

Sorption Behaviour of W, Hf, Lu, U, and Th on Ion Exchangers from HCl/H₂O₂ Solutions. Model Experiments for Chemical Studies of Seaborgium (Sg)

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Summary

In model experiments with W, Hf, Th, and U radionuclides, a chemical system was developed for the separation of seaborgium from element 104 and heavy actinides, i.e., cation exchange on Dowex 50X8 from solutions containing 0.1–1.0 M HCl and 0.5–2.0 vol% H₂O₂. The system should be suitable for fast on-line experiments if seaborgium exhibits a non-uranium-like behaviour. Adding hydrogen peroxide to mixed HCl/HF solutions suppresses the partial sorption of W and, presumably seaborgium, on the cation exchanger. This way, the elution volume can be minimized. Prospects for anion exchange separations of group 6 from group 4 elements are also briefly discussed.

Introduction

In [1], we reported on a chemical system which can be used to separate group 4 elements and lanthanides from the group 6 elements W and Mo through the use of cation exchange from diluted aqueous solutions of HCl/HF. These batch studies were aimed at developing chemical conditions suitable for the separation of seaborgium from heavy actinides and element 104 produced simultaneously in heavy ion reactions. First applications with the ARCA II [2] apparatus showed that a good sorption of Hf onto the cation exchange resin AMINEX A6 can be obtained using the proposed solutions, but the reaction is partially influenced by hydrolysis if very diluted solutions are used [3]. The

first successful separation of seaborgium in aqueous solution was done by use of cation exchange on AMINEX A6 with 0.1 M HNO₃/5 × 10⁻⁴ M HF as eluent [4]. Unfortunately, the concentration of HCl (or HNO₃) and HF cannot be increased, because then adsorption of group 4 elements is incomplete [1, 3]. Hence, the system is very sensitive to small changes in acid concentrations and adsorption on surfaces due to hydrolytic processes can take place in some cases. Another disadvantage is that Mo, and even W, show a partial sorption on the cation exchanger, too [1], which results in a relatively large elution volume using the ARCA apparatus. Therefore, it is desirable to develop chemical systems with a higher content of acid to suppress hydrolysis completely. W and Mo are known to form stable anionic complexes with H₂O₂ in acid solutions up to 10 M HCl [5]. A similar behaviour can be expected for the group 6 element seaborgium. Zr, Hf and lanthanides form positively charged compounds [6] in acid, neutral and slightly basic solutions. This makes the system possibly suitable for the separation of group 6 from group 4 elements.

Relativistic calculations [7] showed that in some cases chemical similarities of transactinide elements with the corresponding lighter actinides might be expected. For instance, similarities in the chemical properties of hahnium with protactinium were observed [8]. Therefore, in the present work, the behaviour of U and Th was taken into consideration. Detailed batch studies were carried out with carrier-free and small amounts of carrier isotopes of Hf, W, Lu, U, and

Th as model elements for the elements 104 and 106 and for trivalent actinides. The aim was to test the utility of HCl/H₂O₂ containing solutions for separating seaborgium on cation exchange resins. Furthermore, H₂O₂ was added to HCl/HF solutions used in [1] with the aim of improving the separation. Separations of seaborgium from HCl/H₂O₂ solutions on anion exchange resins are discussed alternatively.

Experimental

The irradiations for the production of ¹⁷³Lu, ¹⁷⁸W, and ²³²U were carried out with 650 MeV protons at the Phasotron "F" (Laboratory of Nuclear Problems, JINR Dubna, Russia). Metallic Ta was irradiated for 7 hours in the external beam to produce both ¹⁷⁸W and ¹⁷³Lu. Tungsten was separated from the irradiated target by thermochromatography using moist air. Carrier-free W was condensed onto the surface of a thermochromatographic column [9] and was subsequently dissolved in 0.5 M HCl. Rare earth elements were separated by gradient elution with α -HIB as reported in [10].

