Study on the Formation of Ferromagnetic Bimetallic Nanoparticles and Their Application in Trace Metal Ion Collection

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Abstract: In this study, we investigated the collection of trace metal ions using ferromagnetic bimetallic nanoparticles synthesized from ferromagnetic metals and noble metals using $NaBH_4$ reduction. Co-Pd and -Pt and Fe-Pd and -Pt particles rapidly formed aggregates and had large ferromagnetic properties. The ion collection efficacy was evaluated for 40 elements chosen from the noble and rare earth metals. Elements that had recovery rates greater than 90% were Tl, Os, Cd, Sn, Ir, Pb, Ag, Au, Pt, Rh, Se, Ga, Te, Cu, and Ge. On the other hand, alkali, alkaline earth elements and most of the rare-earth elements were not recovered by this method.

Keywords : *Bimetallic ferromagnetic nanoparticles, cobalt, palladium, $NaBH_4$, preconcentration, trace metal ions*

Introduction

Recently, nanoparticle-based materials have received much attention due to their unique chemical and physical properties. In general, nanoparticles have a large collective surface area, which can be used for collecting materials from water samples. Nanoparticles with ferromagnetic property have been used for magnetic collection, where handling are generally easy. Qu et al. have synthesized Fe_2O_3 magnetic particles modified carbon nanotubes (CNTs) as an adsorbent for the magnetic separation of dye contaminants from water. Uheida et al. have used Fe_3O_4 and γ-Fe_2O_3 nanoparticles for adsorption of Co^{2+} from aqueous solution [1,2]. Recently, bimetallic nanoparticles synthesized from a ferromagnetic element (Fe, Co etc.) and a noble metal element (Pt, Pd etc.) have been utilized for magnetic collection[3,4]. Nakashima et al. synthesized FePd nanoparticles, which were used for preconcentration of trace metals in seawater[5]. However, they have not reported the magnetic properties and other combinations of ferromagnetic and noble metals.
Trace metals in hydrosphere environment are used as tracer of mass transfer[6]. Furthermore, metal pollution in the hydrosphere was a common

concern in the world. Therefore, it is necessary to accurately measure and monitor the concentration of metal ions in the hydrosphere. Even inductive coupled plasma mass spectrometry (ICP-MS), which is highly sensitive, is unable to accurately measure these extremely low concentration metal ions. Therefore, separation/concentration of trace metals is required for precise analysis[7]. Magnetic collection has advantages as easy handling and operation in a closed

system compared with other separation methods. In this study, we investigated co-reductive incorporation of trace metal ions into ferromagnetic bimetallic nanoparticles synthesized from ferromagnetic and noble metals. Bimetallic ferromagnetic nanoparticles were synthesized by reduction using $NaBH_4$. To our best knowledge, the investigation of the magnetic properties with formed bimetallic ferromagnetic particles and collection of trace metals in a magnetic field is first attempt. The incorporation of trace metals during formation of the ferromagnetic bimetallic nanoparticles was also investigated.

Materials and Methods

Instrumentation

An inductive coupled plasma atomic emission spectrometry (ICP-AES); model SPS 1500 VS (Seiko Instruments) was used for the determination of major and minor elements in the samples. An inductive coupled plasma mass spectrometer (ICP-MS); model ICPM-8500 (Shimadzu) was utilized for the determination of trace and ultratrace elements. For the ICP-MS measurements, internal standard correction was carried out in order to correct matrix effects due to major elements as well as instrumental drift. The structure and size of the particles were characterized by X-ray diffraction (XRD, Rint-2600-VHF, Rigaku) with CuKα radiation and transmission electron microscopy (TEM, Hitachi H-800), respectively. Magnetic properties of the particles were assessed with a magnetic balance (SHIMADZU MB-2). In addition, we used a pH METER (HM-25G) for the pH measurement. A magnet (Φ 17.5×20 mm, 5500 Oe) was utilized for the collection of magnetic particles.

