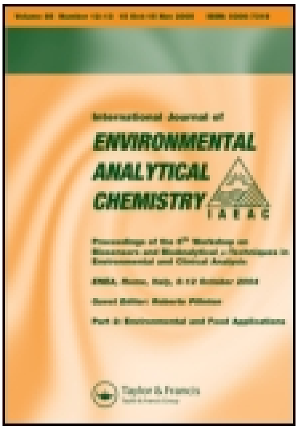

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

# Highly selective determination of rhodium(III) using silica gel surface-imprinted solid-phase extraction

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To cite this article: Hong Zheng, Shuling Yang, Jianchao Wang & Wenfeng Sun (2011): Highly selective determination of rhodium(III) using silica gel surface-imprinted solid-phase extraction, International Journal of Environmental Analytical Chemistry, 91:11, 1013-1023

To link to this article: http://dx.doi.org/10.1080/03067310903402441

*Intern. J. Environ. Anal. Chem.*
Vol. 91, No. 11, 15 September 2011, 1013–1023

# Highly selective determination of rhodium(III) using silica gel surface-imprinted solid-phase extraction

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(*Received 3 May 2009; final version received 6 October 2009*)

A novel Rh(III)-imprinted amino-functionalised silica gel sorbent was prepared by a surface imprinting technique for preconcentration and separation of Rh(III) prior to its determination by inductively coupled plasma atomic emission spectrometry (ICP-AES). Compared with the traditional solid sorbents and non-imprinted polymer particles, the ion-imprinted polymers (IIPs) had higher adsorption capacity and selectivity for Rh(III). The maximum static adsorption capacity of the imprinted and non-imprinted sorbent for Rh(III) was 29.86 $\text{mg g}^{-1}$ and 11.23 $\text{mg g}^{-1}$, respectively. The imprinted Rh(III) was removed with 2 mL of 3% thiourea + 2 $\text{mol L}^{-1}$ HCl. The obtained imprinted particles exhibited excellent selectivity and rapid kinetics process for Rh(III). The relatively selective factor ($\alpha_r$) values of Rh(III)/Ru(III), Rh(III)/Au(III), Rh(III)/Pt(IV), Rh(III)/Ir(IV), Rh(III)/Pd(II) were 26.7, 39.0 29.2, 28.1, 43.7, respectively, which were greater than 1. The detection limit ($3\sigma$) of the method was 0.26 $\mu\text{g L}^{-1}$. The relative standard deviation of the method was 1.79% for eight replicate determination of 10 μg of $Rh^{3+}$ in 200 mL water sample. The method was validated by analysing standard reference material (GBW 07293), the results obtained is in good agreement with standard values. The developed method was also successfully applied to the determination of trace rhodium(III) in geological samples with satisfactory results.

**Keywords:** Rh(III); solid-phase extraction; surface imprinting silica gel; preconcentration; ICP-AES

## 1. Introduction

Inductively coupled plasma atomic emission spectrometry (ICP-AES) has become one of the most attractive detection systems for the determination of trace elements in geological and other biological samples. Noble metals and especially rhodium are very resistant to acids, heat and corrosion, and rhodium is therefore used as a precious metal in jewellery and in some forms of chemical apparatus. It is also an excellent conductor of electricity and is used for electrical contacts and in catalytic converters [1–3]. However, concentrations of rhodium metal in environmental (also geological) materials are usually too low (even below the detection limit of the instrument) to be determined directly by conventional techniques owing to insufficient sensitivity and matrix interference. Thus, an

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903402441
http://www.informaworld.com

effective preconcentration and separation procedure is usually necessary prior to determination.

