Separation of W from Ta, Hf, Lu and Mo by BPHA-$C_5H_{11}OH$/HCl extraction system

(Model experiments for chemical study of seaborgium, the 106th element)

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Abstract In the batch experiment with W, Ta, Hf, Lu and Mo as radiotracers, a new rapid radiochemical isolation procedure for element tungsten has been developed by using radiochemical separation method and γ spectrum measurement technique. With Voltalef powder carried 2% (W/V) BPHA(Benzoylphenylhydroxylamine)-$C_5H_{11}OH$ (iso-amyl-alcohol) organic solution, radioactive W was adsorbed on the Voltalef column in the 4 mol/L hydrochloric acid system. Hf, Lu and Mo fractions passed through the Voltalef column rapidly and partial Ta activities retained on the Voltalef column, respectively. Following this, W fraction was eluted completely with 1%$Na_3C_6H_5O_7$(sodium citrate)-5%(W/V) NH_4OH solution and no Hf, Lu, Ta and Mo activities passed through the Voltalef extraction chromatographic column. The procedure was simultaneously used to isolate W from Er target bombarded with a low energy ^{12}C beams. By means of this separation system, it is one of the possible way to develop an isolation procedure of Sg, supposing the chemical property of Sg is similar to that of tungsten.

Keywords W, Ta, Hf, Lu and Mo tracers, Voltalef-BPHA-$C_5H_{11}OH$, Separation of Sg, Extraction chromatography

CLC numbers O615.4$^+$1, O614.61$^+$3, O652.62

1 INTRODUCTION

In the past years, the study of chemical property of transactinide elements gained a broad interest from both experimental and theoretical chemists to determine their positions in the element periodic table[1~4]. However, due to the "relativistic effect" of

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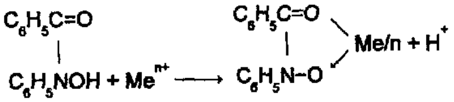
transactinide elements, the deviation from regularity of the periodic table was not suitable for the transactinide elements compared with their lighter homologue elements. A few of modelling experiments aimed at studying the chemical property of Sg with anion and cation exchange resins in low concentration of strong acidic medium were finished[5~7], these batch researches tried to develop some chemical systems which were suitable for the isolation of element Sg from heavy actinides and Rf produced simultaneously in heavy ion nuclear reactions. Wiertczinski *et al.*[8] used its lighter homologue element W as a radiotracer and the SISAK-3 centrifuge system as an on-line rapid experiment test of chemical studies of the elements Db and Sg using trioctylamine extraction. For Sg element, its aqueous chemistry with Automatic Rapid Chemistry Apparatus(ARCA)[9] was carried out in 1995 at the UNILAC accelerator (GSI, Germany)[10] and in 1997 at Berkeley 88 inch cyclotron accelerator (USA)[11]. In these experiments, 0.1 mol/L HNO_3-5 $\times 10^{-4}$ mol/L Hf and 0.1 mol/L HNO_3 were used to adsorb element Rf and heavy actinides on the cation exchanger AMINEX A6. Some conclusions were obtained that the chemical behaviour of Sg was not similar to that of uranium but molybdenum or tungsten. At the same time, in absence of fluoride ion, the behaviour of Sg was not similar to tungsten because of its weaker tendency to hydrolyze. From the theoretical calculations on the electronic structure and the redox potentials, it has been predicted that, within the series of MeO_4^{2-} ions, $(SgO_4)^{2-}$ will be the most stable ion in aqueous solution in subgroup VI[4] and it has been known that Mo and W will form anionic complex with chloride[12].

BPHA, a cupferron analogue[13], was used extensively as an organic precipitant and solvent extraction since it reacts with several metal elements to form stable chelates which are soluble in organic solvents. However, BPHA is superior to cupferron because it exhibits better thermal and chemical stability. Furthermore, BPHA becomes more selective and reacts only with some transition elements in strong acidic medium, particular emphasis was devoted to extraction of easily hydrolyzed transition metals[14~16] in neutral or weak acidic medium. W and Mo fractions can be quantitatively extracted with the system of BPHA-C_6H_6 in strong acidic medium[17]. Its structure formation is as following



where Me^{n+} is a metal ion and $(C_6H_5)_2NCOOH$ is the molecular formation of BPHA.