Chemicals

The standard solutions for the calibration curves used in the ICP-AES and ICP-MS measurements, and evaluation of the adsorption of trace metal ions were prepared in 9 separate groups by mixing the single element standard stock solutions (1000 μg.g^{-1}) for atomic absorption spectrometry, purchased from Wako Pure Chemicals (Osaka, Japan) and Kanto chemicals (Tokyo, Japan). The multi-element standard solutions used for the ICP-AES and ICP-MS measurements are listed in Table 1.

the noble metal ion (90 mg g^{-1} as Pd, Pt, Au, Ag, Rh, Ru, Ir or Os) in solution were mixed together in 20 g of 1 mol kg^{-1} buffer solution (pH 6). Five gram of 0.25 mol kg^{-1} NaBH$_4$ solution was then added, which results in the solution turning black. After 20 minutes of shaking followed by 10 minutes at rest, the supernatant solution was transferred to another vessel. Then, the magnetic aggregate was separated using a magnet, and dissolved in 1 g of aqua regia or concentrated nitric acid, and analyzed with ICP-AES. The magnetic aggregates were also characterized by XRD, TEM and magnetic measurements.

Evaluation of metal ion adsorption onto the

Table 1. Composition of multielement standard solutions for ICP-AES and ICP-MS measurements

Group	Element	Concentration (solvent)
ICP-AES measurement		
Group 1	Co, Fe, Ni	1 μg g^{-1} in 0.1 HNO$_3$
	Rh, Ag	10 μg ml^{-1}
Group 2	Pd, Pt, Au, Ru, Ir, Os	10 μg g^{-1} in 0.1 HCl
ICP-MS measurement[a)]		
Group 3	Ni, Se, Cu, Pb, Cd, Ag, Rh, Zn	10 ng g^{-1} in 0.1 HNO$_3$
Group 4	Ru, Os, Ir, Pt, Au	10 ng g^{-1} in 0.1 HCl
Group 5	Ge, Mo, W	10 ng g^{-1} in 0.01 HNO$_3$
Group 6	Sc, Y, La, Pr, Nd, Sm, Eu, Yb	10 ng g^{-1} in 0.1 HNO$_3$
Group 7	Tb, Dy, Ho, Em, Tm, Gd	10 ng g^{-1} in 0.1 HNO$_3$
Group 8	Ti, Cr, Mn, Ga, Zr, Nb, Hf, Ta, Tl	10 ng g^{-1} in 0.1 HNO$_3$
Group 9	Sn, Sb, Te, Er10 ng g^{-1} in 0.1 HCl	

a)Each of the multielement standard solutions for ICP-MS measurement contains In, Bi (10 ng g^{-1} each)as internal standard elements.

The compositions of the elements in each standard solution were chosen, taking into consideration the stabilities of the elements dissolved in 0.1 mol L^{-1} HNO$_3$ solution (or 0.01 mol L^{-1} HNO$_3$, 0.1 mol L^{-1} HCl) and the concentration ranges of the analytic elements. Nitric acid, acetic acid, hydrochloric acid, ammonia aqueous solution, sodium acetate, Tris, citric acid, and sodium hydroxide were all analytical grade (Kanto Chemical). In addition, CoCl$_2$.6H$_2$O (Kanto Chemicals), FeCl$_3$（Wako Pure Chemicals）, Na$_2$PdCl$_4$ (SIGMA-ALDRICH), HAuCl$_4$.4H$_2$O （Wako Pure Chemicals, H$_2$PtCl$_6$.6H$_2$O (Kanto Chemicals), IrCl$_3$（Wako Pure Chemicals, (NH$_4$)$_2$OsCl$_6$ (SIGMA-ALDRICH), RuCl$_3$ (SIGMA-ALDRICH), AgNO$_3$(Kanto Chemicals), Na$_3$[RhCl$_6$].nH$_2$O (Kanto Chemicals), Co powder (Kanto Chemicals), Pd powder (Kanto Chemicals) and NaBH$_4$（Wako Pure Chemicals, 95 %purity）were used. All chemicals were used without further purification. Purified water was prepared by a Milli-Q purification system (Nihon Millipore Kogyo, Tokyo, Japan).

