Nanocomposite Magnetite-Kaolin for Rh Preconcentration and Determination by Electrothermal Atomic Absorption Spectrometry

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Abstract

A preconcentration technique with magnetite-kaolin adsorbent capable of magnetic separation was developed for the determination of rhodium in the environmental samples. The magnetite-kaolin nanocomposite was prepared for the preconcentration of rhodium in aqueous solution prior to electrothermal atomic absorption spectrometric determination. The detection limit (3S/N) of rhodium was 16 pg mL\(^{-1}\) under the optimum conditions. Even though matrix elements existed in 10\(^3\) fold excess in aqueous solution, the rhodium adsorption could be not affected by the matrix. The present method could be applied to the determination of Rh in aqueous solution. The advantages are easy preparation of adsorbent and fast magnetic separation.

**Keywords:** Preconcentration, magnetic kaolin, rhodium, ETAAS, water
Introduction

Until now, Rh (rhodium) has been widely employed as a raw product of plating in the electronic instruments and as a catalytic converter for the purpose of controlling of automotive emissions.\(^1\) As a consequent, Rh has been extendedly distributed into the environmental field. Hence, it is necessary to develop the sensitive monitoring techniques of rhodium in the environmental samples.\(^1\)

Recently, the analysis of rhodium by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) has been conducted.\(^2\) These techniques are highly sensitive, however the instrumentation is more complex and costly. Electrothermal atomic absorption spectrometry (ETAAS), namely, graphite furnace atomic absorption spectrometry (GFAAS) is very convenient and in much more general use.\(^3\) Since the detection limit of Rh for ETAAS is not superior,\(^3\) the preconcentration method for rhodium is needed for determining Rh with the ultra trace concentration in the environmental sample.\(^4\) Furthermore, the preliminary separation process is often required because of the matrix interferences. The techniques containing coprecipitation, liquid-liquid extraction, electrolytic deposition (electro-deposition), electrophoretic separation, sorption, adsorption and solid phase extraction have been applied into the separation and preconcentration of trace Rh in various samples.\(^4\)

Kaolin (\(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\) or \(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}\)) is abundant in the nature and available, and is a layered silicate consisted of platelets connected by hydrogen bonding. Kaolin has been recently applied many industrial processes owing to its good bonding ability and thermal stability. The removal of heavy metals from aqueous solution by kaolin has been reported by Yavuz et al.,\(^5\) and it was found from the results that kaolinite showed better absorption ability for Cu, Co, Mn and Ni. Because the adsorption materials are generally powder forms, it is
difficult to separate the solid from a liquid phase. In order to solve this problem, magnetic separation using an external magnetic field has attracted great attention due to high separation efficiency, shorter time and less energy consumption.\textsuperscript{6} Although many works has been carried out on magnetic separation method and kaolin separation,\textsuperscript{6,7} there is little information on the preconcentration technique for rhodium with magnetic kaolin. The present work focuses on the determination of Rh in the environmental samples by ETAAS combined with the preconcentration technique with magnetic kaolin.

**Experimental**

**Reagents and chemicals**

All of the chemical reagents were of analytical grade, and used without further purification. Ultrapure water (18.2 MΩ cm) was obtained from the Advantec ultrapure water system CPW–102 (Tokyo, Japan). All of solutions were prepared with ultrapure (deionized) water. An aqueous standard solution of rhodium was prepared by diluting 1 mg mL\textsuperscript{−1} stock solution obtained from KANTO CHEMICAL Co., Inc. (Tokyo, Japan). Iron salts (FeCl\textsubscript{2}·4H\textsubscript{2}O and FeCl\textsubscript{3}) were obtained from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan). Matrix solutions of Ca, Cu, K, Mg, Mn, Ni and Pb were prepared by dissolution of nitrates and hydrochlorides. Kaline was purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan).