To date, no report about the extraction behaviour of element W with BPHA-$C_5H_{11}OH$ system has been seen. In order to give more evidences to determine the chemical property of element 106 (Sg), a rapid radiochemical separation procedure of W aiming at studying the chemical property of Sg has been developed. According to the property of BPHA mentioned above, we tried to extract W as a model of Sg with a BPHA-$C_5H_{11}OH$/HCl system.

2 EXPERIMENTAL

2.1 Materials

BPHA and other chemical reagents were purchased from Merck chemical factory (Darmstadt in Germany), their purity was analytical grade(AP). Voltalef powder from Lehmann & Voss (Hamburg) was used as inert support material for 2% BPHA-$C_5H_{11}OH$ solution. The range of particle sizes was 25~36 μm. Voltalef powder was coated with 2% BPHA-$C_5H_{11}OH$ extraction reagent, weighted ratio Voltalef-2%BPHA-$C_5H_{11}OH$ (10:1) and mixed uniformly by hand stirring, and a slurry of this material in distilled water was packed into 1.6×8 mm chromatographic Teflon column under 0.5 bar of pressure[9].

2.2 Preparation of tracers

Some tracer activities were produced at the Mainz TRIGA reactor by thermal neutron induced nuclear reaction. The thermal neutron flux intensity was $7\times10^{11}\cdot n\cdot s^{-1}\cdot cm^{-2}$. All produced nuclides and their decay properties are shown in Table 1.

Table 1 The decay properties of tracers in the batch experiment

Nuclide	Nuclear reaction	Half-life	γ-energy/keV and branch ratio
^{187}W	$^{186}W(n, \gamma)^{187}W$	23.90 h	685.8(31.6%), 479.5(25.3%)
^{182g}Ta	$^{181}Ta(n, \gamma)^{182g}Ta$	114.4d	100.1(14.1%), 222.1(7.56%)
^{181}Hf	$^{180}Hf(n, \gamma)^{181}Hf$	42.4 d	481.5(85.5%),133.0(43%)
^{177g}Lu	$^{176}Lu(n, \gamma)^{177g}Lu$	6.70 d	208.4(11%), 113.0(6.6%)
^{99}Mo	$^{99}Mo \xrightarrow{\beta^-} {}^{99}Tc$	66.7 h	140.5(89%),181.1(6.82%)

A few drops of 10% NaOH solution were used to dissolve WO_3 powder, then added 4 mol/L HCl solution several times, evaporated, made the final solution into 4 mol/L HCl.

For Ta foil, the mixed solutions of concentrated HNO_3 (68%) and concentrated HF (40%) was added in polyethylene cup and heated to dissolve, evaporated to near dryness, and then stored in 4 mol/L HCl.

For HfO_2 sample, 5 drops of concentrated HF (40%) were added in polyethylene cup, and evaporated to near dryness, the final solution was 4 mol/L HCl.

For Lu_2O_3 sample, 5 drops of concentrated HNO_3 (68%) solution were added, heated to dissolve and evaporated to near dryness, after cooled, make the final solution into 4 mol/L HCl.

Aluminium foil containing radioactive Mo was heated to dissolve with 1mL of 1mol/L HCl solution, after cooled, the dissolved solutions were transferred to AG2×8 anion exchange resin column, and eluted with 5% NH_4OH solution. The elution solution was evaporated to dryness and dissolved in 4 mol/L HCl. All radiotracer solutions were stored in different sealed-up glass bottles.

2.3 Experiment with glass column

For the batch experiment with glass column, 50 μL of carrier-free radioactive solutions were used for each time. A little quartz wool(5~30 μm) was put into the bottom of glass column, 10%(W/W) Voltalef powder containing 2% BPHA-$C_5H_{11}OH$ organic solvent was put into the glass column. Some radiotracers were moved to glass centrifugal test tube, the final volume was made into 1 mL of 4 mol/L HCl. The activity was measured before HPGe detector, then let the measured solutions pass through the glass column packed by Voltalef powder, and the column was washed again by 0.5 mL of 4 mol/L HCl. Following this step, the Voltalef column was eluted with 1 mL of 1% $Na_3C_6H_5O_7$-5% NH_4OH solution, finally the eluted Voltalef powder column was blown into a glass test tube and measured.