Preparation of magnetic particles

Bimetallic nanoparticles were synthesized for characterization of the magnetic properties and their morphologies as follows. 0.02g of the ferromagnetic ion (20 mg g^{-1} as Co or Fe) in solution, and 0.04 g of

Co-Pd particles was performed as follows. 0.02g of ferromagnetic ion (1000 μg g^{-1} as Co or Fe) standard solution, and 0.18 g of noble metal ion (1000 μg g^{-1} as Pd, Pt, Au, Ag, Rh, Ru, Ir, or Os) standard solution were mixed into a 20 g of 1 mol kg^{-1} buffer solution (pH 6). Then, 5 g of 0.05 mol kg^{-1} NaBH$_4$ solution was added. After 20 minutes of shaking followed by 10 minutes at rest, the supernatant solution was transferred to another vessel. Then the magnetic aggregate was separated using a magnet, and dissolved in 1 g of aqua regia or nitric acid, and analyzed with ICP-AES and ICP-MS.

Results and discussion

Particle formation by the combination of a ferromagnetic element and a noble metal element

Figure 1 shows recoveries of the noble metal and ferromagnetic metal for each combination under magnetic separation.

From visual inspection and ICP-AES measurements, it was found that almost all the combinations of ferromagnetic element with noble metal element produce particles. As can be seen Fig.1, the recovery of each element in Co-Pd, Co-Pt, Co-Au, Fe-Pd, Fe-Pt and Fe-Au bimetallic particle show high recoveries than the others. Palladium, Pt, and Au which have high redox potentials are easily reduced by
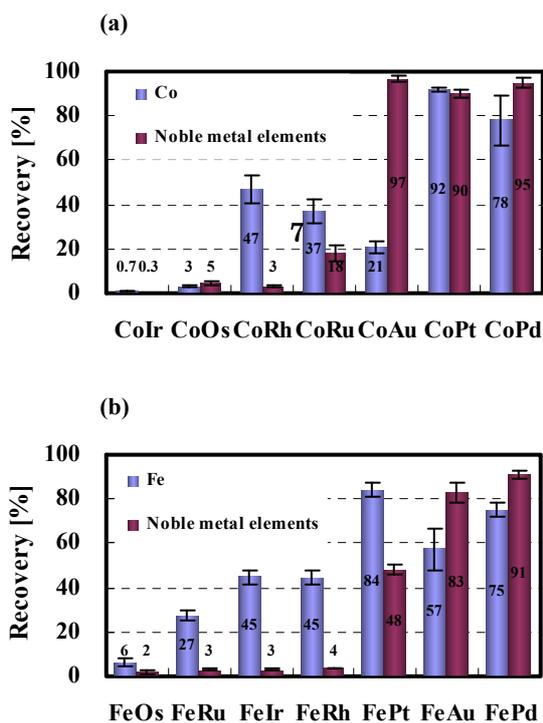
(a)

(b)

Figure.1 Noble metal and ferromagnetic metal recovery rate for various particle combination
The mass ratio of ferromagnetic element and the noble metal element is1:9 (400 μg : 3600 μg), pH 6:1 M $CH_3COOH-NH_4OH$ buffer solution, $NaBH_4$: 0.25 M、n = 3, (a) Co-metallic compounds, (b) Fe-metallic compounds.

$NaBH_4$. Iridium, Ru, Rh particles are also formed, however, they have low solubility in aqua regia and nitric acid, so the recovery for particles with these elements was relatively low.

The Co-Pd, Co-Pt and Fe-Pd particles has 227 emu g^{-1}, 175 emu g^{-1} and 190 emu g^{-1} of the saturation magnetization measured by the magnetic balance. They provided greater than 100 emu g^{-1}, which indicates they are ferromagnetic.