The preconcentration and selection separation of metal ions from aqueous solutions is usually achieved by solid-phase extraction which has many advantages: higher enrichment factor, better absence emulsion and increased safety with respect to hazardous samples, minimal costs due to low consumption of reagents, flexibility and incorporation into automated analytical techniques [4–7]. An efficient adsorbing material should possess a stable and insoluble porous matrix having suitable active groups (typically organic groups) that interact with metal ions. Silica gel is an ideal supporter for organic groups because it is very stable under acidic conditions and non-swelling inorganic material, and has fast and quantitative sorption and elution, high mass exchange and capacity characteristics and very high thermal resistance [8]. Immobilisation and cross-linking of organic compounds with certain functional groups on the surface of silica gel has gained important application in different research and industrial fields [9–12]. However, the basic disadvantage of the traditional solid sorbents is the lack of metal selectivity, which leads to other species interfering with the target metal ion(s). Recently, highly selective molecularly imprinted sol–gel materials have been extensively studied [13–15].

Nowadays, metal ion imprinted polymers (MIIP) have been investigated as highly selective sorbents for SPE in order to concentrate and clean up samples prior to analysis. One potential application that has recently attracted widespread interest is their use for clean up and enrichment of analytes present at low concentrations in complex matrices [16]. Ion-imprinted polymers (IIPs) are similar to MIPs, but they can recognise metal ions after imprinting and retain all the virtues of MIPs [17–18].

IIPs have outstanding advantages such as predetermined selectivity in addition to being simple and convenient to prepare. A particularly promising application of IIPs is the solid-phase extractive preconcentration of analytes present in low concentration or the separation from other coexisting ions or complex matrix. Thus, ion-imprinted polymers for solid-phase extraction are a fast developing area for the application of ion imprinting technology [19]. One of the first ionic template effects in the synthesis of chelating polymers was reported by Nishide *et al.* [20] in the mid-1970s. Recently, Takagi and co-workers [21] introduced a novel imprinting technique called surface template polymerisation. Surface molecular imprinting is one of the important types of molecular imprinting. Surface molecularly imprinted polymer not only possesses high selectivity but also avoids problems with mass transfer [18].

For metal ions, molecular imprinting can be interpreted as ionic imprinting exactly. So far a number of metal ions imprinted polymers have been prepared, including Pb(II) [22], Cu(II) [23–24], Ni(II) [25–26], Pd(II) [27–29], Cr(III) [30], Dy(III) [31], $UO_2$(II) [32], Cd(II) [33], Ca(II) [34], Zr(IV) [35] and Mg(II) [36] imprinted polymers.

However, to the best of our knowledge, solid-phase extraction and preconcentration by Rh(III)-imprinted amino-functionalised silica gel sorbent have not been employed for the separation and preconcentration of Rh(III) from aqueous solution. In this paper, a simple procedure was developed to synthesise a new Rh(III)-imprinted amino-functionalised silica gel sorbent by combining a surface molecular imprinting technique with a sol–gel process for selective separation and preconcentration of Rh(III). The characterisation of this imprinted amino-functionalised silica gel sorbent and its applicability to selective solid-phase extraction of Rh(III) are described and discussed in detail. The prepared Rh(III)-imprinted adsorbent was shown to be promising for the preconcentration and selective separation of rhodium in geological samples with satisfactory results.

## 2. Experimental

### 2.1 *Equipment*

An IRIS Advantage ER/S inductively coupled plasma spectrometer (TJA, USA) was used for all metal-determinations. The operation conditions and the wavelengths were summarised in Table 1.

The pH values were controlled with a pHs-10C digital pH meter (Xiaoshan Instrument Factory, China). A YL-110 peristaltic pump (General Research Institute for Nonferrous Metals, Beijing, China) was used in the separation/preconcentration process. A minimum length PTFE tube (0.5 mm i.d.) was used for flow injection connections. A self-made PTFE micro-column (45 mm × 2.5 mm i.d.) was used.

### 2.2 *Chemicals and reagents*

Reagents of analytical and spectral purity were used for all experiments and doubly distilled deionised water was used throughout. Standard labware and glassware used were repeatedly cleaned with $HNO_3$ and rinsed with pure water, according to a published procedure [37].

