

Articles

Separation of Gold, Palladium and Platinum in Chromite by Anion Exchange Chromatography for Inductively Coupled Plasma Atomic Emission Spectrometric Analysis

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A study has been carried out on the separation of gold, iridium, palladium, rhodium, ruthenium and platinum in chromite samples and their quantitative determination using inductively coupled plasma atomic emission spectrometry (ICP-AES). The dissolution condition of the minerals by fusion with sodium peroxide was optimized and chromatographic elution behaviour of the rare metals was investigated by anion exchange chromatography. Spectral interference of chromium, a matrix of the minerals, was investigated on determination of gold. Chromium interfered on determination of gold at the concentration of 500 mg/L and higher. Gold plus trace amounts of iridium, palladium, rhodium and ruthenium, which must be pre-concentrated before ICP-AES was separated by anion exchange chromatography after reducing Cr(VI) to Cr(III) by H_2O_2 . AuCl_4^- retained on the resin column was selectively eluted with acetone- HNO_3 - H_2O as an eluent. In addition, iridium, palladium, rhodium and ruthenium remaining on the resin column were eluted as a group with concentrated HCl. However, platinum was eluted with concentrated HNO_3 . The recovery yield of gold with acetone- HNO_3 - H_2O was $100.7 \pm 2.0\%$, and the yields of palladium and platinum with concentrated HCl and HNO_3 were $96.1 \pm 1.8\%$ and $96.6 \pm 1.3\%$, respectively. The contents of gold and platinum in a Mongolian chromite sample were $32.6 \pm 2.2 \mu\text{g/g}$ and $1.6 \pm 0.14 \mu\text{g/g}$, respectively. Palladium was not detected.

Keywords : Chromite, Ion exchange separation, Gold, Platinum group elements, ICP-AES.

Introduction

Perchloric acid and perchloric-phosphoric acid mixture are the principal reagents used for dissolving chrome ores, chromite.¹ Manganese dioxide as an oxidizing agent with sulphuric acid is generally used to dissolve the chromite.^{2,3} A fusion procedure with Na_2O_2 alone⁴ or Na_2O_2 combined with NaOH is also frequently applied to attack ores containing chromium, a refractory element. Recently, a microwave digestion system has been introduced with aqua regia-perchloric-hydrofluoric acid mixture.⁵ A fire assay, which can dissolve 20-30 g samples and collect the platinum group elements (PGEs) into lead metal or nickel sulphide, has been frequently applied to dissolve rocks, soils and sediments for the determination of PGEs, the contents of which are ultra-trace amounts. In recent years, the nickel sulphide fire assay is the preferred method over lead fire assay for multi-element analysis and the absence of the cupellation step.⁶ In addition, partial digestion such as aqua regia leaching is also employed in the analysis of geological and environmental samples.⁷ Tsimbalist *et al.*⁸ effectively dissolved chromite powder by mixing and grinding with ammonium chloride to intensify dissolution and enhance the degree of homogenization of mineral substances.

Inductively coupled plasma mass spectrometry (ICP-

MS),^{9,10} laser ablation ICP-MS,¹¹ graphite furnace atomic absorption spectrometry (GFAAS),¹² neutron activation analysis (NAA)¹³ and inductively coupled plasma atomic emission spectrometry (ICP-AES)¹⁴ have been employed to analyze gold and PGEs. In particular, ICP-AES has been widely selected as the technique of choice to do the analysis of trace amounts of metal elements. This is due to ICP-AES's wide analytical dynamic range, high sensitivity, simultaneous measurement capability and relative freedom from matrix interferences. In spite of these advantages, however, direct analysis of the mineral was not possible for trace amounts of gold and PGEs because severe spectral interference was found in the intensely complex atomic emission spectra of the mineral matrix such as chromite. Thus, an adequate pre-separation procedure is needed before ICP-AES analysis. Ion exchange chromatography,^{15,18} coprecipitation,^{19,20} solvent extraction,²¹⁻²³ nickel sulphide fire assay^{24,28} and lead fire assay^{29,30} have been used to separate gold and PGEs from the sample matrix.