The γ radioactivity of tracers before and after separation were measured with a HPGe detector which has 2.3 keV energy resolution at the 1332 keV for ^{60}Co source, respectively. Since the geometric position of source is the same for each time measurement, its decay rate of γ rays energy peaks corresponding to nuclides will be used to determine the chemical yield of the elements.

2.4 Experiment with ARCA device

The progress of filling in ARCA II column described in 1), 20μL of radioactive solutions were moved into the sliders, then connected ARCA device and operated by a computer control program. Firstly, the slider valve was washed 10 s with 4 mol/L HCl solution, and the solution collected in a glass test tube. Secondly, the column containing radioactives was eluted at the flow rate of 1 mL/min with 1%$Na_3C_6H_5O_7$-5% NH_4OH solution, this mixture solutions were continuously collected more than 7 times, and the collection time was 5 s for each time. The collected solutions were measured with a HPGe detector. It took 30 min for each circular experiment, the decay correction of nuclides can be ignored since the half-life of all used nuclides was more than one day. The elution efficiency of W fraction as a function of elution time was depicted in Fig.1. As can be seen in this figure, there was no activity of W before 5 s elution time with 1% $Na_3C_6H_5O_7$-5% NH_4OH, this was probably caused by the dead volume of ARCA[9] device. Since it was very difficult to determine the original radioactive intensity, the collected 4 mol/L HCl solution, 1% $Na_3C_6H_5O_7$-5% NH_4OH solution and Voltalef powder column were measured simultaneously, the total radioactive count rates were regarded as the initial activity which was taken.

2.5 Heavy ion nuclear reaction

In order to test the reliability of the chemical separation procedure developed in this paper. 5 mg/cm^2 of Er target was bombarded with 6.7 MeV/u ^{12}C beam at an average beam current intensities of 5 nA in the UNILAC accelerator. The nuclear reaction products were transmitted from the target chamber to ARCA equipment with a *helium-gas-jet along a stainless steel tube with 1 mm inner diameter and 20 meters in* length. After the products was collected for 2 min in the slider valve, the separation of W was performed using the methods described above. Since this was a fusion-evaporation reaction, the main product was ^{173}W($T_{1/2}$=7.6 min). When 4 mol/L HCl was used to wash the product, and 1% $Na_3C_6H_5O_7$-5% NH_4OH was used to elute the products, more than 70% W product was eluted in 20 s. The result was similar to the tracer experiment, therefore this procedure can suit separation of tungsten fraction.

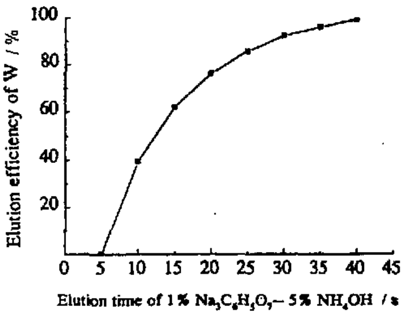


Fig.1 Elution efficiency of W as a function of *elution time with* 1% $Na_3C_6H_5O_7$-5% NH_4OH solution

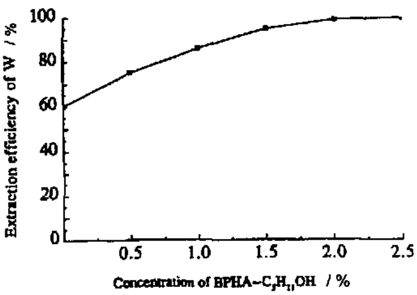


Fig.2 Extraction efficiency of W as a *function of concentration of* BPHA-$C_5H_{11}OH$

3 RESULTS AND DISCUSSION

While only $Na_3C_6H_5O_7$ (sodium citrate) solution was used to elute W and Mo fractions, less than 50% of W and a few of Mo (<4%) activities eluted in the concentration interval (0.1%-10%). However, Mo fraction retained completely in the Voltalef column and only tungsten activity was rapidly eluted when combining sodium citrate with NH_4OH solution. Therefore tungsten can be isolated from Mo with 1% $Na_3C_6H_5O_7$-5% NH_4OH mixture solution, and this system opened the possibility that not only well suits the separation and identification of Sg but also the determination of its chemical property in comparison to its lighter homologues (Mo and W).

The Voltalef powder of different particle size from 25μm to more than 80μm was tested, the best size was 25~36μm for this extraction system, and some tungsten fraction passed through the column for bigger size.