Silica gel (200–300 mesh, Mouping Kangbinuo Chemical Factory, Yantai, China) was used as the support to prepare the ion-imprinted functionalised sorbent.

In this study 3-aminopropyltrimethoxysilane (APS, Qingdao Ocean University Chemical Company, Qingdao, China) was used.

Stock solution ($1.0\,g\,L^{-1}$) of the Rh(III), Ru(III), Au(III), Pd(II), Ir(III) and Pt(II) were purchased from the National Research Center for Certified Reference Materials (Beijing, China). The standard working solution was diluted daily prior to use.

Table 1. ICP-AES operating conditions and wavelengths examined.

| Parameter | |
|---|---|
| R.F. Power (kw) | 1.15 |
| Carrier gas (Ar) flow rate ($L\,min^{-1}$) | 0.6 |
| Auxiliary gas (Ar) flow rate ($L\,min^{-1}$) | 1.0 |
| Coolant gas (Ar) flow rate ($L\,min^{-1}$) | 14 |
| Nebuliser flow (psi) | 30 |
| Pump rate ($r\,min^{-1}$) | 100 |
| Observation height (mm) | 15 |
| Integration time (s) on-axis | 20 |
| Off-axis | 5 |
| Wavelength (nm) | Rh(III) 233.477 nm,<br>Ru(III) 240.272 nm,<br>Au(III) 267.595 nm,<br>Pd(II) 340.458 nm,<br>Pt(IV) 265.945 nm,<br>Ir(IV) 224.272 nm |

### 2.3 *Preparation of the Rh(III)-imprinted and non-imprinted amino-functionalised silica gel sorbent*

The silica gel surfaces were activated by refluxing in concentrated hydrochloric acid under stirring for 8 h, then filtered off, and washed repeatedly with doubly distilled water until neutral and dried in an oven at 80°C for 12 h.

To prepare the Rh(III)-imprinted amino-functionalised silica gel sorbent, 2.074 g of $RhCl_3$ was dissolved in 80 mL of methanol under stirring and heating, then 4 mL of APS was added into the mixture. The solution was stirred and refluxed for 1 h, then 6 g of activated silica gel was added. After 20 h of stirring and refluxing the mixture, the product was first recovered by filtration, then washed by ethanol to remove the remnant of APS, and finally stirred into 50 mL of 3% thiourea $+ 6\,\text{mol L}^{-1}$ HCl for 2 h to remove the metal ions from the polymer. The final product was filtered, washed with doubly distilled water to neutral and dried under vacuum at 80°C for 12 h. The non-imprinted functionalised silica gel sorbent was also prepared using an identical procedure without adding $RhCl_3$.

### 2.4 *Recommended procedure*

#### 2.4.1 *Batch procedure*

A portion of standard or sample solution containing $Rh^{3+}$ was transferred into a 10 mL beaker, and the pH values were adjusted to the desired value with $0.1\,\text{mol L}^{-1}$ $HNO_3$ or $0.1\,\text{mol L}^{-1}$ $NH_3 \cdot H_2O$. Then the volume was adjusted to 10 mL with doubly distilled deionised water. Then 50 mg of sorbent was added, and the mixture was mechanically shaken for 30 min to attain equilibrium. After the solution was centrifuged, the concentrations of the metal ions in the solution were directly determined by ICP-AES.

#### 2.4.2 *Column procedure*

Firstly, the glass column (45 mm in length and 2.5 mm in diameter) was packed with a mixture of 50 mg of the Rh(III)-imprinted functionalised silica gel sorbent. A small amount of glass wool was placed at both ends to retain the sorbent in the column. Before the usage, pH = 4 of $HNO_3$ solution and doubly distilled and deionised water were successively passed through the micro column for equilibration. Portions of aqueous standard or sample solutions that contain Rh(III) were also prepared on the site. Then the pH value was adjusted to the desired value with $0.10\,\text{mol L}^{-1}$ of $HNO_3$ and $NH_3 \bullet H_2O$. Each solution was passed through the column at a flow rate of $1.0\,\text{mL min}^{-1}$ by using a peristaltic pump. Afterwards, the metal ions retained on microcolumn were eluted with 2 mL of 3% thiourea $+ 2\,\text{mol L}^{-1}$ HCl solution. The analytes in the elution were determined by ICP-AES.

