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

Mai FURUKAWA,^{*,†} Ikki TATEISHI,^{**} Hideyuki KATSUMATA,^{*} Risako KUSUNOKI,^{*} and Satoshi KANECO^{*,**}

^{*}Department of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu, Mie 514-8507, Japan

^{**}Global Environment Center for Education & Research, Mie University, Tsu, Mie 514-8507, Japan

A preconcentration technique with a magnetite-kaolin adsorbent capable of magnetic separation was developed for the determination of rhodium in environmental samples. The magnetite-kaolin nanocomposite was prepared for the preconcentration of rhodium in an aqueous solution prior to an 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 10³ 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 an aqueous solution. The advantages are easy preparation of the adsorbent and fast magnetic separation.

Keywords Preconcentration, magnetic kaolin, rhodium, ETAAS, water

(Received September 5, 2019; Accepted November 15, 2019; Advance Publication Released Online by J-STAGE November 29, 2019)

Introduction

Until now, Rh (rhodium) has been widely employed as a raw product of plating in electronic instruments and as a catalytic converter for the purpose of controlling automotive emissions.¹ As a consequence, Rh has been extendedly distributed into the environmental field. Hence, it is necessary to develop the sensitive monitoring techniques of rhodium in 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, though 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 a preconcentration method for rhodium is needed for determining Rh for an ultra-trace concentration in the environmental sample.⁴ Furthermore, a preliminary separation process is often required because of matrix interferences. Techniques containing coprecipitation, liquid-liquid extraction, electrolytic deposition (electrodeposition), electrophoretic separation, sorption, adsorption and solid-phase extraction have been applied to the separation and preconcentration of trace Rh in various samples.⁴

Kaolin (Al₂Si₂O₅(OH)₄ or Al₂O₃·2SiO₂·2H₂O) is abundant in nature and is available. It is a layered silicate consisting of platelets connected by hydrogen bonding. Kaolin has recently been applied to 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 has 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, a shorter time and less energy consumption.⁶ Although many works has been carried out using the magnetic separation method and kaolin separation,^{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 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 an Advantec ultrapure water system (CPW-102; Tokyo, Japan). All solutions were prepared with ultrapure (deionized) water. An aqueous standard solution of rhodium was prepared by diluting a 1 mg mL⁻¹ stock solution obtained from KANTO CHEMICAL Co., Inc. (Tokyo, Japan). Iron salts (FeCl₂·4H₂O and FeCl₃) were obtained from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan). Matrix solutions of Ca, Cu, K, Mg, Mn, Ni and Pb were prepared by the dissolution of nitrates and hydrochlorides. Kaolin was purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan).

[†] To whom correspondence should be addressed.
E-mail: chem.mie-u.ac.jp

Preparation of magnetic $\text{Fe}_3\text{O}_4/\text{kaolin}$

Kaolin- Fe_3O_4 composites were synthesized according to the literature with some modification.⁸ A suspension of 0.5 g kaolin of a 200-mL solution including 0.32 g FeCl_3 and 0.2 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was heated at 80°C for 80 min. Then, 25 mL of 4 mol L^{-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 h. The characterization of kaolin- Fe_3O_4 composites are shown in Figs. S1 to S4 and Tables S1 to S3 (Supporting Information).

Preconcentration procedure

The initial pH of the solution (100 mL) was adjusted to 5 using 0.1 mol L^{-1} HNO_3 and 0.1 mol L^{-1} NaOH. Then, 50 mg of magnetic kaolin was added into the analyzed solution, and the magnetic kaolin nanopowders were sonicated for 7 min for dispersing the 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 decantation of the supernatant solution, the obtained adsorbent was washed with 1.0 mL of a 0.5 mol L^{-1} HNO_3 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

An analysis for rhodium determination was carried out with a SHIMADZU AA-7000 equipped with an electrothermal graphite atomizer (GFA-7000A), an auto-sampler (ASC-7000) and a deuterium lamp background corrector (Kyoto, Japan). A Rh hollow cathode lamp was carried out for 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. Pyrolytically coated graphite tubes were 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 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 $\text{Fe}_3\text{O}_4/\text{kaolin}$, $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$, $\text{Fe}_3\text{O}_4/\text{TiO}_2$ and $\text{Fe}_3\text{O}_4/\text{halloysite}$ nanoclay were fabricated for the preconcentration of Rh. Photographs of the eluents after the preconcentration of rhodium using different magnetic adsorbents are illustrated in Fig. S5 in Supporting Information. The colors of eluents with magnetic Al_2O_3 , TiO_2 and halloysite nanoclay were not transparent, and these phenomena mean peeling of Fe_3O_4 , and the dissolution of iron may occur owing to worse adhesion. However, in the case of $\text{Fe}_2\text{O}_3/\text{kaolin}$, 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

Fig. 1 Effect of the 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.

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

Effect of the pH

It has been reported that deposition, sorption and adsorption methods can be frequently effected by the solution pH.⁹⁻¹¹ Therefore, the influence of the 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 a lower pH (<5.0), there was competition between H^+ ions and Rh ions to occupy the active

Fig. 3 Effect of the 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).

sites of magnetic kaolin. Hence, in light of the results, the solution pH 5.0 was chosen as the optimum condition.

Effect of the eluent

The influence of the type of eluent on the Rh enrichment factor was investigated. As can be seen in Fig. 1, the 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 eluents, as shown in Fig. 2. From the results elution with a 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 the adsorbent amount

In the solid extraction (adsorption onto the solid), the amount (suspension concentration) of magnetic adsorbent becomes one of the main factors effecting on the extraction of analytes. Therefore, the effect of the 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. This fact could be caused by the availability of a greater sorption situation and a larger surface area. At over a value of 0.5 mg mL^{-1} , the factor of Rh decreased. Consequently, a suspension concentration of 0.5 mg mL^{-1} was selected as the optimum magnetic kaolin content for subsequent experiments.

