 93.2 | 90.1 | 87.2 |
| 3.0 | 16.9 | 84.9 | 87.6 | 83.9 | 79.3 |
| 5.0 | 9.7 | 80.1 | 78.5 | 75.2 | 73.8 |
| 7.0 | 7.8 | 67.9 | 54.1 | 65.4 | 64.2 |
| 9.0 | 7.1 | 49.3 | 38.9 | 54.2 | 59.8 |
| Washing volume (mL) | | | | | |
| 1 | 4.9 | 69.7 | 65.2 | 67.6 | 59.2 |
| 2 | 9.7 | 80.1 | 78.5 | 75.2 | 73.8 |
| 3 | 12.5 | 84.9 | 79.8 | 80.2 | 77.0 |
| 4 | 15.6 | 85.4 | 82.2 | 85.0 | 79.1 |
| 5 | 18.7 | 84.6 | 85.7 | 86.4 | 81.4 |
| Flow rate (mL $min^{-1}$) | | | | | |
| 0.1 | 24.5 | 89.2 | 90.8 | 92.3 | 87.6 |
| 0.5 | 18.3 | 85.2 | 83.9 | 83.4 | 79.3 |
| 1.0 | 9.7 | 80.1 | 78.5 | 75.2 | 73.8 |
| 1.5 | 6.1 | 77.5 | 74.2 | 73.9 | 71.4 |
| 2.0 | 5.3 | 74.9 | 71.3 | 72.8 | 72.6 |

Sorbent stability in the working conditions was evaluated for several repetitive loading, watching and eluting operations. The good reproducibility of the results, obtained after 20 sorption–desorption cycles, proved good sorbent stability in the working conditions. The sorbent in dry state can be stored at room temperature for long period of time.

### 3.6. *Calibration graph, detection limit and precision of IIP-SPE–RLS method*

The analytical figures of merit of IIP-SPE coupled with RLS for the determination of trace amount of rhodium were evaluated under the optimal experimental conditions. To construct the calibration graph for the determination of rhodium by the IIP-SPE–RLS method, 2 mL of Rh(III) standard solution (pH 6.0) with different concentration was submitted to IIP-SPE procedure represented in Section 2.6, and the eluent was collected and analyzed by RLS (see Section 2.3 for details). A linear relationship is found between difference in the light-scattering intensity between the ion-associated system and reagent blank ($\Delta I$) and the concentration of Rh(III) in the final determination system of 25 mL over 0.06–1.5 ng $mL^{-1}$ with a correlation coefficient ($r$) of 0.9991 and a linear regression equation of $\Delta I=3.72+38.71c$ (ng $mL^{-1}$). The limit of detection (LOD) of 0.024 ng $mL^{-1}$ was calculated from the method recommended by IUPAC as $LOD=3S_{bl}/S$, where $S_{b1}$ is the standard deviation of 9 blank measurements and $S$ is the slope of the calibration graph. The relative standard deviation (RSD) was found to be 2.76% and 1.98% for the determination of 0.1 ng $mL^{-1}$ and 1.0 ng $mL^{-1}$ of Rh (III) ($n=9$), respectively.

### 3.7. *Selectivity of the IIP-SPE–RLS method*

To examine the reliability of the proposed method, different foreign ions were added individually to a standard solution containing 20 ng of Rh(III) prior to separation by IIP-SPE. The results (Table 2) indicate that the selectivity of IIP-SPE–RLS is better than that of RLS. In IIP-SPE–RLS, at least 10-fold excess of the platinum group metals and 75-fold excess of the other

**Table 4**
Comparison of the present method with other methods for preconcentration, separation and determination of rhodium.

| Determination methods[a] | Preconcentration and separation methods[b] | EF[c] | LOD[d] (ng $mL^{-1}$) | Linear range (ng $mL^{-1}$) | RSD[e] (%) | Sample | Ref. |
|---|---|---|---|---|---|---|---|
| FAAS | IL-USA-DLLME | 29.1 | 0.37 | 4.0–500 | 1.63 | Water, plant | [7] |
| LI-TLS | CPE | 450 | 0.06 | 0.5–50 | < 5.0 | Water | [8] |
| FAAS | CPE | 50 | 0.052 | 0.16–1.5 | – | | [9] |
| ICP-AES | ETV | – | 0.8 | – | 2.4 | Biological and environmrntal samples | [10] |
| ETAAS | IEM with Dowex 1 × 8–200 as sorbent | 20 | 0.3 | 0.9–50 | 1.8 | Environmental samples | [12] |
| FIA-FAAS | SPE with cross-linked polystyrene as sorbent | – | 3 | – | – | Alloy, ores | [13] |
| FAAS | SPE with MWCNTs | 120 | 0.01 | 20–25000 | 0.97 | Alloy, water | [14] |
| ICP-AES | SPE with amberlite XAD-4-m-phenylendiamine as sorbent | – | 80 | – | 4.1 | Water | [15] |
| RLS | SPE with Rh(III) ion-imprinted polymers as sorbent | 10 | 0.024 | 0.06–1.5 | < 3.0 | Water, alloy, catalyst | This work |

[a] The abbreviation of the determination methods as follows: FIA: Flow injection analysis; FAAS: Flame atomic absorption spectrometry; ETAAS: Electrothermal atomic absorption spectrometry; LI-TLS: Laser induced-thermal lens spectrometry; ICP-AES: Inductively coupled plasma atomic emission spectrometry; RLS: Resonance light-scattering technique.

