Asian Journal of Chemistry;   Vol. 24, No. 8 (2012), 3741-3744

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Determination of Iridium by Graphite Furnace Atomic Absorption Spectrometry After Preconcentration with SEPABEADS®SP825 Resin as Sorbent

WANQIU LIU, ZHONGQI YANG and ZHANGJIE HUANG*

Department of Chemistry, Yunnan University, Kunming 650091, P.R. China

*Corresponding author: Fax: +86 871 5032180; E-mail: zhjhuang2010@163.com

(*Received*: 24 September 2011; *Accepted*: 26 March 2012) AJC-11229

A solid phase extraction and graphite furnace atomic absorption spectrometry (GFAAS) for the determination of iridium with SEPABEADS®SP825 resin as sorbent was studied. Iridium are preconcentrated on a nonpolar resin SEPABEADS®SP825 in the form of $(L_2{\cdot}H_3O^+)_2IrCl_6^{2-}$ ion-pairs,where L = diphenyl sulfoxide and water was used as eluent. The effects of various parameters such as acidity, flow rate of sample and eluent, type of eluent, amount of adsorbent and interfering ions have been studied. The iridium in 100 mL solution can be concentrated to 1 mL, representing an enrichment factor of 100 was achieved. The detection limit and quantification limit of the method were found to be 0.03 μg L^{-1} and 0.1 μg L^{-1}, respectively. The analytical results for the certified reference samples (GBW07290 and GBW07291) were in a good agreement with the certified value. The relative standard deviation for ten replicate measurements of 0.40 μg L^{-1} iridium was 4.1 %. The method was applied to the determination of trace amount iridium in ore samples with good result.

Key Words: Solid phase extraction, Iridium, Diphenyl sulfoxide, Graphite furnace atomic absorption spectrometry.

INTRODUCTION

Iridium is commonly used in various jewellery, dental alloys, electrical equipments, corrosion-resistant chemical wares, crucibles for high temperature reactions and extrusion dyes for high melting glasses[1,2]. Iridium commonly coexists with other platinum metals in Earth's rock at a very low content, so high sensitive and selective methods are required for its determination.

The most widely used methods for determination of iridium in ore samples include graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), neutron activation analysis (NAA) and spectrophotometric methods[3-10]. However, the determination of iridium in ore samples by spectrometric techniques is strongly hampered by numerous spectral and non-spectral interferences arising from a complicated sample matrix.

In ore samples, the low concentration of iridium (ng mL^{-1} levels) together with the high concentration of interfering matrix components often requires an enrichment step combined with a matrix separation. Several methods have been reported for the separation and preconcentration of iridium, such as liquid-liquid extraction, high-performance liquid chromatography and solid-phase extraction[11-13]. Among these techniques, solid-phase extraction is one of the most important preconcentration methodologies because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability to combine with different detection techniques in on-line or off-line mode.

The aim of this work is to combine solid-phase extraction with graphite furnace atomic absorption spectrometry and develop a new method for the determination of iridium. In this method diphenyl sulfoxide (DPSO), which reacts with iridium(IV) forming a stable $[(DPSO)_2{\cdot}H_3O^+]_2IrCl_6^{2-}$ ion-pairs. Subsequently, water sample containing $[(DPSO)_2{\cdot}H_3O^+]_2IrCl_6^{2-}$ ion-pairs was passed through SEPABEADS®SP825 cartridge. Iridium ion-pairs with DPSO were preconcentrated on a nonpolar resin SEPABEADS®SP825. The $[(DPSO)_2{\cdot}H_3O^+]_2IrCl_6^{2-}$ ion-pairs adsorbed on SEPABEADS®SP825 cartridge was eluted with water. The levels of analyte ions in the samples were determined by the graphite furnace atomic absorption spectrometry. The optimum analytical conditions for the quantitative recoveries of iridium on SEPABEADS®SP825 adsorption resin were investigated.