Carrier-free ²³²U was obtained as a decay product of ²³²Pa (β^- , $T_{1/2} = 1.31$ d) which was produced via the nuclear reaction ²³²Th(p,n)²³²Pa(β^-). After decay of ²³²Pa, a pure sample was obtained which contained only ²³²U and its decay products. ²²⁸Th, the α -decay product of ²³²U, was separated immediately before the experiments by adsorbing the ²³²U on the anion exchange resin Dowex 1X8 from 9 M HCl solution. The ²²⁸Th passes through the column without sorption. ²³²U can then be eluted from the column with 2 M HCl.

¹⁸¹Hf was produced by irradiating ¹⁸⁰HfO₂ at the IBR-2 reactor (neutron flux 5×10^{12} n/cm²s, Laboratory of Neutron Physics, JINR Dubna, Russia) for two weeks. A specific activity of 63 MBq/mg Hf was obtained. Sample preparation has been described earlier [11].

For the batch experiments, 5 ml of the radioactive solutions were contacted with 200 mg of either Dowex 50WX8 or Dowex 1X8 (20–50 mesh) for one hour. The γ -activities of the solutions containing ¹⁷³Lu or ¹⁸¹Hf were measured before and after the contact with the resin using a Ge(Li) detector. The distribution of ²³²U was determined by evaporating 0.1 ml of the solution before and after contact and measuring the α -activity using a Si(Au) detector (resolution 35 keV). The results on ²²⁸Th were obtained by determining the γ -activity of its decay products (²¹²Pb) one month after the experiment using a Ge(Li) detector. The distribution coefficients were calculated, by use of the following formula, as described in [1, 11]:

$$D = \frac{A_i V_s}{A_s m_i}$$

with A_i activity on the ion exchanger (Bq) A_s activity of the solution (Bq)
 m_i amount of ion exchanger (g) V_s volume of the solution (ml).

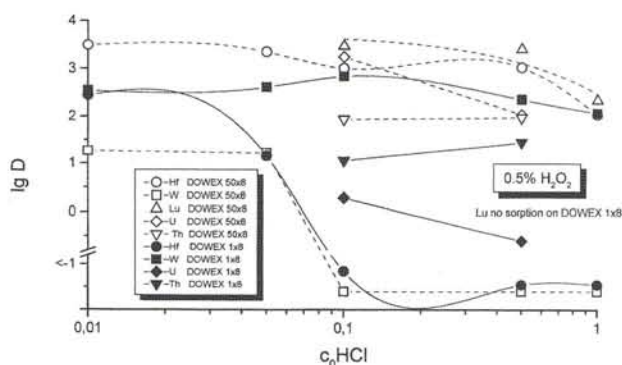


Fig. 1. Distribution coefficients of Lu, Hf, W, Th and U on Dowex 50X8 and Dowex 1X8 as a function of the HCl concentration at a fixed concentration of 0.5 vol.% H₂O₂.

Results and discussion

1zn1. Sorption of Hf, Lu, W, and Th as a function of the HCl concentration

In Fig. 1, the $\lg D$ values of Hf, Lu, W, Th, and U on Dowex 50X8 and Dowex 1X8 as a function of HCl concentration in the presence of 0.5 vol.% H₂O₂ are plotted. The suitable concentration range of H₂O₂ was determined in preliminary studies. It can be seen that W exhibits strong sorption on the anion exchanger over the whole range of HCl concentrations, while the sorption is very weak on the cation exchanger at concentrations higher than 0.05 M HCl. This is due to the formation of anionic compounds. At concentrations lower than 0.05 M HCl, W shows also sorption on Dowex 50X8.

The behaviour of hafnium is influenced by hydrolysis. This group 4 element is known to hydrolyze strongly in weak acid solution [12]. While it is completely sorbed on Dowex 50X8 over the whole HCl concentration interval, it shows also strong sorption on the anion exchange resin at concentrations lower than 0.1 M HCl. With increasing HCl concentration, the sorption on Dowex 1X8 decreases but the strong sorption on Dowex 50X8 remains. From this, one can propose the formation of a positively charged complex, which is (partially) hydrolyzed in weak acid solution.