Many organic reagents (such as $CHCl_3$, C_6H_6, C_7H_8, $C_4H_6O_3$, $C_5H_{11}OH$) combined with BPHA were tested to extract tungsten, too. Most of them had an extent effect to extract W fraction and some of them was not suitable for this aim. However, BPHA-$C_5H_{11}OH$ extraction system was the best one for extraction of tungsten. The extraction efficiency of W as a function of concentration of BPHA-$C_5H_{11}OH$ was plotted in Fig.2. The curve in Fig.2 shows that the extraction efficiency increases while increasing the concentration of BPHA-$C_5H_{11}OH$. It is seen that the extraction efficiency of W is more than 95%, while the concentration of BPHA-$C_5H_{11}OH$ is more than 1.8%, therefore, 2% BPHA-$C_5H_{11}OH$ will be fixed to extract tungsten. 60% of tungsten is extracted while only $C_5H_{11}OH$ is used as an extracting agent. After combining BPHA with $C_5H_{11}OH$ organic solvent, the extraction efficiency of tungsten increases.

As for the concentration of HCl solution, the extraction efficiency of tungsten fraction will decrease at the concentrations lower than 3 mol/L HCl. However, W fraction was adsorbed completely on the Voltalef column with 4 mol/L HCl system, Hf, Lu, Mo and half of Ta fractions passed completely through the Voltalef column rapidly. The residual Ta activities retained on the Voltalef column, since tantalum partially precipitated with BPHA reagent forming the stable chloro-complexes in hydrochloric acid[14]. There was the same tendency for extraction tungsten in BPHA-$CHCl_3$ system[16]. Lu served as analogous element for trivalent actinide, Hf and Ta was the lighter homologue for the transactinide elements Rf and Db. This separation procedure can be used to isolate Sg. According to a decay chain of transactinide elements, Sg-Rf-No, its daughters (Rf and No) can be actually separated out in this isolation procedure.

4 DISCUSSION

As shown from the above experimental results, a new rapid extraction column separation procedure of tungsten has been developed with the extraction system of 2% BPHA-$C_5H_{11}OH/HCl$, in which 1% $Na_3C_6H_5O_7$-5% NH_4OH is used to back-extract W fraction. In this step, there is no Hf, Lu, Ta and Mo fractions existed in the tungsten sample. Therefore, the procedure presented above is one of the possible way to study the aqueous chemistry of element Sg for rapid on-line extraction experiment supposing the chemical property of Sg is similar to that of W.

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References

1 Schädel M. Radiochim Acta, 1995, **70/71**:207

2 Gregorich K E. The Transactinide Elements, Proceedings of Welcb Foundation 41st Conference on Chemical Research, Houston: 1997, 95

3 Kratz J V. The Transactinide Elements, Proceedings Welch Foundation 41st Conference on Chemical Research, Houston: 1997, 65

4 Pershina V G, Fricke B. GSI-Preprint-96-26

5 Schumann D, Fischer S, Andrassy M *et al.* Radiochim Acta, 1996, **72**:137

6 Schumann D, Andrassy M, Nitsche H *et al.* Radiochim Acta, 1998, **80**:1

7 Szeglowski Z, Bruchertseifer H, Brudanin V B et al. J Radioanal Nucl Chem Letters, 1994, **186**:353

8 Wierczinski B, Alstad J, Eberhardt K *et al.* Radiochim Acta, 1995, **69**:77

9 Schädel M, Brüchle W, Gäger E *et al.* Radiochim Acta, 1989, **48**:171

10 Schädel M, Brüchle W, Schausten B *et al.* Radiochim Acta, 1997, **77**:149

11 Paulus W, Günther R, Brüchle W *et al.* GSI Scientific Report, 1998, 13

12 Stary J, Smizanska J. Anal Chim Acta, 1963, **29**:545

13 Hogfled E. Stability constants of metal ion complexes, Part A: Inorganic Ligands, IUPAC chemical data series, No21,Oxford: Perhamon Press,1982

14 Vita C A, Levier W A, Litteral E. Anal Chim Acta, 1968, **42**:87

15 Shendrikar A D. Talanta, 1969, **16**:51

16 Yi Z M, Zhu Z F, Liang S Q. Acta Chimica Sinica, 1963, **29**:249

17 Wang B W. Anal Chem, 1973, **3**:64