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High- Technologies Corpotation, Japan) was used in the studies. Hitachi hollow cathode lamps (HCL) were used for the determination of iridium (264.0 nm) operated at 10 mA. High-purity argon (99.999 %, Messer Chemical

Corpotation, Kunming, China) was used as the purge and sheath gas throughout at a flow rate of 200 mL min^{-1}. The output signals were collected and processed with peak-height mode. Other operating conditions were carried out according recommendations of manufacturer.

The pH Values were measured with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

Standard stock solutions of iridium (1000 mg L^{-1}) and the ore reference materials(GBW07290 and GBW07291) were obtained from the National Institute of Standards (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solution.

0.3 % (w/v) Solution of DPSO was prepared by dissolving appropriate amount of DPSO in ethanol. Ultra-pure water was used throughout. Pipettes and vessels in the experiments were kept in 10 % nitric acid for at least 24 h and subsequently washed four times with ultra-pure water. All other reagents used were of the highest available purity and of at least analytical reagent grade. Ultra-pure water of resistivity 18 MΩ cm obtained from a UPHW purification device (Ulupure Co. Shanghai, China) was used to prepare all the solutions.

Diphenyl sulfoxide was obtained from Alfa Aesar. SEPABEADS®SP825 was purchased from Mitsubishi Chemical Corporation (Tokyo, Japan). SEPABEADS®SP825 resin is an aromatic type adsorbent. It is based on cross-linked polystyrenic matrix. Its surface area is 1000 m^{2}g^{-1}. SEPABEADS®SP825 is widely used in different industrial fields[14]. It was washed successively with methanol, water, 1.0 mol L^{-1} HNO_3 in acetone, water, 1.0 mol L^{-1} NaOH and water, sequentially.

Preconcentration procedure: An off-line column procedure was applied for the preconcentration process. The Teflon column was 3.5 cm long and 0.8 cm in diameter. The 2.0 µm of sieve plate was placed to prevent loss of the resin beads during sample loading. Then, 600 mg of SEPABEADS® SP825 resin was poured into the column. The resin bed was washed with plenty of ultra-pure water until neutral pH and subsequently reused. The method was tested with model solutions before its application to real samples. 100 mL of solutions containing 10-300 ng iridium, 35 mL of 12 mol L^{-1} hydrochloride acid solution and 4 mL of 0.3 % DPSO was passed through the column at a flow rate of 5 mL min^{-1} using a vacuum aspirator. The retained iridium ions were eluted from the column by 1 mL H_2O and the concentrations of iridium ions were determined by graphite furnace atomic absorption spectrometry. A blank solution was also run under the same conditions without adding the analytes.

Sample preparation: The developed method has been successfully applied to the determination of iridium in ore reference materials and ore samples (Tables 1 and 2).

The 10 g of ore reference materials or ore samples were transferred into a porcelain crucible and roasted for 2 h in a muffle furnace at 620 ºC. After roasting, the sample was transferred to 500 mL glass beaker and 80 mL of freshly prepared aqua regia was added to sample. 1.5 g of NaCl was added to stabilize the iridium chloride complex during evaporation on a hot plate. The beaker was covered with a watch glass and heated on a hot plate. Heating was continued for at least 3 h and enough aqua regia was added at regular intervals to maintain the free acid level at about 1 cm above the sample level. The watch glass was removed and the content was evaporated slowly until the residue became nearly dry. Then, 50 mL of 2 mol L^{-1} HCl was added to the beaker and the solution was warmed until clear solution was obtained. Afterwards, sample solution was cooled and filtered using whatman No.1 filter paper (pore size, 11µm). The residue was washed with minimum amounts of 0.1 mol L^{-1} HCl. The final residue was discarded and the filtrate was then dissolved and diluted to 100 mL with distilled water. Finally, iridium in ore sample was determined by the proposed method.