In the present study, we tried to measure gold directly in Mongolian chromite dissolved by the sodium peroxide fusion technique by ICP-AES. But the best sensitive gold wavelength, 242.795 nm, was spectrally interfered by chromium. To separate gold from chromium matrix, anion exchange chromatography was selected because the distri-

bution coefficient of gold in a hydrochloric acid medium is very high and other major constituents do not adsorb on the resin due to the formation of positive charge species. Because Cr(VI) oxidized by sodium peroxide fusion dissolution is adsorbed on the resin, Cr(VI) must be reduced to Cr(III) as a first step before ion chromatography. Adsorbed AuCl_4^- was eluted with acetone-nitric acid-water. After the desorption of gold, our task was to find the best desorbent for Ir(III), Pd(II), Pt(IV), Rh(III) and Ru(III) retained on the resin. The method was applied to measure gold, palladium and platinum in a Mongolian chromite.

Experimental Section

Instruments. A Jobin Yvon JY 38 PLUS, the sequential type of ICP-AES, was used to measure gold and PGEs, and from the same company, a JY 50 P, the simultaneous type of ICP-AES, was used to determine sodium in the eluate of gold. Analyses were done using a two-point calibration. The operation conditions of ICP-AES for the determination of PGEs, including gold and sodium, are shown in Table 1. The wavelengths for measurement of gold and PGEs are shown in Table 2. UV-Vis spectrophotometer (Varian, U.S.A.) was used to confirm the reduction of Cr(VI) to Cr(III) by H_2O_2 . An electric muffle furnace (Fisher Scientific, U.S.A.) and zirconium crucible (B-J Scientific Products, U.S.A.) were used.

Reagents and synthetic chromite solution. All chemicals such as hydrochloric acid (Merck Co., Germany), nitric acid (Merck Co., Germany), hydrogen peroxide (Merck Co., Germany), chromic oxide (Yakuri Chemicals Co., Japan), acetone (Dongyang Chemicals Co., Korea) and sodium peroxide (Fisher Co., U.S.A.) were of analytical grade. The distilled and demineralized water (DDW) was further purified by Milli-Q plus Ultra Pure Water System (Millipore Co., U.S.A.).

Table 1. Operating conditions of the ICP-AES

System	Sequential type (JY 38 PLUS) Simultaneous type (JY 50 P)
Focal length	1 m (JY 38 PLUS) 0.5 m (JY 50 P)
Mounting	Czemey Turner (JY 38 PLUS) Paschen Runge (JY 50 P)
Grating	3600 grooves/mm (JY 38 PLUS, JY 50 P) 1200 grooves/mm (JY 50 P)
Torch	Fassel type
Nebulizer	Meinhard TR 50-C1
Spray chamber	Scott type
Outer gas flow	12 L/min
Sheath gas flow, G1	0.4 L/min (JY 38 PLUS, JY 50 P)
G2	0.6 L/min (JY 50 P)
Injector gas flow	0.4 L/min
Sample uptake rate	1 mL/min
Incident power	1000 W
Integration time	5 × 0.5
Observation height	15 mm above the loading coil

Table 2. Wavelength selected for determination of Au, Ir, Pd, Pt, Rh and Ru

Element	Wavelength (nm)	Element	Wavelength (nm)
Au	242.795	Pt	214.423
Ir	224.268	Rh	343.489
Pd	340.458	Ru	240.272

To increase the surface area of sodium peroxide, Na_2O_2 was ground with an agate mortar. The concentrations of Au(III), Ir(III), Pt(IV), Ru(III) (Spex Certiprep., Metuchen, NJ, U.S.A.) Pd(II), Rh(III) (AccuStandard, New Haven, CT, U.S.A.) in stock solution were 1,000 mg/L, and each stock solution was diluted to the proper concentration for preparing a working standard solution and synthetic chromite solution. The chromite sample was supplied by the Central Geological Laboratory of Mongolia. Anion exchange resin, AG IX8 (chloride form, 100-200 mesh) was purchased from Bio-Rad Laboratories. To measure the recovery of gold and PGEs, a synthetic chromite solution was prepared by adding Au(III), Ir(III), Pd(II), Pt(IV), Rh(III) and Ru(III) to a Cr_2O_3 solution dissolved by the same procedure as the chromite sample.