Palladium provides a hydrogen absorption effect and is a non-magnetic metal, but can be alloyed with a small quantity of magnetic metal (e.g. Fe, Co) and subsequently tends to order ferromagnetically [8]. Furthermore, palladium can be alloyed with noble metal elements easily. The Co-Pd had the larger saturation magnetization property than other ferromagnetic particles and showed high recoveries of Co and Pd as mentioned above. Therefore, we selected CoPd to trial the magnetic separation method in further research.

Evaluation of Co-Pd particles

The effects of the amount ratio of Co^{2+} to Pd^{2+} on the composition of the Co-Pd particles formed were investigated. Specifically, the amount ratios of Co to Pd were 1:15, 1:12, 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1. The recovery of Co^{2+} and Pd^{2+} from supernatant solution and magnetic particles under different ratios is shown in Table 2.
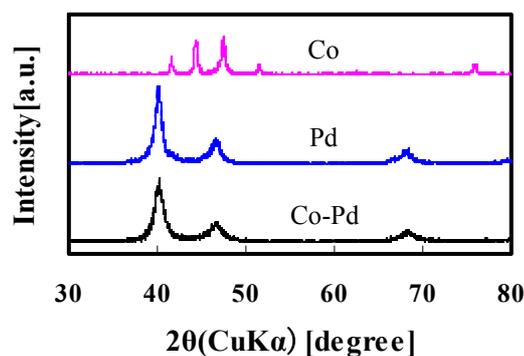

Figure.2 X-ray diffraction patterns of pure Co, pure Pd and synthesized Co-Pd particles
The mass ratio of ferromagnetic element and noble metal element was 1:9, pH 6 buffer solution.

From the results in Table 2, almost all of the Pd^{2+} was reduced and collected as magnetic aggregate. The recovery of the Co in the aggregate dropped when the quantity of Co^{2+} was higher than Pd^{2+}. This result indicates that Pd has a very important function in forming particles and incorporating trace metals into the particles, while cobalt is necessary to make Co-Pd particles aggregate with ferromagnetic property.

The XRD diffraction diagram of pure Co, pure Pd and synthesized Co-Pd particles (1:9 mass ratio) are shown in Fig.2. Three peaks (40°, 47°, 68°) attributable to Pd are observed. For the Co-Pd, no peaks appear at 41°, 44°, 47°, 51° and 76° which would correspond to Co, indicating that all Co is dissolved into the Pd matrix. TEM images and size distributions of (a) Co particles, (b) Pd particles, and (c) Co-Pd particles are shown in Fig.3. The Co and Pd particle was synthesized using addition of $NaBH_4$ to a Co or Pd only containing solution. When reducing Co^{2+} alone to Co, well-dispersed particles with an average particle size of around 50 nm were obtained. It was found that the synthesized Co particles were approximately 10 times bigger than the Pd particles.

The size and morphology of the Co-Pd particles(Fig.3b) are very similar to the Pd particles(Fig.3c). This result indicates that the Co layer was extremely thin compared with Pd phase, which can be expected from the TEM image and the XRD result. In the case of coreduction of $Co^{2+}$and Pd^{2+}, Pd^{2+} are reduced firstly because Pd has higher reductive property than Co [3].

Table 2. Recovery of Co and Pd from supernatant solution and magnetic particles under various amount of ratio of Co to Pd

Co:Pd amount ratio	Recovery [%]			
	Magnetic particles		Supernatant solution	
	Co	Pd	Co	Pd
1:15	77	95	22	n.d.
1:12	80	99	18	n.d.
1:9	71	93	21	1
2:8	68	96	27	n.d.
3:7	68	97	31	n.d.
4:6	58	96	37	n.d.
5:5	40	96	56	n.d.
6:4	34	98	59	n.d.
7:3	28	98	67	n.d.
8:2	25	100	67	n.d.
9:1	7	95	87	n.d.