**Preparation of magnetic Fe\textsubscript{3}O\textsubscript{4}/kaolin**

The kaolin-Fe\textsubscript{3}O\textsubscript{4} composites were synthesized according to the literature with some modification.\textsuperscript{8} A suspension of 0.5 g kaolin of a 200 mL solution including 0.32 g FeCl\textsubscript{3} and 0.2 g FeCl\textsubscript{2}·4H\textsubscript{2}O was heated at 80 °C for 80 min. Then, 25 mL of 4 mol L\textsuperscript{−1} NaOH was added
dropwise to fabricate iron oxide. The composites were aged at 100 °C during 90 min, and then were washed 3 times with pure water. The obtained composites were dried under vacuum conditions for 24 hours. The characterization of kaolin-Fe₃O₄ composites are shown in Figs. S1 to S4 and Tables S1 to S3.

Preconcentration procedure

The initial pH of the solution (100 mL) was adjusted to 5 using 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NaOH. Then, 50 mg of the magnetic kaolin was added into the analyzed solution, and the magnetic kaolin nanopowders were sonicated for 7 min for the dispersion of adsorbent using an ultrasonic cleaner (SIBATA SCIENTIFIC TECHNOLOGY Ltd., SUP-10, 100 W, Saitama, Japan). Next, the magnetic adsorbent was magnetically removed from the sample solution using a powerful magnet. After the decantation of the supernatant solution, the obtained adsorbent was washed with 1.0 mL of 0.5 mol L⁻¹ HNO₃ solution in order to desorb the Rh ions. The concentrated solution for Rh was obtained by the magnetic removal of adsorbents with a powerful magnet.

Analysis by ETAAS

The analysis for rhodium determination was carried out with an SMIMAZU AA-7000 equipped with an electrothermal graphite atomizer (GFA-7000A), an auto-sampler (ASC-7000) and deuterium lamp background corrector (Kyoto, Japan). A Rh hollow cathode lamp was carried out for the absorbance measurements at a wavelength of 343.5 nm and was operated at 10 mA with a spectral bandwidth of 0.7 nm. The peak height absorbance mode was adapted. The pyrolytically coated graphite tubes was used. Argon was used as a sheathing gas, and the internal Ar gas flow in the graphite atomizer was interrupted in the atomization step. The furnace temperature programs are described in Table S4 in the supporting information. The
analytical data were the average values obtained with more than three samples.

**Results and Discussion**

**Choice of kaolin**

In order to confirm the higher adsorption affinity for kaolin, various magnetic adsorbents containing $\text{Fe}_3\text{O}_4$/kaolin, $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$, $\text{Fe}_3\text{O}_4/\text{TiO}_2$ and $\text{Fe}_3\text{O}_4$/halloysite nanoclay were fabricated for the preconcentration of Rh. The photographs of the eluents after the preconcentration of rhodium using different magnetic adsorbents are illustrated in Fig. S5 in the supporting information. The colors of eluents with magnetic $\text{Al}_2\text{O}_3$, $\text{TiO}_2$ and halloysite nanoclay were not transparent, and these phenomena means the peeling of $\text{Fe}_3\text{O}_4$ and the dissolution of iron may occur owing to worse adhesion. However, in the case of $\text{Fe}_3\text{O}_4$/kaolin, the color was transparent. Furthermore, the maximum enrichment factor was observed with the adsorption of magnetic kaolin. Hence, in the present work, the optimum conditions for the preconcentration of Rh was explored with magnetic kaolin.