Dissolution of chromite. An accurately weighed, finely powdered 0.8 g sample was transferred to a zirconium crucible, then 5.5 g of sodium peroxide was added to the crucible. After thorough mixing of its contents with a glass rod, the crucible was covered with a zirconium lid, then it was placed in the cold furnace. The mixture was ignited at 600 °C for 20-30 min. The crucible was removed from the furnace and swirled at 30 min intervals to ensure thorough mixing. The swirling process was repeated 10 times. After cooling, the crucible was immersed in a pyrex beaker containing 1 M HCl for chromic oxide or 2 M HCl for chromite sample and heated on a hot plate. The dissolution continued for approximately 8 hrs. Because fine black particles were observed, the solution was filtered (Watman No. 42 filter paper) and the filter paper containing the residue was washed thoroughly with 1 M HCl. The filtrate was saved for use later.

The filter paper, including the residue, was transferred to the crucible and burnt off at 500 °C. About 2.0 g of sodium peroxide was then added to the crucible. After thorough mixing, the temperature was raised to 600 °C for 20-30 min. The crucible was removed from the furnace and swirled at 30 min intervals to ensure mixing. The swirling process was repeated 10 times. The crucible and lid were immersed in the pyrex beaker containing filtrate and heated on a hot plate. For the chromite sample, filtration, burning the filter paper and the fusion process (0.5 g of Na_2O_2) were repeated once more. Finally, a clear orange color solution without the black particles was obtained. The volume of solution was adjusted to 100 mL.

Separation of gold and PGEs using anion exchange chromatography.

Column preparation: An appropriate amount of AG IX8,

100-200 mesh resin was washed with excess DDW 3 to 4 times. A polyethylene column (i.d. 0.7 cm) was plugged with glass wool on the bottom. The column was packed with washed resin using a conventional slurry packing technique. The resin bed height was adjusted to 4 cm. The resin in the column was pre-equilibrated with 2 to 3 times the loading solution before use. Since Ir(III), Rh(III) and Ru(III) might be retained on the used column, a new column was used for every separation process.

Separation procedure: A 5 mL synthetic chromite solution was transferred to a 100 mL pyrex beaker. To reduce Cr(VI) to Cr(III), 0.5 mL of 30% H_2O_2 was added to the beaker. In the case of chrome ore, a 10-30 mL sample solution was taken and 1 mL of 30% H_2O_2 was used. The solution was evaporated to dryness on a hot plate and subsequently dried under an infrared lamp. The residue was dissolved with 5 mL of 0.1, 1 and 3 M HCl, respectively. The solution was transferred to the column. The beaker was rinsed with 10 mL of each loading solution and the rinsed solution was transferred to the column to completely elute any Cr(III) still remaining on the column. 25 mL of acetone-nitric acid-DDW (100 : 5 : 5, v/v) as an eluent was passed through the column to desorb the gold. The flow rate of the eluent was 5 mL/40 min. The eluate collected in a 50 mL pyrex beaker was evaporated to near dryness on a water bath (80 °C) and the residue was dissolved with 5 mL of 0.1 M HCl. It was transferred to a 5 or 10 mL volumetric flask, according to sample size. The beaker was rinsed with 0.1 M HCl. The rinsed solution was transferred to the volumetric flask and the volume was made up with 0.1 M HCl.

After desorption of gold, 20 mL of concentrated hydrochloric acid and 20 mL of concentrated nitric acid were sequentially passed through the column to desorb the iridium, palladium, platinum, rhodium and ruthenium retained on the column. During the elution, the flow rate of the eluent was maintained at 5 mL/40 min. The eluate collected in a 100 mL pyrex beaker was evaporated to near dryness on a hot plate and the residue was dissolved with 5 mL of 0.1 M HCl. It was transferred to a 2, 5 or 10 mL of volumetric flask according to sample size.