TABLE-1
DETERMINATION OF Ir (ng g^{-1}) IN THE CERTIFIED REFERENCE MATERIALS AFTER APPLICATION OF THE PRESENTED PROCEDURE (n=5)

Sample	Certified value (ng g^{-1})	Present value (ng g^{-1})
GBW07290	4.3 ± 0.5	4.2 ± 0.6
GBW07291	4.7 ± 1.1	4.8 ± 0.9

TABLE-2
DETERMINATION OF Ir (µg g^{-1}) IN ORE SAMPLES (n=5)

Samples	Added	Found[a] by present method	Recovery (%)
Ore1	0	0.9 ± 0.1	-
	5	6.0 ± 0.1	102
	10	10.5 ± 0.2	96
Ore2	0	0.8 ± 0.1	-
	5	5.6 ± 0.1	96
	10	10.9 ± 0.3	101

-, not determined; [a]Mean ± S.D.

The ore samples were collected from Jin Bao Mountain (Dali, P.R. China).

Graphite furnace atomic absorption spectrometry analysis: The graphite furnace atomic absorption spectrometry analysis condition is listed in Table-3. For samples analysis, a 20 µL aliquot of the samples or standard solution was injected into the graphite cuvette for the graphite furnace atomic absorption spectrometry determination. The atomic absorption signals were measured with the Zeeman background corrector in operation. The measurement was repeated three times and the obtained signals were averaged.

TABLE-3
SETTING OF ANALYTICAL CONDITIONS

Analytical condition	Parameter for measurement of iridium
Calculation mode	Peak height
Wavelength (nm)	264.0
Slit Width (nm)	0.2
Time constant (s)	0.1
Lamp current (mA)	10 mA
Cuvette type	Pyro tube HR
Dry start/end temp (ºC)	80/140
Dry ramp time(s)	40
Ash start/end temp (ºC)	520/520
Ash ramp time (s)	20
Atomize start/end temp (ºC)	2400/2400
Atomize hold time (s)	5
Clean start/end temp (ºC)	2700/2700
Clean hold time (s)	4
Gas flow (mL min^{-1})	200
Sample injection volume (µL)	20

RESULTS AND DISCUSSION

Effect of acidity: The acidity of the sample solution is one of the important factors affecting the formation of $[(DPSO)_2{\cdot}H_3O^+]_2IrCl_6^{2-}$ ion-pairs and the subsequent solid phase extraction. According to the results (Fig. 1), quantitative recoveries (> 95 %) for analytes were obtained in the presence of HCl in the concentration range: 3-5 mol L^{-1}. Thus, 35 mL of 12 mol L^{-1} HCl solutions was recommended to control acidity.

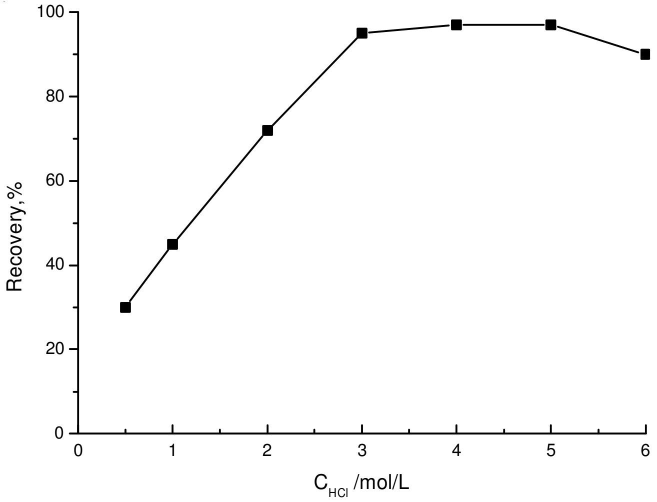

Fig. 1. Influences of acidity on the recovery of iridium; Conditions: sample volume: 100 mL; flow rate: 5 mL min^{-1}; amount of the resin: 600 mg

Influences of DPSO amount: In order to determine the amounts of DPSO required for quantitative recovery for iridium(IV), the proposed method was applied. Changing the DPSO amounts (0.3 % solution) at the range of 1-6 mL. The results showed that the recovery values of the analyte iridium(IV) were increased with increasing amounts of DPSO added. The recovery reaches a constant value with at least 3 mL of 0.3 % DPSO solution used. On this basis, studies were carried out at DPSO amounts of 4 mL. This amount of DPSO is enough for the separation and preconcentration procedure because of the low level of the investigated iridium(IV) concentrations in real samples.