#### 2.4.3 *Constants*

The adsorption capacity, the distribution ratio, the selectivity coefficient and the relative selectivity coefficient were calculated as the following equations:

$$Q = (C_0 - C_e)V/W;\ \ E = (C_0 - C_e)/C_e;\ \ D = 1000Q/C_e;\ \ \alpha_{Rh/M} = D_{Rh}/D_M;\ \ \alpha_r = \alpha_i/\alpha_n;$$

where $Q$ represents the adsorption capacity ($\text{mg g}^{-1}$), $C_0$ and $C_e$ represent the initial and equilibrium concentration of $Rh^{3+}$ ($\mu\text{g mL}^{-1}$), W is the mass of Rh(III)-imprinted amino-functionalised silica gel polymer (mg) and V is the volume of metal ion solution (mL), $E$ is the extraction percentage (%), $D$ is the distribution ratio (mL $g^{-1}$), $\alpha_{Rh/M}$ is the selectivity coefficient, $D_{Rh}$ and $D_M$ represent the distribution ratios of Rh(III) and Ru(III), Au(III), Pt(IV), Ir(IV), Pd(II); $\alpha_r$ is the relative selectivity coefficient, $\alpha_i$ and $\alpha_n$ represent the selectivity factor of imprinted sorbent and non-imprinted sorbent.

## 3. Results and discussion

### 3.1 *Preparation of the Rh(III)-imprinted amino-functionalised silica gel sorbent*

Silica gel immobilised chelating groups are gaining increasing is an ideal support for organic groups because it is a stable under acidic conditions and non-swelling inorganic material, and has high mass exchange characteristics and very high thermal resistance. The crucial factor is that many silanol groups (Si-OH) on its surface are responsible for its chemical modification. Because commercial silica gel has adsorbed some metal ions and also possesses a low content of surface silanol groups suitable for modification, it is necessary to activate the silica gel surface. According to the literature [38], concentrated hydrochloric acid was chosen for activation reagent. The complex was formed between Rh(III) and APS, then cohydrolysed and co-condensed with the activated silica gel. Thus, the activated silica gel surface was grafted with the complex of Rh(III) and APS rather than just the free APS. After the remnant APS and Rh(III) had been removed by ethanol and 3% thiourea + 6 mol $L^{-1}$ HCl, respectively, the imprinted functionalised silica gel sorbent which contained a tailor-made cavity for Rh(III) was formed. The ratio of APS to the activated silica gel is directly related to the moles of the active groups with respect to the weight of the functionalised silica gel sorbent. It was found that 1 mL APS/1.5 g activated silica gel was the optimal proportion, so this proportion was used in the present work.

### 3.2 *Characteristic of the FT-IR spectra*

To identify and confirm the presence of APS in the functionalised silica gel sorbents, the FT-IR spectra of activated silica gel, rhodium(III)-imprinted and non-imprinted amino-functionalised silica gel sorbents were obtained. From Figure 1(A), the observed features around 1102.71 and 967.75 $cm^{-1}$ related to Si–O–Si and Si–O–H stretching vibrations, respectively. The peak 469.95 $cm^{-1}$ was assigned to Si-O stretching vibrations and valence link curve. The presence of adsorption water was reflected by $\nu$OH vibration at 3436.64 and 1631.88 $cm^{-1}$. The peaks around 803.24 and 469.85 $cm^{-1}$ resulted from Si–O vibrations. The characteristic features of the imprinted adsorbent (Figure 1(C)) compared with activated silica gel are N–H bond around 1537.68 $cm^{-1}$ and C–H bond around 2926.12 $cm^{-1}$, 2863.85 $cm^{-1}$ and 1454.32 $cm^{-1}$. A characteristic feature of the imprinted and non-imprinted sorbents is a N–H peak around 3437.12 $cm^{-1}$. It shows that $-NH_2$ was grafted onto the surface of the activated silica gel after modification. Imprinted and non-imprinted sorbent showed a very similar location and appearance of the major peaks. It indicates that $-NH_2$ was recovered after removal of rhodium(III) in the imprinted sorbent.

