ELSEVIER

Journal of Chromatography A, 932 (2001) 159–163

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Short communication

Selective concentration of gold in water to a polystyrene-embedded fiber disk with polyoxyethylene(10)–*p*-isononylphenyl ether

Tohru Saitoh[a,*], Shigendo Akita[b], Takahiro Torii[a], Masataka Hiraide[a]

[a]*Department of Molecular Design and Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan*
[b]*Nagoya Municipal Industrial Research Institute, Rokuban, Atsuta, Nagoya 456-0058, Japan*

Received 15 May 2001; received in revised form 30 August 2001; accepted 30 August 2001

Abstract

A new surfactant-mediated separation method was developed for concentrating traces of gold ion in water. The methodology is based on the combination of selective complexation of gold(III) with polyoxyethylene(10)–*p*-isononylphenyl ether, PONPE-10, and strong binding of surfactant complex to hydrophobic polystyrene resins embedded in a PTFE fiber disk (Empore disk). A 400-fold concentration of gold(III) was achieved by 400 ml load of the sample containing 0.01% (w/v) PONPE-10 and 0.10 *M* nitric acid and by the subsequent elution with 1.0 ml of aqueous buffer solution of 0.01 *M* *N*-(dithiocarboxyl)sarcosine diammonium. Traces of gold (0.40 ng/l) in river water samples were successfully determined with inductively coupled plasma MS. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Fiber disks; Gold; Polystyrene; Polyoxyethylene(10)–*p*-isononylphenyl ether

1. Introduction

Complexation of polyoxyethylene nonylphenyl ether (PONPE)-type nonionic surfactants with gold(III) has been often utilized for the selective solvent extraction of gold ion from acidic media [1]. This unique property of PONPEs has been also extended to micelle-mediated separation methodologies such as cloud point extraction and micellar-enhanced ultrafiltration. In the former, gold(III) can be concentrated into a very small surfactant phase resulting from temperature-induced phase separation of aqueous PONPE solution [2,3]. In the latter, gold(III) is concentrated on the ultrafiltration membrane together with PONPE due to the complexation with PONPE [4]. All these methods seem to also be available for the concentration of traces of gold in water samples prior to instrumental analyses.

However, difficulties lie in the analytical application of these methodologies due to the requirement of heating, centrifuging, or ultrafiltrating the solution [2–7]. Additionally, it is arduous to reproducibly handle a very small volume of viscous surfactant solution [5]. Thus, the concentration factor to be achieved using these methods could not be set to so high (ca. 20-fold in our experiments). Potential interference of large amount of surfactant into analytical signals is another reason for eliminating the use of these methods.

On the other hand, the strong interaction of PONPE with hydrophobic solid materials may solve these problems. It has been reported that polyoxy-

---

*Corresponding author. Tel.: +81-52-789-3579; fax: +81-52-789-3241.

E-mail address: saitoh@numse.nagoya-u.ac.jp (T. Saitoh).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)01251-1

ethylene-type nonionic surfactants in environmental water could be efficiently collected by the use of several types of sorbent [8]. Among them, polystyrene resin seems to be the most adequate, because of its tolerance against acid and of its strong ability for the adsorption of nonionic surfactants [8,9]. Furthermore, a recently developed membrane filter composed of fine polystyrene particles and PTFE fibers (Empore disk) seems to enable the use this adsorbent for analytical purposes [10,11].

In the present work, we developed a new method for concentrating traces of gold in water on the basis of selective complexation with PONPE surfactants and the adsorption to polystyrene resin. The conditions for achieving rapid and efficient concentration were investigated. The method was applied to the concentration of gold in river water prior to determination by inductively coupled plasma mass spectrometry (ICP-MS).

2. Experimental

2.1. Materials

An Empore disk (SBD-XC, ϕ 47 mm) was purchased from GL Science (Tokyo, Japan). The disk set in a 50-ml glass holder (I.D. 35 mm) was pretreated with 10 ml of ethanol and then washed with 50 ml of 0.10 *M* nitric acid before use. Polyoxyethylene(10)–*p*-isononylphenyl ether (PONPE-10) was purchased from Tokyo Kasei Kogyo (Tokyo, Japan) and used as 1.0% (w/v) aqueous solution. An eluting solution was made by adding 11.9 mg of *N*-(dithiocarboxyl)sarcosine diammonium salt (DTCS; Dojindo Lab., Kumamoto, Japan) to 10 ml of aqueous solution of 0.05 *M* ammonium acetate just before use. Foreign ions, sodium(I), potassium(I), calcium(II), magnesium(II), iron(III), copper(II), and lead(II), obtained as 1000 ppm standard solution for atomic absorption spectrometry (AAS) were purchased from Wako (Tokyo Japan). Other chemicals used were of analytical grade. Milli-Q water (18 MΩ) was used.