Results and Discussion

Dissolution of chromite. Sodium peroxide fusion procedure was better than perchloric acid or perchloric-phosphoric acid mixture digestion procedure in dissolution of a Mongolian chromite sample.³¹ To prevent contamination of silica from a pyrex beaker, a Teflon beaker was used to dissolve the fused sample. For determination of gold and PGEs in the chromite sample, however, since fine particles do not cascade easily down the wall of a Teflon beaker, a pyrex beaker was used. The schematic diagram of the overall fusion dissolution procedure is shown in Figure 1.

Interference of chromium on gold wavelength. Since the gold content was several $\mu\text{g/g}$ in most of the chromites, sensitive instrumental techniques such as GFAAS or ICP-MS were needed for measurement. Since the gold content in

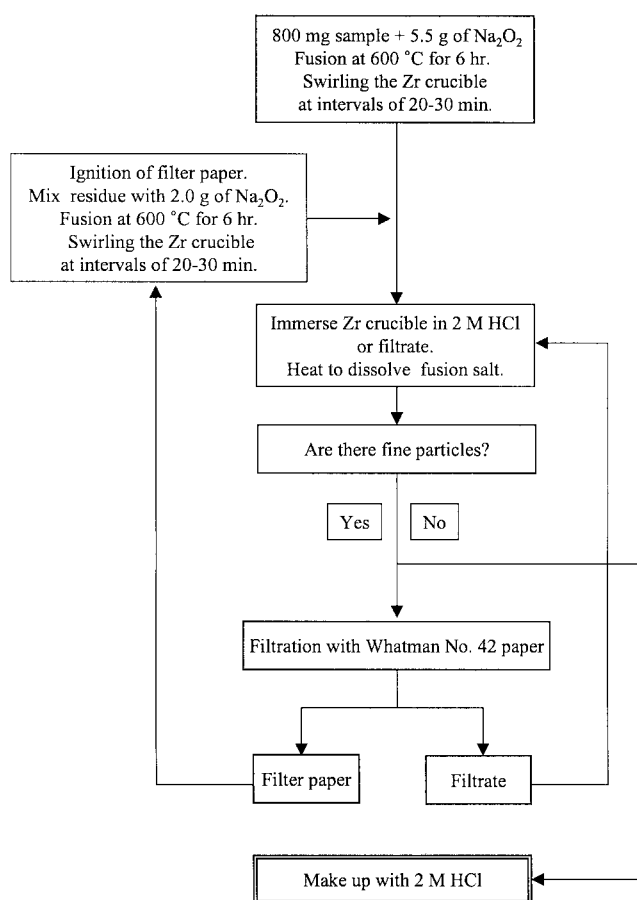


Figure 1. Fusion dissolution procedure for 0.8 g chromite sample.

a Mongolian chromite sample was tens of $\mu\text{g/g}$. ICP-AES was used for direct measurement without separation. However, the best sensitive gold wavelength, 242.795 nm, was spectrally interfered by chromium, as shown in Figure 2. Because this peak could not be confirmed in "Massachusetts Institute of Technology(MIT) Wavelength Tables", which collects more than 100,000 wavelengths from Mo (200.004 nm) to Co (999.97 nm) by electric arc or spark atomization sources, we supposed that 242.757 nm, which is the second order of 485.5146 nm chromium line, appears at 242.788 nm, slightly shifted from 242.757 nm. This 242.788 nm wavelength interfered the gold determination at 242.795 nm. The effect of chromium concentration on Au intensity at 242.795 nm is shown in Table 3. The background position was set at -0.015 nm. Table 3 shows that the emission intensity of gold was not influenced up to 250 mg/L of chromium. In the case of 0.1 mg/L of Au(III) containing 500 mg/L of chromium, the net intensity of gold increased to 11%, compared with 0.1 mg/L of Au(III) standard solution without chromium. The net intensity of gold increased with increasing chromium concentration. Thus, the separation procedure should be done to measure gold in chromium matrix if the gold concentration is not enough high. For 0.5 mg/L of Au(III) containing 500 mg/L of chromium, the net intensity of gold increased to 3.3% compared to the net intensity of 0.5 mg/L of pure Au(III) standard solution.