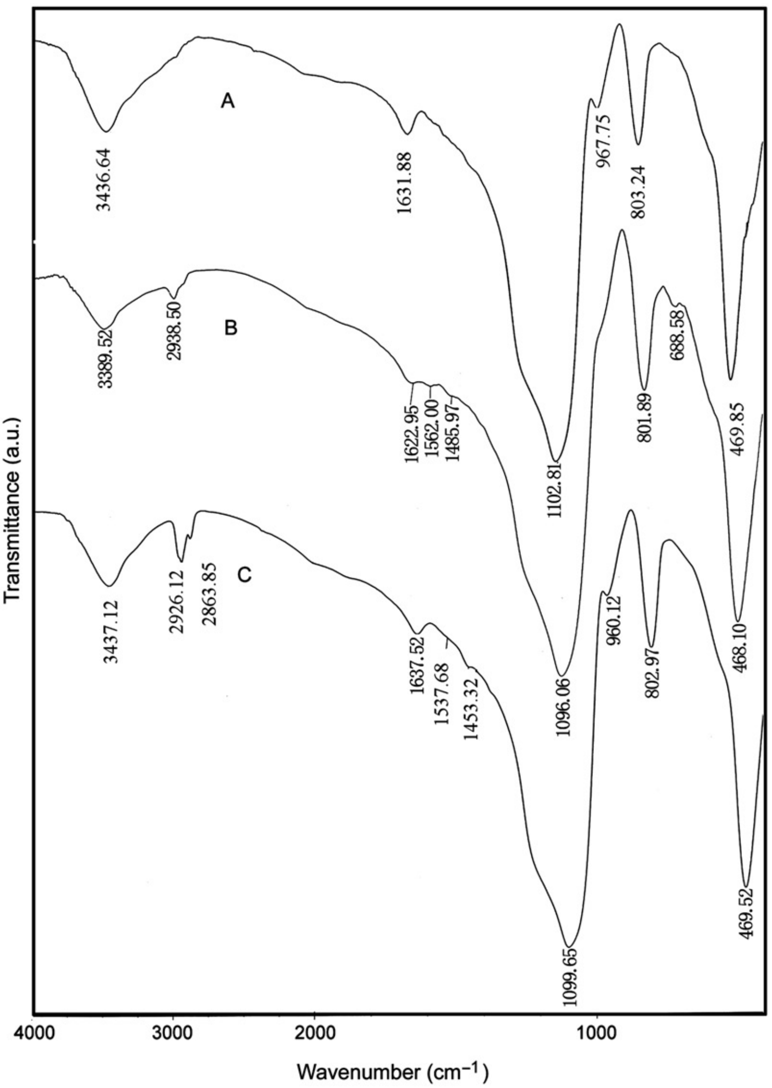

Figure 1. FT-IR spectra of the activated silica gel (A), non-imprinted (B) and Rh(III)-imprinted (C) adsorbent.

### 3.3 *Adsorption capacity of Rh(III)-imprinted sorbent for Rh(III)*

The adsorption capacity was tested following recommended procedure (batch procedure) described above. As can be seen in Figure 2, the amount of Rh(III) adsorbed per unit mass of IIPs increased with the initial concentration of Rh(III). The initial Rh(III) concentrations were increased till the plateau values (adsorption capacity values) were obtained. The static adsorption capacity of the imprinted amino-functionalised silica gel sorbent for Rh(III) was calculated as 29.86 $\mathrm{mg\,g^{-1}}$. It was about 3 times the non-imprinted sorbent (11.23 $\mathrm{mg\,g^{-1}}$). The result shows that the ion-imprinted polymers have a high adsorption capacity for Rh(III).