[b] The abbreviation of the preconcentration and separation methods as follows: SPE: Solid phase extraction; IEM: Ion exchange microcolumn; CPE: Cloud point extraction; MWCNTs: Modified multiwalled carbon nanotubes; IL-USA-DLLME: Ionic liquid ultrasound assisted dispersive liquid–liquid microextraction; ETV: Electrothermal vaporization.

[c] EF: enrichment factors.

[d] LOD: Limit of detection.

[e] RSD: Relative standard deviation.

**Table 5**
Determination of rhodium in the sample solutions by IIP-SPE–RLS method.

| Samples[a] | Standard value (ng mL$^{-1}$) | Found[b] (ng mL$^{-1}$, $n$=4) | Rh(III) added (ng mL$^{-1}$) | Total value found (ng mL$^{-1}$) | Recovery (%) |
|---|---|---|---|---|---|
| Automotive catalyst | 10.80 | 11.18 ± 0.26 | 10.00 | 21.05 | 98.8 |
| GBW07293 | 8.80 | 8.41 ± 0.31 | 10.00 | 17.96 | 94.6 |
| River water | N.D.[c] | N.D. | 10.00 | 10.26 | 102.6 |

[a] Automotive catalyst sample is obtained from Kunming Institute of Precious Metals (Yunnan, China) with the composition of Pt (976 μg g$^{-1}$), Pd (175 μg g$^{-1}$), Rh (108 μg g$^{-1}$) and a few of Ce, La as well as a large number of Al. GBW07293 obtained from Tianyu Chengxiang Experimental Equipment Sales Center, Beijing, China) is a Geochemical reference sample for the analysis of precious metals. The certified value of precious metals in GBW07293 is Pt (0.440 μg g$^{-1}$), Pd (0.568 μg g$^{-1}$), Rh (0.022 μg g$^{-1}$), Ir (0.028 μg g$^{-1}$), Ru (0.013 μg g$^{-1}$), Os (0.016 μg g$^{-1}$) and Au (0.045 μg g$^{-1}$). The river water sample was collected in Kunming (Yunnan, China) and filtered through a 0.45 μm pore size membrane filter before analysis.

[b] Mean ± S.D.

[c] N.D.: not detected.

transition metals have no effect on the determination of rhodium, which suggest that the proposed method can be used for the determination of rhodium in the complicated samples.

In comparison with other techniques for separation and determination of Rh(III) (Table 4), the developed analysis procedure showed a comparatively low detection limit (0.024 ng mL$^{-1}$), higher selectivity, together with a tolerable enrichment factor (10) and dynamic range (0.06–1.5 ng mL$^{-1}$) for Rh(III).

### *3.8. Application of the IIP-SPE–RLS method*

Some real samples, including an automotive catalyst material, a geochemical reference sample of GBW07293 and a natural water sample, were analyzed by the IIP-SPE–RLS method to evaluate the precision and accuracy of the proposed analytical procedure further. For this purpose, 1.0 mL of each sample solution was separated and determined in accordance to the proposed method. The results of these analyses are presented in Table 5. The recoveries of rhodium, which was carried out with the standard addition method by adding 10.0 ng mL$^{-1}$ of Rh(III) to the sample solution prior to the IIP-SPE process, are in the range 95.5–102.6%. The reproducibility of the procedure, expressed as RSD, is less than 4.0%. These results not only indicate the suitability of the Rh(III)-imprinted polymers for selective extraction of rhodium from the complicated samples but also prove the availability of the IIP-SPE–RLS method for the accurate determination of rhodium in the complicated samples.

## 4. Conclusions

In this work, the combination of the high sensitivity of RLS technique with the good selectivity of IIP-SPE method for the determination of trace rhodium in the complicated samples was considered. Hence, a Rh(III) ion-imprinted polymer as SPE material for the selective separation of Rh(III) and a RLS method for the determination of Rh(III) based on a ion-association complex formed among Rh(III), $WO_4^{2-}$ and ethylrhodamine B were investigated at the first time so far as we know. The results demonstrate that the combination method, employing RLS technique after IIP-SPE, possesses a low limit of detection (0.024 ng mL$^{-1}$), high sensitivity, good precision (RSD < 4.0%) and selectivity. It can suffer the interference from at least 10-fold excess of the platinum group metals and 75-fold excess of the other transition metals. The tolerable enrichment factor (10) along with easy operation and low cost is another advantage of the IIP-SPE–RLS method.

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