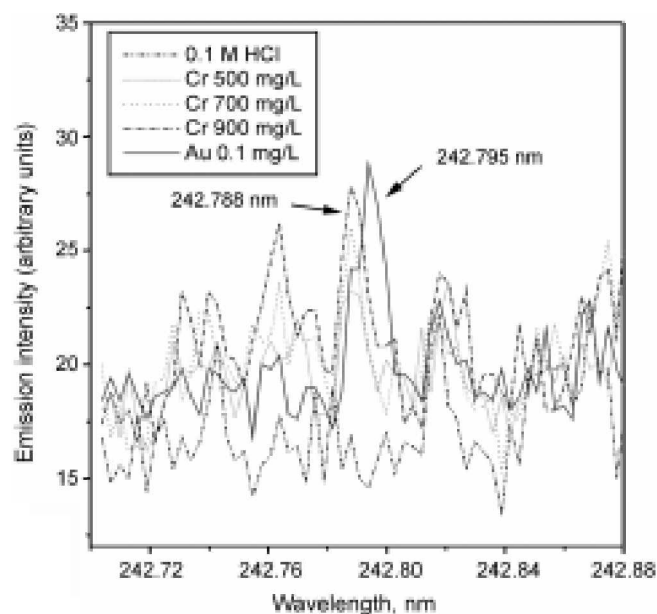


Figure 2. Spectral interference of Cr on Au 242.795 nm.

Table 3. Effect of Cr concentration on Au intensity at 242.795 nm

Cr concentration (mg/L)	Au intensity ^a	Background	Net intensity ^b	Relative diff. ^c (%)
0	27.5 ± 1.1	11.4 ± 0.25	16.0 ± 0.95	0
250	28.2 ± 0.64	11.9 ± 0.31	16.2 ± 0.65	1.2
500	30.4 ± 0.40	12.5 ± 0.12	17.9 ± 0.31	11.2
750	33.9 ± 0.25	13.1 ± 0.15	20.7 ± 0.40	29.2
1000	34.7 ± 0.79	13.7 ± 0.15	21.0 ± 0.81	30.4
1100	35.6 ± 1.05	13.9 ± 0.10	21.7 ± 0.95	34.8

^aConcentration of Au in each sample: 0.1 mg/L. ^bn = 3. ^cDifference from standard solution without chromium.

Reduction of Cr(VI) to Cr(III) using H₂O₂. The oxidation state of chromium dissolved with the sodium peroxide fusion procedure was the orange-red dichromate ion, Cr₂O₇²⁻. At pH's below 1 the main species, chromate ion, CrO₄²⁻, and dichromate ion, Cr₂O₇²⁻, are quantitatively converted into the chlorochromate ion, CrO₃Cl⁻, in hydrochloric acid medium.³² Since this chlorochromate ion is adsorbed on the anion exchange resin, some CrO₃Cl⁻ adsorbed on the resin was eluted with the gold. On the other hand, Cr(III) passed through the column without adsorption because cationic species such as Cr(H₂O)₆³⁺ is formed in acidic solution (pK = 4).³³

Therefore, Cr(VI) should be reduced to Cr(III) before separation and pre-concentration of the gold from chromium matrix with anion exchange resin.³⁴ Since the reduction potentials of Cr(VI) and H₂O₂ are 1.33 and 0.88 volts, respectively, and a metal reductant like Ce(IV) may interfere with the inductively coupled plasma conditions, hydrogen peroxide was selected as a reducing agent.⁴ UV-Vis spectra are shown in Figure 3 for synthetic chromite solution to which hydrogen peroxide was added for reduction. Figure 3 shows that Cr(VI) was completely reduced to Cr(III) by adding 0.5 mL 30% H₂O₂. The chromium concentration in