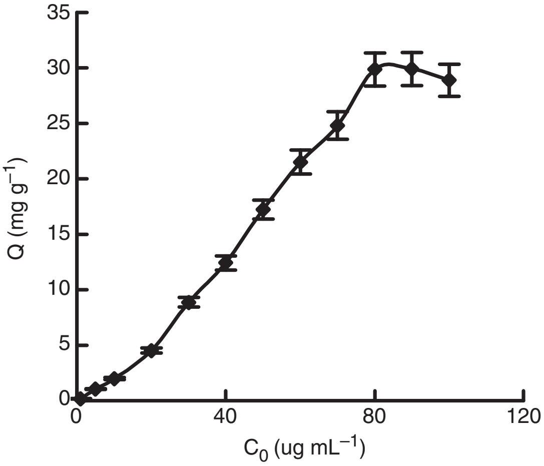

Figure 2. The effect of Rh(III) initial concentration on the adsorption quantity of Rh(III)-imprinted amino-functionalised silica gel sorbent. Other conditions: 50 mg of Rh(III)-imprinted sorbent, pH value of 4, shaking time of 30 min, temperature of 25°C.

### 3.4 *Uptake kinetics of Rh(III) by the imprinted adsorbent*

In this work, different shaking time (ranging from 2 to 60 min) was studied at room temperature. The result revealed that the 95% uptake of Rh(III) was achieved within 10 min. It is clear that the solid phase extraction process of the present adsorbent is faster than most of the traditional ion-imprinted adsorbents [25,26]. This indicate that the surface imprinting greatly facilitates diffusion of Rh(III) to the binding site.

### 3.5 *Influence of solution acidity*

Investigation of the influence of pH on adsorption is of great importance, because the adsorption for metal ions from aqueous solution is dependent on acidity. According to the recommended procedure (batch procedure), the solutions were enriched at pH 1–10 and then analysed by ICP-AES. The experimental results show, $Rh^{3+}$ could be adsorbed quantitatively on Rh(III)-imprinted amino-functionalised silica gel sorbent with a pH range of 4–10. In order to avoid hydrolysing at higher pH values, pH 4 was selected as the enrichment acidity for subsequent work.

### 3.6 *Elution condition on recovery*

Since the adsorption of cations at $pH < 2$ is negligible, one can expect that elution will be favoured in acidic solution. Elution of $Rh^{3+}$ from the column containing the Rh(III)-imprinted amino-functionalised silica gel sorbent was investigated by passing 2 mL several kinds of elating reagents following the general procedure(column procedure). The result (Table 2) shows that $Rh^{3+}$ was quantitatively desorbed with about 2 mL of 3% thiourea + 2 mol L$^{-1}$ HCl solution. Therefore, 2 mL of 3% thiourea + 2 mol L$^{-1}$ HCl was used as eluent in subsequent experiments.

Table 2. Elution recovery (%) for metal ions adsorbed on Rh(III)-imprinted sorbent. Eluent volume: 2 mL.

| Eluting solution | Rh(III) recovery, % |
|---|---|
| 5% $(NH_4)SCN$ | 77.5 |
| 5% thiourea | 85.9 |
| 2% thiourea + 1 mol $L^{-1}$ HCl | 90.1 |
| 3% thiourea + 2 mol $L^{-1}$ HCl | 95.7 |
| 4% thiourea + 2 mol $L^{-1}$ HCl | 97.3 |
| 3% thiourea + 3 mol $L^{-1}$ HCl | 96.6 |
| 4% thiourea + 3 mol $L^{-1}$ HCl | 97.3 |
| 5% thiourea + 3 mol $L^{-1}$ HCl | 97.4 |
| 6% thiourea + 3 mol $L^{-1}$ HCl | 98.1 |

The repeated use of a commercial adsorbent is likely to be a key factor. To test the stability, it was subjected to several adsorption and elution batch operations under the above experiment conditions. The results from both tests agreed within <5% error up to 20 cycles of repeated experiments. The adsorbent shows better reusability and stability. Therefore, the surface imprinted adsorbent is suitable for repeated use without decreasing their adsorption capacities significantly.