**Effect of aging processes**

Since the aging (heating) temperatures during the fabrication of adsorbent affected the surface color of magnetic kaolin, their surface conditions for the magnetic kaolin may be dependent on the dry processes. Therefore, the effect of heating (aging) conditions on the enrichment factor of rhodium was studied. The aging temperatures was tested in the range of 25 °C to 200 °C. The results are shown in Figs. S6 and S7. The aging temperatures and times could affect the enrichment factors for the preconcentration of Rh. The maximal enrichment factor was observed with the aging of 100 °C for 90 min. Therefore, these aging conditions were used for the fabrication of magnetic kaolin.
Effect of pH

It has been reported that deposition, sorption and adsorption methods can be frequently effected by the solution pH. Therefore, the influence of solution pH on the enrichment factor of analyte was investigated in the range of 3 to 9 when the other parameters were kept constant. The results are shown in Fig. 1. The enrichment factor of Rh increased gradually as the solution pH decreased from 9 to 5. The maximum enrichment factor was obtained at pH 5. At lower pH (<5.0), there was competition between H\(^+\) ions and Rh ions to occupy the active sites of magnetic kaolin. Hence, in the light of the results, the solution pH 5.0 was chosen as the optimum conditions.

Effect of eluent

The influence of type of eluent on the Rh enrichment factor was investigated. As seen in Fig. 1, adsorption of Rh onto the magnetic kaolin at pH 3 was relatively low, which means that desorption in acidic media can be useful for the magnetic kaolin adsorbent. Therefore, a variety of acid solutions were tested as the eluents as shown in Fig. 2, and from the results the elution with the concentration of 0.5 mol L\(^{-1}\) HCl gave the maximum factors. Hence, 1 mL of 0.5 mol L\(^{-1}\) HCl eluent was selected for the elution conditions.

Effect of adsorbent amount

In the solid extraction (adsorption onto the solid), the amount (suspension concentration) of magnetic adsorbent become one of the main factors effecting on the extraction of analytes. Therefore, the effect of suspension concentration of magnetic kaolin on the Rh enrichment factor was evaluated in the range of 0.2 to 0.5 mg mL\(^{-1}\), as illustrated in Fig. 3. The enrichment factor for Rh increased with an increase in the adsorbent. The fact could be caused by availability of more sorption situation and larger surface area. Over the value of 0.5 mg mL\(^{-1}\),
the factor of Rh decreased. Consequently, the suspension concentration of 0.5 mg mL\(^{-1}\) was selected as the optimum magnetic kaolin content for the subsequent experiments.

**Interferences**

The interferences from the coexisting elements has been described for the determination of rhodium by ETAAS.\(^3\),\(^4\),\(^12\) Therefore, the effects of Ca, Cu, K, Mg, Mn, Ni and Pb, which are generally present as the matrix elements in environmental waters, on the enrichment factors for Rh were investigated. The concentration of matrix elements was 10\(^3\) times larger relative to that of Rh. The results are shown in Fig. 4. Most of the matrix elements could not interfere with the enrichment factor of Rh. It has been reported in the previous paper\(^12\) that interferences by matrix elements for Rh could be associated with adsorption power of elements. Therefore, the interference for Rh was tried to be evaluated in the base of standard potentials related with the adsorption power. The standard potentials of typical existing ions are as follows:\(^13\) \(E^\circ\)\((\text{Rh}^{3+}/\text{Rh})=0.758\ \text{V},\ \ E^\circ\)\((\text{Ca}^{2+}/\text{Ca})=-2.3419\ \text{V},\ \ E^\circ\)\((\text{Cu}^{2+}/\text{Cu})=0.3419\ \text{V},\ \ E^\circ\)\((\text{K}^+/\text{K})=-2.931\ \text{V},\ \ E^\circ\)\((\text{Mg}^{2+}/\text{Mg})=-2.372\ \text{V},\ \ E^\circ\)\((\text{Mn}^{2+}/\text{Mn})=-2.690\ \text{V},\ \ E^\circ\)\((\text{Ni}^{2+}/\text{Ni})=-0.257\ \text{V},\ \ E^\circ\)\((\text{Pb}^{2+}/\text{Pb})=-0.1262\ \text{V}.\) From these data, it could be speculated that the adsorption of rhodium may occur predominantly. Therefore, it is reasonable that the these matrix elements tested did not interfere with rhodium preconcentration, by considering these data. Since the magnetic kaolin preconcentration appears relatively interference-free, the method was applied into the determination of Rh in the environmental samples. The mechanism for the preconcentration process may include ion exchange, physical adsorption and the interaction between the element Rh and the magnetic kaolin surface. From the information in the literatures, it could not be clarified which process is predominant for the adsorption of Rh onto the magnetic kaolin.