2.2. Analytical procedure

A water sample was passed through a 0.45-μm Durapore membrane filter (pre-washed with 2 *M* nitric acid, Millipore, Bedford, MA, USA), and acidified to pH 1.0 with 14 *M* nitric acid. To a 400-ml aliquot of the sample was added 0.4 ml of 10.0% (w/v) PONPE-10 aqueous solution. Then, the resulting solution was slowly passed through an Empore disk to collect gold. After the disk was washed with 10 ml of Milli-Q water, the gold was eluted by 1.0 ml of the eluting solution and determined with a Seiko (Tokyo, Japan) SPQ6500 ICP mass spectrometer. A Seiko SAS-760 graphite furnace atomic absorption spectrometer was used for optimizing experimental conditions. Their instrumental parameters are listed in Table 1.

Table 1
Operating conditions for GFAAS and ICP-MS

GFAAS	
Furnace program	
Drying	0–150°C/20 s, 150°C for 15 s
Ashing	150–650°C/5 s, 650°C for 15 s
Atomization	2400°C for 2 s
Clean up	2550°C for 3 s
Wavelength for Au	242.8 nm
Lamp current	10 mA
Slit width	1.08 nm
Sample volume	10 μl
ICP-MS	
Gas flow-rate	
Outer	16 l/min
Intermediate	0.8 l/min
Carrier	1.0 l/min
RF power	1.2 kW
Sampling depth	12 mm
m/e for Au^+	196.97

3. Results and discussion

3.1. Effect of PONPE-10 concentration

The kind or the concentration of surfactant is the most important factor that influences the recovery of gold(III), because the surfactant molecules or their aggregates work as the chelating agents. PONPE-7.5, having 7.5 oxyethylene units and being extensively employed for cloud point extraction [5,12–15], was not appropriate because it is immiscible with water at room temperature. On the other hand, PONPE-10 having 10 oxyethylene units seems to be a good choice, because the cloud point (ca. 60°C [2,3]) of its acidic solution is higher than room temperature.

As shown in Fig. 1, the adsorption yield on the Empore disk increased with increasing PONPE-10 concentration. In the concentration range from 0.005 to 0.04% (w/v), more than 98% of gold was recovered. This concentration is extremely lower than that required for the cloud point extraction or micellar-enhanced ultrafiltration [2–4]. It is reported that some ordered structures are formed by the adsorption of polyoxyethylene-type nonionic surfactants on the polystyrene surface [16]. Thus, such structures may provide favorable circumstances for improving the stability of gold–PONPE complex. Above 0.10% (w/v) PONPE-10, however, the adsorption yields of gold(III) significantly decreased due to the overload of PONPE-10. In marked contrast, the leakage of the surfactant was apparently recognized from the foaming properties of the percolates. The concentration of PONPE-10 was thus set to be 0.01% (w/v).

3.2. Effect of acid concentration

It has been reported that some acids were necessary for extracting gold(III) in the cases of liquid–liquid extraction and cloud point extraction with the use of PONPE [1–4]. Thus, the acid seems to play an important role also in the present system. As depicted in Fig. 2, the gold(III) adsorption increases with increasing in acid concentration. In the present extraction method, quite small amounts of acid were required for quantitative recovery of gold(III). Indeed, extremely high concentration of hydrochloric or nitric acid is necessary for obtaining sufficient gold recovery (94% in 7 *M* HNO_3–diethyl ether, 95% in 3 *M* HCl–diethyl ether [17–20]) in the conventional solvent extraction using oxygenic solvents. This different behavior can be ascribed to strong binding of gold(III) to polyoxyethylene moieties of PONPE molecules. The higher recovery in the nitric acid system may be attributed to the strong binding ability of $[Au(NO_3)_4]^-$ to rather than $[AuCl_4]^-$. Above 0.05 *M* of nitric acid, the recovery was more than 98%. In the following study, the concentration of nitric acid was set to 0.10 *M*.