### 3.7 *Influence of flow rate*

The flow rate of the $Rh^{3+}$ solution through the packed column is a very important parameter because the time of analysis and the sorption of elements on adsorbent depend upon the flow rate of the sample solution. Its influence was studied under the optimum conditions (pH, eluent, etc.) by passing 50 mL of sample solution through the column with a peristaltic pump. The flow rates were adjusted in the range of 0.5 to 3.0 mL $min^{-1}$. The experimental results show that quantitative recoveries of the metal ions will decrease with the further increasing of the flow rate that is over 1.5 mL $min^{-1}$. Thus, a flow rate of 1.0 mL $min^{-1}$ was selected in this work.

### 3.8 *Maximum sample volume and enrichment factor*

The enrichment factor was researched by recommended column procedure by increasing volume of $Rh^{3+}$ solution and keeping the total amount of loaded $Rh^{3+}$ constant to 1.0 µg. For this purpose, 10, 50, 100, 150, 200, 250, 300 and 400 mL of sample solutions containing 1.0 µg of $Rh^{3+}$ were passed through the column at the optimum flow rate. The experimental results show, the maximum sample volume can be up to 300 mL with the recovery >95%. Therefore, 300 mL of sample solution was adopted for the preconcentration of $Rh^{3+}$ from sample solutions. And a high enrichment factor of 150 was obtained when 2 mL of 3% thiourea + 2 mol $L^{-1}$ HCl was used as eluent in these experiments.

### 3.9 *Influence of co-existing ions*

Different foreign ions were added to equal quantities of the diluted mixed standard solutions and adsorbed and desorbed according to the general procedure. The results

Table 3. The selectivity parameters of adsorbents for Rh(III).

| Metal ions[a] | $D_i$ (imprinted) ($mL\,g^{-1}$) | $D_n$ (non-imprinted) ($mL\,g^{-1}$) | $\alpha_i$ | $\alpha_n$ | $\alpha_r$ |
|---|---|---|---|---|---|
| Rh(III) | 16823 | 4670 | | | |
| Ru(III) | 137 | 1010 | 123 | 4.6 | 26.7 |
| Au(III) | 108 | 1155 | 156 | 4.0 | 39.0 |
| Pt(IV) | 151 | 1220 | 111 | 3.8 | 29.2 |
| Ir(IV) | 162 | 1260 | 104 | 3.7 | 28.1 |
| Pd(II) | 110 | 1350 | 153 | 3.5 | 43.7 |

Note: [a]Initial concentration: $10.0\,\mu g\,mL^{-1}$.

showed that up to $4000\,\mu g\,mL^{-1}$ of $K^+$ and $Na^+$, $200\,\mu g\,mL^{-1}$ of $Ca^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Ba^{2+}$, and $Ni^{2+}$, $100\,\mu g\,mL^{-1}$ of $Cd^{2+}$, $50\,\mu g\,mL^{-1}$of $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$ had no significant interferences with the determination of $1\,\mu g\,mL^{-1}$ of $Rh^{3+}$. There are three possible factors for this reason [18]. One is the amino-functionalised group inherent selectivity. The amino group is a soft base and it would not interact with alkali metal and alkali earth metal ions that are classified as hard acids. The second is the hole-size selectivity. The size of Rh(III) exactly fits the cavity of the Rh(III)-imprinted sorbent. The third is the coordination-geometry selectivity because the Rh(III)-imprinted silica gel sorbent can provide the ligand groups arranged in a suitable way required for coordination of Rh(III) ion. Although some ions have similar size with Rh(III) ion, and some ions have high affinity with the amino ligand, the Rh(III)-imprinted amino-functionalised silica gel sorbent still exhibits high selectivity for extraction of Rh(III) in the presence of other metal ions. These results suggest that the coordination-geometry selectivity may dominate in the selectivity enhancement.