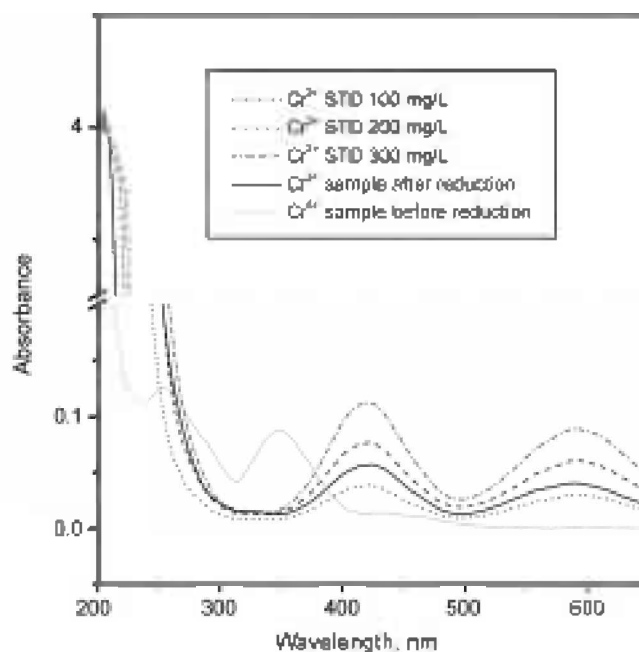


Figure 3. Absorption spectra of Cr³⁺ and Cr⁶⁺ solution.

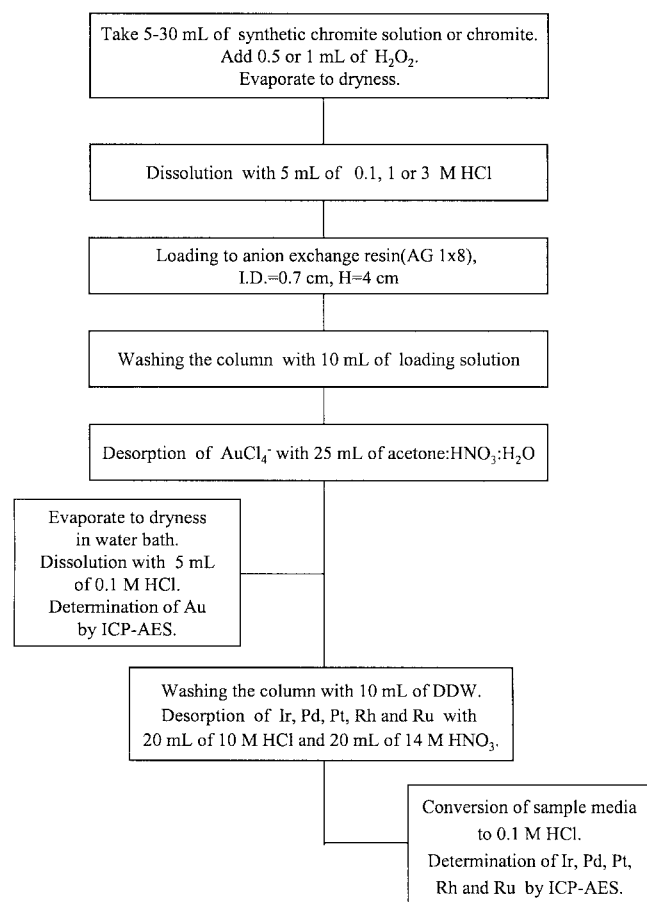
the eluate of gold was less than 1 mg/L in this case. But in the case where there was no addition of hydrogen peroxide, chromium concentration in the eluate of gold ranged from tens to hundreds of mg/L. The sodium concentration in the eluate of gold was less than 10 mg/L. Because major constituents such as iron, aluminum and magnesium and excess sodium were eluted along with chromium, they did not affect gold determination.