n.d.:not detected
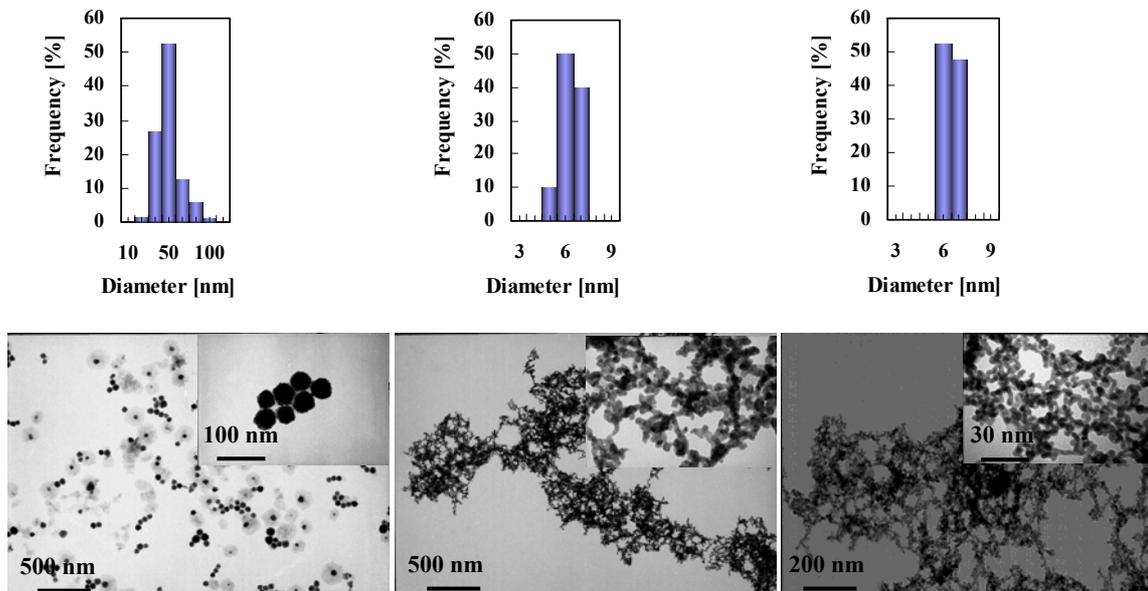
Figure.3 TEM photographs of the synthesized Co(a), Pd(b) and Co-Pd(c) particles synthesized by $NaBH_4$ reduction method.

Furthermore, the crystal lattice constants (CLC) of Co and Pd are 0.4060 nm and 0.3890 nm, respectively. So it is unlikely that cobalt atoms penetrate into the palladium bulk. For these reasons, it is concluded that thin layer of Co forms the Pd particles to form a Pd core-Co shell structure. This is in good agreement with the report by Noce et al.[9].

The incorporation of metal ions into ferromagnetic particles

Figure 4 shows the influence of the Co:Pd mass ratio on the recovery rate of selected metal ions. The results indicate that the mass ratio of Co^{2+} to Pd^{2+} did not significantly affect the recovery of metal ions.

It was thought that pH has an effect on collection of metal ions. The collection of metal ions from pH 2 to 9 was investigated. The results was shown in Fig.5. When the pH of the solution was 2.1 or 3.2, particle formation was very slow and produced non-magnetic particles, so a quite low recovery was obtained.

When the pH of the solution was 4.1, 5.3 and 6.8, the particle formation was very fast within 3 minutes. At the pH conditions, there was a high recovery rate for almost all elements. When the pH of the solution was above 7, particle formation was very slow and some part of the produced particles in the solution was attracted to the magnet. In this pH region, a low recovery and large variation was observed for almost all the elements. Cobalt can be easily dissolved at low pH values, while Co and Pd form hydroxides at high pH values.
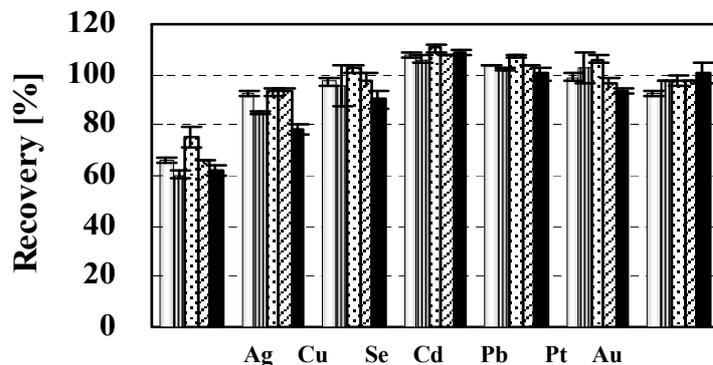
Figure.4 Effect of Co:Pd amount ratio in the recovery of metal ions.