### 3.10 *Analytical precision and detection limit*

Under the optimal conditions, eight portions of standard solutions were enriched and analysed simultaneously following the recommended procedure. The relative standard deviations (RSDs) of the method was lower than 1.79% that was lower than 2.0%, which indicated that the method had good precision for the analysis of trace rhodium in solution samples. In accordance with the definition of IUPAC [39], the detection limit of the method was calculated based on three times of the standard deviation of 11 runs of the blank solution. The detection limit ($3\sigma$) of the proposed method was $0.26\,ng\,mL^{-1}$.

### 3.11 *Selectivity of the imprinted sorbent*

In order to evaluate the selectivity of the imprinted adsorbent, competitive enrichment of Rh(III)/Ru(III), Rh(III)/Au(III), Rh(III)/Pt(IV), Rh(III)/Ir(IV) and Rh(III)/Pd(II) from their mixture was investigated in batch procedure because these ions often coexisted in their minerals and products or held the similar ionic radius or the same ionic charge. As can be seen in Table 3, the distribution ratio ($D$) values of Rh(III)-imprinted adsorbent for Rh(III) was highly greater than that of other metals. The relatively selectivity factor ($\alpha_r$) of Rh(III)/Ru(III), Rh(III)/Au(III), Rh(III)/Pt(IV), Rh(III)/Ir(IV), Rh(III)/Pd(II) were 26.7,

Table 4. Analysis of standard reference material samples.

| Analyte | Found value | Certified value |
|---|---|---|
| [a]GBW 07293 Rh | $376 \pm 21\,\mathrm{ng\,g^{-1}}$ | $381 \pm 23\,\mathrm{ng\,g^{-1}}$ |
| Copper sediment Rh | $1.06 \pm 10\,\mathrm{\mu g\,g^{-1}}$ | $1.09 \pm 11\,\mathrm{\mu g\,g^{-1}}$ |

Note: [a]GBW 07293 contains Ru, Rh, Pd, Ir and Pt elements.

39.0 29.2, 28.1, 43.7, respectively, which were greater than 1. The results indicate that the Rh(III)-imprinted adsorbent had higher selectivity for Rh(III). This means that Rh(III) can be determined even in the presence of Ru(III), Au(III), Pt(IV), Ir(IV) and Pd(II).

### 3.12 *Analytical application*

The proposed method has been applied to the determination of trace rhodium in geological samples. A 20.00 g amount of water deposit samples (GBW 07293 reference sample and one copper sediment sample) were roasted at 600°C for 1 hour, and then transferred into beakers right after. About 50 mL of diluted aqua regia (1 : 1) (v/v) were added into beakers. The solutions were digested for 30 minute. They were further diluted to 100 mL and filtered afterwards. The filtrates were detected as mentioned above. The analytical results are shown in Table 4. It is obvious results that all the results agree with the certified values.

## 4. Conclusion

In this paper, a selective and sensitive method for the determination of trace levels of rhodium was developed by a surface imprinted sorbent. The preparation of Rh(III)-imprinted amino-functionalised silica gel sorbent by a surface imprinting technique was relatively simple, rapid and economical. It had higher adsorption capacity and selectivity for Rh(III), and the method was successfully applied to the analysis of trace rhodium in geological samples. The precision and accuracy of the method are satisfactory.

## Acknowledgements

The authors are thankful for financial support from the Key Project of Chinese Ministry of Education (No. 208155) and QingHai Science and Technology Department (No. 2008-G-166).

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