**Detection limit, enrichment factor and reproducibility**
The detection limit (3S/N) of rhodium by the combination of magnetic kaolin preconcentration and ETAAS was 16 pg mL\(^{-1}\) under the optimum conditions. The value was better, compared with the detection limits with ICP-OES (8 ng mL\(^{-1}\))\(^{14}\) and the combination of cloud point extraction and ETAAS (23 pg mL\(^{-1}\))\(^{3}\). The enrichment factor was 38. Also, the reproducibility for the ETAAS with combination of the magnetic kaolin preconcentration was investigated. The relative standard deviation (RSD) in the case of 1.0 ng mL\(^{-1}\) only was 5.7\% for eight measurements.

*Determinations of rhodium in environmental samples*

The developed preconcentration techniques were applied into the environmental samples (rain and mineral waters). The environmental samples spiked with 1.0 ng mL\(^{-1}\) were determined by GFAAS after the preconcentration method. Under the optimum conditions, the dynamic range for calibration curve fabricated from the standard Rh solution was up to 3 ng mL\(^{-1}\). Table 1 gives the determination results obtained for the environmental samples. The recovery value from rhodium spiked water samples was in the range of 100\% to 121\%. The RSD (relative standard deviation) for the spiked samples were better than 6\% for three replicate analyses. It was noted from the analytical determination results that the developed preconcentration method was suitable for the determination of trace Rh in the environmental waters.

**Conclusions**

The magnetic nano composite kaolin-Fe\(_3\)O\(_4\) was successfully applied into an adsorbent for solid extraction and the preconcentration of Rh. The combination of solid phase extraction by magnetic kaolin and ETAAS offered significant analytical performance. The advantages of the present preconcentration methods are easy preparation of adsorbent, fast extraction, fast magnetic separation, simple, low cost and convenient.
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Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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Table 1  Determination of rhodium in water

| Sample       | Concentration of rhodium (ng mL$^{-1}$) | Added | Found  | Recovery (%) |
|--------------|------------------------------------------|-------|--------|--------------|
|              |                                          | 1.0   | 1.21±0.07 | 121          |
| Rain water   |                                          | –     | n.d.   | –            |
| (Mie, Japan) |                                          | 1.0   | 1.21±0.07 | 121          |
| Mineral water|                                          | –     | n.d.   | –            |
|              |                                          | 1.0   | 1.00±0.06 | 100          |

n.d.: not detected.

Number of analysis >3.
**Figure Captions**

Fig. 1  Effect of solution pH on the enrichment factor of Rh.
Sample: Rh 1 ng mL\(^{-1}\) (100 mL); adsorbent: magnetite/kaolin 50 mg; eluent: HNO\(_3\) 0.1 mol L\(^{-1}\) (2 mL).

Fig. 2  Effect of eluent type on the enrichment factor of Rh.
Sample: Rh 1 ng mL\(^{-1}\) (100 mL); solution pH: 5; adsorbent: magnetite/kaolin 50 mg.

Fig. 3  Effect of adsorbent amount on the enrichment factor of Rh.
Sample: Rh 1 ng mL\(^{-1}\) (100 mL); solution pH: 5; eluent: HCl 0.5 mol L\(^{-1}\) (1 mL).

Fig. 4  Effect of matrix elements on the enrichment factor of Rh.
Sample: Rh 1 ng mL\(^{-1}\) (100 mL); matrix elements; 1 μg mL\(^{-1}\); solution pH: 5; adsorbent: magnetite/kaolin 50 mg; eluent: HCl 0.5 mol L\(^{-1}\) (1 mL).
Figure 1
Figure 2
Figure 3
Figure 4
Easy separation using magnetic kaolin for Rh preconcentration