The total amount of the addition of Co^{2+} and Pd^{2+} were 200 μg. The color of the bar indicates the amount ratio of Co^{2+} to Pd^{2+} :1:9(☐),2:8(▥), 3:7(⬚), 4:6(▨), and 5:5(■). The error bar was estimated from three times independent analysis.
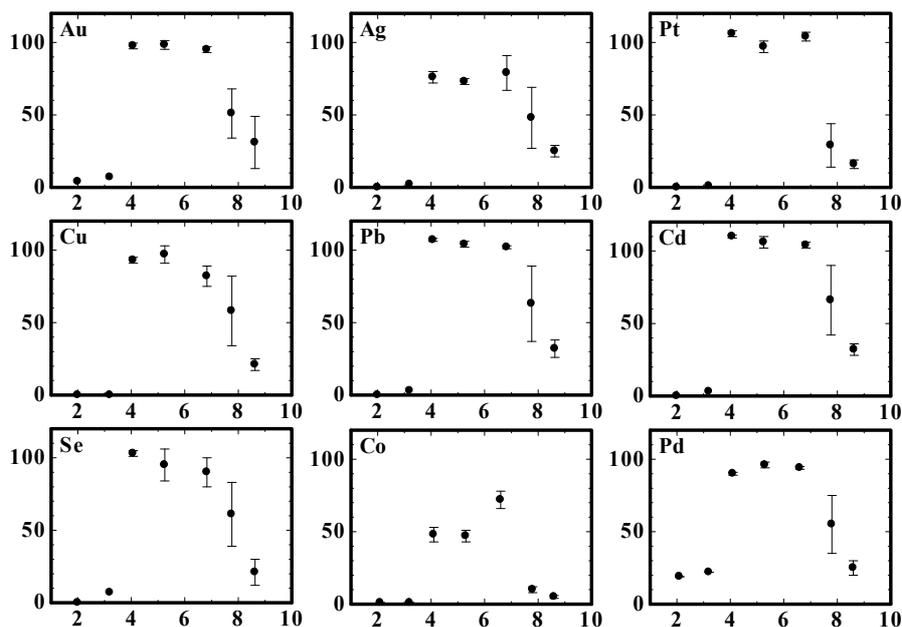

Figure.5 Effect of pH in the recovery of Co, Pd and metal ions
The amount ratio of ferromagnetic element and the noble metal element was set at 1:9 (20 μg : 180 μg). The added amount of the trace metals into the analytical solution was each 0.1 μg. The error bar was estimated from three times replicate measurements

Table 3. Recoveries of trace metal on Co-Pd nanoparticles

Element	m/z	Recovery [%] Mean ± s.d.[a]			Element	m/z	Recovery [%] Mean ± s.d.[a]		
Tl	205	107	±	2	Mn	55	41	±	4
Os	188	106	±	13	Cr	52	39	±	10
Cd	111	104	±	1	Ta	181	38	±	4
Sn	118	104	±	3	Ni	62	32	±	1
Ir	191	102	±	1	Mo	95	31	±	2
Pb	208	101	±	0.2	Sc	45	20	±	2
Ag	107	101	±	1	W	182	15	±	1
Au	197	100	±	7	La	139	7.7	±	0.4
Pt	195	99	±	3	Pr	141	7.1	±	0.3
Rh	103	97	±	1	Nd	146	6.4	±	0.5
Se	82	97	±	2	Gd	157	6.4	±	0.5
Ga	69	97	±	4	Sm	147	5.8	±	0.4
Te	125	94	±	3	Yb	172	5.6	±	0.2
Cu	63	92	±	9	Tm	169	5.6	±	0.3
Ge	72	90	±	4	Er	166	5.5	±	0.7
Ti	47	81	±	11	Dy	163	5.5	±	0.2
Nb	93	76	±	3	Tb	159	5.4	±	0.4
Zn	66	63	±	4	Y	89	5.3	±	0.3
Zr	90	62	±	5	Ho	165	5.1	±	0.3
Hf	178	62	±	6	Eu	153	3.6	±	0.4