Recovery test of gold and PGEs. The effect of HCl as a loading solution on gold recovery was examined by a column method. The HCl concentration of loading solution had not any effect on gold recovery at 0.1, 1 and 3 M HCl concentration, respectively. The recovery yields were 99.3 ± 2.1% (n = 6), 97.7 ± 0.7% (n = 3) and 102.0 ± 1.4% (n = 4) at each HCl concentration, respectively. After Au(III) was eluted with acetone-nitric acid-DDW mixture, the concentrated HCl and HNO₃ in series were used to desorb the Ir(III), Pd(II), Pt(IV), Rh(III) and Ru(III) still retained on the resin. Even though the elements such as Ir(III), Pd(II), Rh(III) and Ru(III) were eluted mostly with concentrated HCl, Pt(IV) was rarely eluted with concentrated HCl. However, Pt(IV) and small portions of Ir(III), Pd(II) and Ru(III) were eluted with concentrated HNO₃. Au(III), Pd(II) and Pt(IV) retained on the Amberlite IRC 718 chelating resin were quantitatively eluted with 0.25 M thiourea, which forms to complex with both Au(III) and Pt(IV).³⁵ The eluted elements in various eluent conditions and the schematic diagram of separation procedure are shown in Table 4 and Figure 4, respectively.

Au(III), Pd(II) and Pt(IV) were adsorbed mostly on anion exchange resin from 0.1 to 3 M HCl. While some portions of Ir(III), Rh(III) and Ru(III) not adsorbed on the resin were passed through the column at a range of 0.1 to 3 M HCl. The content of Ir(III) detected was not largely affected by the

Table 4. Elution sequence of anion exchange procedure for the separation of Au, Ir, Pd, Pt, Rh and Ru from chromite simulated

Eluent	Volume (mL)	Eluted
0.1-3 M HCl	10	major elements, Na
acetone : HNO ₃ : H ₂ O (100 : 5 : 5, v/v)	25	Au
H ₂ O	10	None
10 M HCl	20	Ir, Pd, Rh, Ru
14 M HNO ₃	20	Pt, Ir, Pd, Ru

**Figure 4.** Analytical scheme for Au, Ir, Pd, Pt, Rh and Ru separation.

HCl concentration of loading solution. Rh(III) was detected only in 0.1 M HCl loading solution. However, Jacinta and Philip reported that Rh(III) forms RhCl_5^{+} in 0.1-0.5 M HCl solutions, and it is not adsorbed by anion exchange resins⁴. The amount of Ru(III) passed through the column decreased as the HCl concentration of loading solution increased.

The recovery yield of PGEs with synthetic chromite solution containing 1 mg/L of Au(III) and PGEs is shown in Table 5. The Ru(III) recovery yield increased with increasing HCl concentration of loading solution because $[\text{Ru}(\text{H}_2\text{O})_6]^{4+}$ is formed by the substitution of Cl^- group of the complex $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ for an aquo group in 0.1 M HCl.³⁶ The contents of cationic, neutral and anionic species of ruthenium are 1.2, 1 and 97.8% in 0.5 M HCl, respectively.³⁷ It

Table 5. Effect of HCl loading solution on Au, Ir, Pd, Pt, Rh and Ru recovery

HCl (M) Element ^a	Recovery yield (%)				
	0.1 ^a	0.1 ^b	1 ^a	3 ^a	3 ^c
Au(III) ^d	100.7 ± 2.0	97.8 ± 4.1	97.7 ± 0.7	101.0 ± 2.0	103
Ir(III)	78.0 ± 0.59	69.8 ± 4.7	59.9 ± 9.7	65.2 ± 8.1	78.3
Pd(II)	65.3 ± 13.3	96.1 ± 1.8	69.1 ± 2.7	77.0 ± 3.0	94.9
Ru(III)	23.9 ± 1.2	18.5 ± 2.5	53.1 ± 1.7	61.4 ± 4.5	85.8
Rh(III)	52.9 ± 2.8	36.4 ± 10.4	ND ^e	ND	ND
Pt(IV)	85.7 ± 2.8 ^e	96.6 ± 1.3	ND	ND	79.2