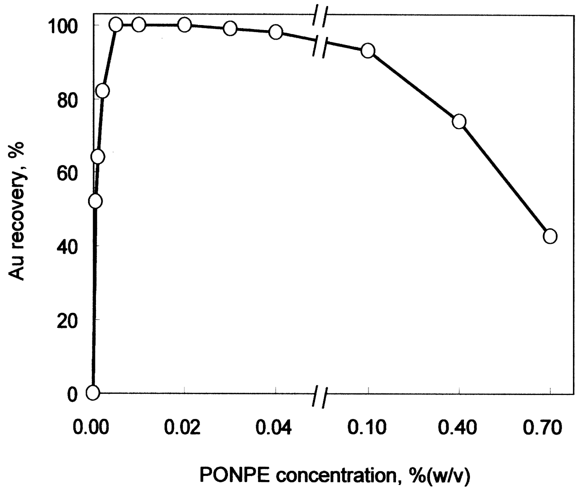

Fig. 1. Effect of PONPE-10 concentration on gold(III) adsorption to the Empore disk. Sample volume 50 ml, Au(III) 50 μg/l, 0.10 *M* HNO_3. Each point represents the average of three experiments.

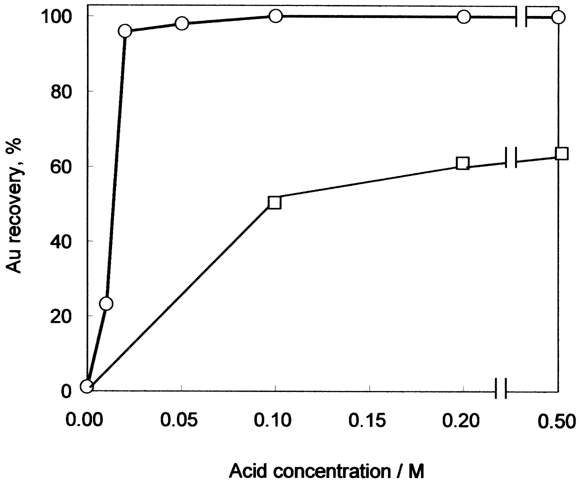

Fig. 2. Effect of hydrochloric acid (□) or nitric acid (○) concentration on gold(III) adsorption to the Empore disk. Sample volume 50 ml, Au(III) 50 μg/l, PONPE-10 0.01% (w/v). Each point represents the average of three experiments.

3.3. Influences of foreign ions

For applying the present method to environmental waters, tolerance limits of foreign ions were confirmed. Sodium(I), potassium(I), calcium(II), and magnesium(II) ions at 100 mg/l each or iron(III), copper(II), and lead(II) at 1 mg/l each negligibly interfered with the adsorption of 250 ng of gold(III) in 50 ml of water. Highly selective adsorption against foreign ions indicates the feasibility for applying the present method to environmental waters.

3.4. Sample loading capacity

In order to determine the sample loading capacity, increasing volumes of aqueous PONPE-10 solution containing gold(III) were passed through the Empore disk, and the effluent monitored. The recoveries of gold(III) were quantitative up to 400 ml of sample loading. At higher sample volumes the analyte recovery rapidly decreased and, simultaneously, the effluent started to become foamy. This probably reflects that the decreasing yield can at least partly be attributed to a loss of PONPE-10. In the present study, the sample volume was 400 ml.

3.5. Elution of gold

Several organic solvents and alkaline solutions tested were ineffective as eluents for desorbing gold from the PONPE-modified polystyrene resins. In contrast, the use of a chelating agent, DTCS, that has a couple of sulfurs as the coordination atoms and that can form stable water-soluble chelates with several heavy metal ions [21,22], was found to be an useful eluting agent. Above 0.005 *M* of DTCS in the aqueous buffer (pH 7.0) solution of 0.05 *M* ammonium acetate, the extent of gold elution reached constant (92±4%). In this study, the DTCS concentration was fixed at 0.01 *M*.