Effects of the amount of resin: The amounts of solid phase extraction material are another important factor on the column studies for the quantitative recoveries of $[(DPSO)_2{\cdot}H_3O^+]_2IrCl_6^{2-}$ ion-pairs. The effect of the amount of SEPABEADS®SP825 on the sorption of metal ions was examined in the range of 300-900 mg. The results demonstrated that, quantitative recoveries (> 95 %) of iridium was observed in the range of 500-700 mg. Above 700 mg the recoveries were below 95 % with 1.0 mL of the eluent. Therefore, in the proposed procedure, 600 mg of SEPABEADS®SP825 resin is recommended.

Effect of flow rate of sample solution and eluent: The influence of flow rate on the adsorption of $[(DPSO)_2{\cdot}H_3O^+]_2IrCl_6^{2-}$ ion-pairs was also studied. Flow rate in the range of 4-6 mL min^{-1} had no significant effect on the recoveries of iridium(IV). Therefore, in the proposed procedure, 5 mL min^{-1} flow rate is recommended.

Among several media investigated as eluent (H_2O, HNO_3, ethanol, methanol acetone, pentanol, NH_3, thiourea, ethyl acetate), only H_2O showed satisfactory elution characteristics. 1 mL of H_2O provided quantitative recovery (> 95 %) and reproducibility. The elution was performed in the opposite direction to avoid the clogging of the column. The iridium in 100 mL solution can be concentrated to 1 mL, representing an enrichment factor of 100 was achieved.

The flow rate of eluent solution was examined in the range of 0.5-1.2 mL min^{-1}. Maximum recoveries for iridium was obtained in the range of 0.5-1.0 mL min^{-1}. The flow rate of 1 mL min^{-1} was chosen as optimum value.

Effect of interfering ions on recovery: The effects of common coexisting ions in the ore samples on the extraction recovery of iridium were studied. In these experiments, 100 mL solutions contains 0.5 μg L^{-1} of iridium and various amounts of interfering ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of iridium less than 95 %. The results obtained are given in Table-4.

TABLE-4
TOLERANCE OF FOREIGN IONS IN THE DETERMINATION OF 0.50 μg L^{-1} IRIDIUM

Interferent	Concentration (μg L^{-1})	Interferent/ iridium ratio	Recovery (%)
Cu^{2+}	650,000	1,300,000	97.5
Fe^{3+}	400,000	800,000	101.2
Zn^{2+}	300,000	600,000	99.2
Ni^{2+}	200,000	400,000	95.8
Co^{2+}	100,000	200,000	98.1
Pd^{2+}	80,000	160,000	95.9
Pt^{4+}	60,000	120,000	97.1
Au^{3+}	50,000	100,000	96.8
Rh^{3+}	50,000	100,000	97.4

Loading capacity: To 0.1 g of SEPABEADS®SP825 resin was placed in the conical flasks. Stock solution of iridium(IV) and DPSO were added to the flask. HCl in the concentration range: Acidity of the solution was adjusted to 3-5 mol L^{-1} using 12 mol L^{-1} HCl solution. After shaking for 3 h, the mixture was filtered. Concentration of Ir(IV) was measured by ICP-AES. The loading capacity of SEPABEADS®SP825 was 13 mg g^{-1} for iridium.

Calibration curve and detection limit: Using the optimized conditions of preconcentration, calibration curve was prepared for iridium(IV). The limit of detection (LOD) value (blank + 3σ) and limit of quantification (LOQ) value (blank + 10σ)[15-18], where s is standard deviation of blank determination (n = 12), were found to be 0.03 μg L^{-1} and 0.1 μg L^{-1}, respectively. The results were also shown in Table-5. SEPABEADS®SP825 resin can be reused at least 100 times.

Applications of the presented procedure: In order to establish the validity of the proposed procedure, the method has been applied to the determination of iridium in the ore reference materials samples (GBW07290 and GBW07291). The results were given in Table-1. The proposed method was applied to determine of iridium in the ore samples. The results for the ore samples were given in Table-2. The results indicate that the recoveries in the range of 96-102 % are reasonable well for trace analysis.