a)The mean and standard deviation were obtained by the 3-times replicate measurements.
20 μg of Co and 180 μg of Pd and 0.1 μg of each trace element were added in the pH 6 buffer solution in the formation of Co-Pd particles.

The elements incorporated in the synthesized Co-Pd magnetic particles were investigated. The results are shown in Table 3. The recoveries for Tl, Os, Cd, Sn, Ir, Pb, Ag, Au, Pt, Rh, Se, Ga, Te, Cu and Ge were over 90%; between 60% and 80% for Ti, Nb, Zn, Zr, and Hf; between 10% and 40% for Mn, Cr, Ta, Ni, Mo, Sc and W. However, the recovery for the rare-earth elements such as La, Pr, Nd, Sm, Yb, Gd, Tm, Er, Ho, Dy, Tb, Y and Eu were under 10%. From these results, it can be seen that elements which have a low ionization tendency and metalloid elements from group 8 to 16 (especially noble metals) could be collected. However, elements from group 3 to 7 could be recovered by this method. Most elements showed good repeatability for the recovery. However, a few elements Os, Ti and Cr had standard deviation greater than 10%. The mechanism of collecting trace metal ions by using a strong $NaBH_4$ reducing agent allows the reduction of many metallic elemental ions to metal. Co^{2+} and trace metal ions are reduced easily and incorporated into Pd particles.

In order to evaluate the analytical reliability, the present method was applied to the analysis of some elements in river water conference material (NMIJ CRM 7202-a) issued from National Metrology Institute of Japan (NMIJ). The results are shown in Table 4. The results of Zn, Cd, Pb and Fe were well agreed with the certified values.

Table 4. Analytical results for determination of trace metals in NMIJ CRM 7202-a

Element	Wavelength or m/z	Mean ± s.d. /ng g^{-1}			Certified value /ng g^{-1}		
Zn	66	10.2	±	0.2	10.3	±	0.3
Cd	111	1.03	±	0.02	1.02	±	0.02
Pb	208	0.90	±	0.12	1.01	±	0.02
Fe	259.940	31	±	1	30.1	±	0.9

Mean and standard deviation of 3 times replicate measurements, total of Co and Pd are 400 μg (Co:Pd=1 μg g^{-1} :9 μg g^{-1}), pH 6, 0. 5 M $NaBH_4$

Conclusion

In this study, we succeeded in preparing magnetic particles from an inorganic solution at low concentration (several $\mu g\ g^{-1}$). In the screening ferromagnetic bimetallic nanoparticles formed by various combinations of ferromagnetic elements (Co and Fe) with noble metal elements (Pd, Pt, Au, Ag, Rh, Ru, Ir, Os), the Co-Pd was the most effective in the view of the magnetic property and recovery of Co and Pd. We were able to confirm that trace metal ions coexisting with Co2+ and Pd2+ (the major components) could be recovered to Co-Pd particles. This method can be used to separate these metals from alkali elements, alkaline earth elements and most of the rare-earth elements. Consequently, this method is suitable for recovering some trace metals (Au, Ag, Pt etc.) from high salt content samples such as river water, seawater and soil. This method outlined in this paper is simple. This provides easy separation through magnetic force, and can be performed in a single reaction vessel without need of filtration.

Acknowledgement

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