Interferences

Interferences from the coexisting elements have 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 matrix elements in environmental water, on the enrichment factors for Rh were investigated. The concentration of the 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 was reported in a previous paper¹² that interferences by matrix elements for Rh could be associated with the adsorption power of the elements. Therefore, the interference for Rh was tried to

Fig. 4 Effect of matrix elements on the enrichment factor of Rh. Sample, Rh 1 ng mL^{-1} (100 mL); matrix elements, $1 \mu\text{g mL}^{-1}$; solution pH, 5; adsorbent, magnetite/kaolin 50 mg ; eluent, HCl 0.5 mol L^{-1} (1 mL).

be evaluated in the base of standard potentials related to the adsorption power. The standard potentials of typical existing ions are as follows:¹³ $E^0(\text{Rh}^{3+}/\text{Rh}) = 0.758 \text{ V}$, $E^0(\text{Ca}^{2+}/\text{Ca}) = 2.3419 \text{ V}$, $E^0(\text{Cu}^{2+}/\text{Cu}) = 0.3419 \text{ V}$, $E^0(\text{K}^+/\text{K}) = 2.931 \text{ V}$, $E^0(\text{Mg}^{2+}/\text{Mg}) = 2.372 \text{ V}$, $E^0(\text{Mn}^{2+}/\text{Mn}) = 2.690 \text{ V}$, $E^0(\text{Ni}^{2+}/\text{Ni}) = 0.257 \text{ V}$, $E^0(\text{Pb}^{2+}/\text{Pb}) = 0.1262 \text{ V}$. From these data, it could be speculated that the adsorption of rhodium may occur predominantly. Therefore, it is reasonable that these tested matrix elements did not interfere with rhodium preconcentration, by considering these data. Since magnetic kaolin preconcentration appears to be relatively interference-free, the method was applied for the determination of Rh in 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 information in the literature, it could not be clarified which process is predominant for the adsorption of Rh onto magnetic kaolin.

Detection limit, enrichment factor and reproducibility

The detection limit ($3S/N$) of rhodium by the combination of the 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 the cloud point extraction and ETAAS (23 pg mL^{-1})³. The enrichment factor was 38. Also, the reproducibility for the ETAAS with the 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.

Determination of rhodium in environmental samples

The developed preconcentration techniques were applied into the environmental samples (rain and mineral water). 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 the calibration curve fabricated from the standard Rh solution was up to 3 ng mL^{-1} . Table 1 gives the determination results obtained for 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 environmental water samples.

Table 1 Determination of rhodium in water

Sample	Concentration of rhodium/ng mL ⁻¹		
	Added	Found	Recovery, %
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.

Conclusions

The magnetic nano composite kaolin-Fe₃O₄ 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 a significant analytical performance. The advantages of the present preconcentration methods are easy preparation of the adsorbent, fast extraction, fast magnetic separation, simple, low cost and convenient.

Acknowledgements

All experiments were conducted at Mie University. The present research was partly supported by a Grant-in-Aid for Scientific Research (C) 18K11709 from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. Any opinions, findings, conclusions, or recommendations expressed in this paper are those of the authors and do not necessarily reflect the view of the supporting organizations.

Supporting Information

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

References

1. C. Almécija, A. Cobelo-García, and J. Santos-Echeandía, *Talanta*, **2016**, 146, 737.
2. J. Rinkovec, P. Gordana, S. Zuzul, and S. Roncevic, *Bull. Environ. Contam. Toxicol.*, **2017**, 98, 672.
3. Q. Han, Y. Huo, J. Wu, Y. He, X. Yang, and L. Yang, *Molecules*, **2017**, 22, 487.
4. P. P. Ndibewu, A. Marais, and M. Crindle, “PGMs Preconcentration & Spectroscopy: Trace/Ultratrace Levels Analysis: Socio-economic importance of PGMs, Chemistry/ Spectroscopy, Adsorption/Preconcentration, Separation/ Determination of PGMs”, **2014**, LAP LAMBERT Academic Publishing, Latvia.
5. Ö. Yavuz, Y. Altunkaynak, and F. Güzel, *Water Res.*, **2003**, 37, 948.
6. L. Qin, L. Yan, J. Chen, T. Liu, H. Yu, and B. Du, *Ind. Eng. Chem. Res.*, **2016**, 55, 7344.
7. P. Zong, S. Wang, and C. He, *Water Sci. Technol.*, **2013**, 67, 1642.
8. M. Amjadi, A. Samadi, and J. L. Manzoori, *Microchim. Acta*, **2015**, 182, 1627.
9. S. Kaneco, K. Hayashi, H. Katsumata, and T. Suzuki, *Int. J. Environ. Anal. Chem.*, **2013**, 93, 1381.
10. M. Furukawa, I. Tateishi, H. Katsumata, and S. Kaneco, *ChemEngineering*, **2019**, 3, 67.
11. T. Kusutaki, M. Furukawa, I. Tateishi, H. Katsumata, and S. Kaneco, *ChemEngineering*, **2019**, 3, 74.
12. S. Kaneco, J. Ogawa, K. Ohta, S. Itoh, and T. Mizuno, *Talanta*, **1998**, 46, 139.
13. D. R. Lide (ed.), “*Handbook of Chemistry and Physics*”, 85th ed., **2004**, CRC Press, Boca Raton, FL, 8 – 23.
14. K. Sawada (ed.), “*Wakate Kenkyusya Notameno Kikibunseki Labogaido (A Laboratory Guide to Instrumental Analysis for Young Chemists, in Japanese)*”, **2006**, Kodansha Scientific, Tokyo, 151.