TABLE-5
ANALYTICAL CHARACTERISTICS OF THE PROPOSED METHOD

Parameter	Analytical feature
Regression equation(C_{Ir} in μg L^{-1})[a]	$A = 5.82 \times 10^{-5} C + 6.74 \times 10^{-3}$
Linear range (μg L^{-1})[a]	10.0-300.00
Correlation coefficient	0.9992
Enrichment factor	100
The relative standard deviation (0.40 μg L^{-1}, n = 10)[b]	4.1
Detection limit (μg L^{-1})[b] (LOD = bland +3σ, n = 12)	0.03
Quantification limit (μg L^{-1})[b] (LOQ = bland +10σ, n = 12)	0.1

[a]In the pre-concentrated solution; [b]In the original samples before applying the pre-concentration procedure

Conclusion

The described method using the SEPABEADS®SP825 resin combined with DPSO has a good potential for the enrichment and separation of iridium ions from the ore samples and their determinations by graphite furnace atomic absorption spectrometry. The method is simple, sensitive, precise, reliable and accurate technique. The advantages of this method is its selective adsorption in a wide range of sample acidity (3-5 M HCl). The method is also low cost. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of SEPABEADS®SP825 was as high as greater than 100 cycles without any loss in its sorption behaviour. The tolerance limits of interfering ions on the recovery of iridium ions are quite high. The results acquired from the analyses of the two standard reference materials confirmed the reliability of the method. The proposed method possesses lower limit of detection and higher enrichment factor, which makes it suitable for the determination of trace amount of iridium in ore samples.

ACKNOWLEDGEMENTS

This work was supported by Development Program of China (2011AA03A405D), Key Natural Science Foundation of China (U0937601) and Science and Technology Support Program of China (2008BAB32B10).

REFERENCES

1. C. Locatelli, *Talanta*, **85**, 546 (2011).
2. B. Tang, F. Han and G.Y. Zhang, *Talanta*, **56**, 603 (2002).
3. X. Dai, C. Koeberl and H. Froschl, *Anal. Chim. Acta*, **436**, 79 (2001).
4. R. Brajter and U. Kozicka, *Anal. Chim. Acta*, **156**, 323 (1984).
5. S.C. Shome, M. Mazumdar and P.K. Haldar, *J. Indian Chem. Soc.*, **57**, 139 (1980).
6. S.P. Chaudhury and S.C. Shome, *J. Indian Chem. Soc.*, **68**, 430 (1991).
7. A. Wasey, B.K. Puri and M. Satake, *Analyst*, **111**, 757 (1986).
8. V. Hodge, M. Stallard, M. Koide and E.D. Goldberg, *Anal. Chem.*, **58**, 616 (1986).
9. S.J. AI-Bazl and A. Chow, *Anal. Chem.*, **53**, 1073 (1981).
10. Z. Aneva, *Anal. Chim. Acta*, **236**, 385 (1990).
11. V. Druskovic, V. Vojkovic and S. Miko, *Talanta*, **62**, 489 (2004).
12. M.A. Taher, S. Puri, R.K. Bansal and B.K. Puri, *Talanta*, **45**, 411 (1997).
13. J.M. Sanchez, O. Obrezkov and V. Salvado, *J. Chromatogr. A*, **871**, 217 (2000).
14. Z. Molnar, M. Nagy, A. Aranyi, L. Hanak, J. Argyelan, I. Pencz and T. Szanya, *J. Chromatogr. A*, **1075**, 77 (2005).
15. D. MacDougall and W.B. Crummett, *Anal. Chem.*, **52**, 2242 (1980).
16. G.L. Long and J.D. Winefordner, *Anal. Chem.*, **55**, 712A (1983).
17. A. Santalad, S. Srijaranai, R. Burakham, T. Sakai and R.L. Deming, *Microchem. J.*, **90**, 50 (2008).
18. I. Narin, A. Kars and M. Soylak, *J. Hazard. Mater.*, **150**, 453 (2008).