^aSynthetic chromite solution containing 10 μg of gold and PGEs in 10 mL of 0.1 M HCl, respectively. ^bEluent : 10 M HCl, 0.5 mL H₂O₂, n = 3. ^cEluent : 10 M HCl - 14 M HNO₃, 1 mL H₂O₂, n = 3. ^dEluent : 10 M HCl + 14 M HNO₃, 0.5 mL H₂O₂. ^eEluent : acetone : HNO₃ : H₂O = 100 : 5 : 5, v/v. ^fEluent : 14 M HNO₃. ^gND : not detected.

was confirmed that the content of Ru(III) passed through the column decreased with increasing HCl concentration of loading solution. After Rh(III) was loaded on the column using 1 and 3 M HCl, it was not detected in the cases with concentrated hydrochloric acid as an eluent, regardless of the addition of reducing agents. The distribution coefficient of Rh(III) decreased with increasing HCl concentration, while Rh(IV) was strongly adsorbed.³⁴ Thus, we concluded that Rh(III) in 1 and 3 M HCl was passed through the column in both cases without adsorption. We confirmed that most Rh(III) was passed through the column in 3 M HCl. According to other experimental results reported,³⁸ Rh(III) was not adsorbed on the resin and was passed through the column in the range of 2-12 M HCl. As mentioned above, Pt(IV) was not eluted regardless of the HCl concentration of desorbent. As shown in Table 5, Pt(IV) was quantitatively recovered using concentrated HNO₃ as an eluent with 0.1 M HCl loading solution and the relative standard deviation of Pt(II) was 1.3%. Table 5 shows that Pd(II) recovery yield was 96.1 ± 1.8% (n = 3), using concentrated HCl and HNO₃ as eluents with 0.1 M HCl loading solution.

From the above results, we concluded that the gold recovery yield was not affected by the HCl concentration of loading solution within 0.1-3 M HCl, and Pd(II) and Pt(IV) in synthetic chromite solution were quantitatively determined after gold desorption. To get good accurate and precise results for gold and PGEs, evaporation and dryness processes should be carefully done so as not to burn off during dryness. Further study will be done to improve the recovery yields and precision of Ir(III), Rh(III) and Ru(III).

Analysis of gold, palladium and platinum from a Mongolian chromite sample. After the separation and pre-concentration of Au(III), Pd(II) and Pt(IV) using anion exchange chromatography with 0.1 M HCl loading solution, we obtained analytical results for a Mongolian chromite sample as shown in Table 6. Because the content of gold in the sample was higher than the contents of palladium and platinum, the determination was possible even with 100 dilution factors. The gold content in the sample was 32.6 ± 2.2 μg/g (n = 5), which is much higher than in other chromites. Pd(II) and Pt(IV), however, which were quantitatively

Table 6. Analytical results of Au, Pd and Pt determined by ICP-AES and NAA for a Mongolian chromite sample

Method Element	ICP-AES ($\mu\text{g/g}$)	NAA ($\mu\text{g/g}$)	Relative diff. (%)
Au(III)	32.6 ± 2.2^a	29.1 ± 5.6^b	10.7
Pd(II)	ND	ND ^d	
Pt(IV)	1.6 ± 0.14^c	ND	

^an = 5, ^bn = 3, ^cn = 2 (from the same solution dissolved), ^dND : not detected.

recovered from synthetic chromite solution were not detected in the sample because of low concentrations. From the same dissolved solution with 10 times dilution factors, the platinum content of the sample was $1.6 \pm 0.14 \mu\text{g/g}$ (n = 2) and palladium was not detected by ICP-AES. To confirm this method, neutron activation analysis (NAA) was carried out by 'HANARO' research reactor. The two data were in agreement within 11% of relative difference as shown in Table 6.

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