3.6. Application to river water

Finally, the proposed method was applied to the determination of gold in river water by ICP-MS. A linear relationship was obtained in the concentration range of 0–3 ng/l ($n=5$ for each of five data points) within 10% RSD in the signal intensity–gold concentration curve obtained by the standard addition method. From the intercept of the x-axis of the linear curve, the concentration of gold in Shonai River (Nagoya, Japan) water estimated was 0.4 ng/l. It has been recently reported that gold mostly exists as water-soluble salts in natural waters such as river, lake, and spring waters, with the concentration from sub-ppt to ppt (ng/l) [23–25]. The application of the proposed method to these samples would be beneficial to the monitoring traces of gold in environmental waters.

4. Conclusion

The combination of selective complexation of gold with PONPE-10 and hydrophobic binding of the complex to polystyrene resin created a novel medium for efficiently concentrating traces of gold in water. The present concentration method was successfully applied prior to ICP-MS analysis without giving any appreciable interference in the determination of gold. The application of this method to environmental or waste waters will propagate the determination of traces of gold and therefore contribute the development of gold geochemistry or effluent control.

Acknowledgements

This study was supported by a Grant-in-Aid for Scientific Research Japan (B) (12 558 071).

References

[1] S. Akita, L. Yang, H. Takeuchi, Hydrometallurgy 43 (1996) 37.
[2] H. Koshima, H. Onishi, Nippon Kagaku Kaishi 1986 (1986) 889.
[3] S. Akita, M. Rovira, A.M. Sastre, H. Takeuchi, Sep. Sci. Technol. 33 (1998) 2159.
[4] S. Akita, L. Yang, H. Takeuchi, J. Membr. Sci. 133 (1997) 189.
[5] T. Saitoh, Y. Kimura, T. Kamidate, H. Watanabe, K. Haraguchi, Anal. Sci. 5 (1989) 577.
[6] T. Saitoh, W.L. Hinze, Anal. Chem. 63 (1991) 2520.
[7] T. Saitoh, T. Matsudo, C. Matsubara, J. Chromatogr. A 879 (2000) 121.
[8] H.-B. Lee, Water Qual. Res. J. Canada 34 (1999) 3.
[9] A.K. Burnham, G.V. Calder, J.S. Fritz, G.A. Junk, H.J. Svec, R. Willis, Anal. Chem. 44 (1972) 139.
[10] J.W. Eichelberger, T.D. Behymer, W.L. Budde, in: Methods for the Determination of Organic Compounds in Drinking Water, US Environmental Protection Agency, Washington, DC, 1988, p. 325.

[11] J.F. Pankow, W. Luo, L.M. Isabelle, K.M. Hart, D.F. Hagen, J. Chromatogr. A 732 (1996) 317.
[12] H. Watanabe, H. Tanaka, Talanta 25 (1978) 585.
[13] H. Hoshino, T. Saitoh, H. Taketomi, T. Yotusyanagi, H. Watanabe, K. Tachikawa, Anal. Chim. Acta 147 (1983) 339.
[14] W.L. Hinze, E. Pramauro, CRC Crit. Rev. Anal. Chem. 24 (1993) 133.
[15] R.C. Martinez, E.R. Gonzalo, B.M. Cordero, J.L.P. Pavon, C.G. Pinto, E.F. Laespada, J. Chromatogr. A 902 (2000) 251.
[16] M.S.R. Cano, A.M. Rodriguez, G. Chauveteau, F.J. de las Nieves, Colloid Surfaces A: Physicochem. Eng. Aspects 140 (1998) 347.
[17] R. Bock, Z. Anorg. Allg. Chem. 263 (1950) 146.
[18] H.M. Irving, Quart. Rev. 5 (1951) 200.
[19] H. Goto, S. Suzuki, M. Saito, M. Kishimoto, Nippon Kagaku Zashi 85 (1964) 75.
[20] N. Ichinose, Talanta 18 (1971) 105.
[21] H. Watanabe, N. Yamaguchi, H. Tanaka, Bunseki Kagaku 27 (1978) 368.
[22] Y. Sakai, K. Kuroki, Bunseki Kagaku 28 (1979) 429.
[23] R. Cidu, L. Fanfani, P. Shand, W.M. Edmunds, L. Van't Dack, R. Gijbels, Anal. Chim. Acta 296 (1994) 295.
[24] R. Cidu, L. Fanfani, P. Shand, W.M. Edmunds, L. Van't Dack, R. Gijbels, Appl. Geochem. 10 (1995) 517.
[25] M.M.G. Gomez, C.W. Mcleod, J. Anal. Atom. Spectrom. 10 (1995) 89.