Th like Hf, is sorbed on the cation exchange resin as expected for a typical tetravalent element. On Dowex 1X8, it also exhibits a somewhat high distribution coefficient. This is probably caused by formation and partial sorption of neutral compounds.

From this work and from literature [5, 13] it can be expected that Lu as the model element for trivalent lanthanides and actinides, shows strong sorption on Dowex 50X8 and no sorption on the anion exchange resin over the whole range of HCl concentration (Fig. 1).

From these results, it is expected that conditions for a good separation of W from tri- and tetravalent elements can be found at HCl concentrations between 0.1 and 1.0 M. Over this range of HCl concentrations,

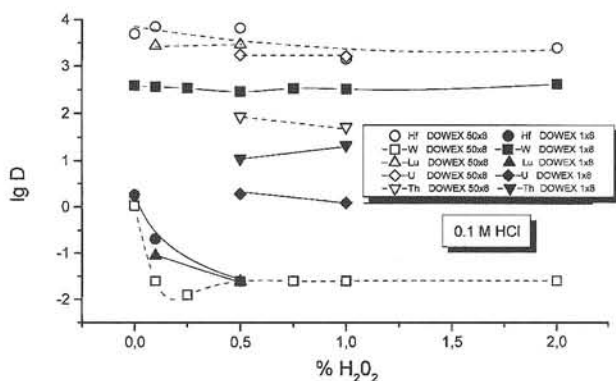


Fig. 2. Distribution coefficients of Lu, Hf, W, Th, and U on Dowex 50X8 and Dowex 1X8 as a function of the H₂O₂ concentration at a fixed concentration of 0.1 M HCl.

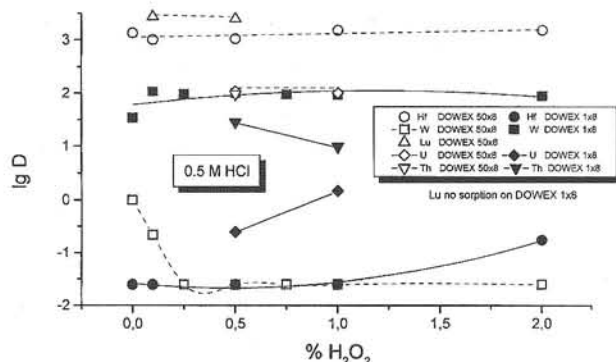


Fig. 3. Distribution coefficients of Lu, Hf, W, Th and U on Dowex 50X8 and Dowex 1X8 as a function of the H₂O₂ concentration at a fixed concentration of 0.5 M HCl.

the influence of H₂O₂ concentration was studied in detail.

2. Sorption of Hf, Lu, W, and Th as a function of the H₂O₂ concentration

The dependence of the lg *D* values for sorption of the elements investigated on Dowex 50X8 and Dowex 1X8 on the H₂O₂ concentration with several concentrations of HCl is shown in Figs. 2–4. With the exception of very low H₂O₂ concentration (<0.5 vol.%), the sorption of Hf, Lu, W, and Th is nearly independent of the H₂O₂ concentration both on the cation and on the anion exchange resin. This behaviour does not change if the concentration of HCl is varied (0.1 M HCl Fig. 2, 0.5 M HCl Fig. 3, 1.0 M HCl Fig. 4). This means that solutions containing 0.5–2.0 vol.% H₂O₂ and 0.1–1.0 M HCl are useful as eluting agents for the separation of W from tri- and tetravalent elements on a cation or anion exchange resin. This chemical system is not as sensitive to small changes in the concentrations as the HNO₃/HF system and conditions can be selected which allow the suppression of hydrolytic effects completely. Therefore, if a W-like behaviour of

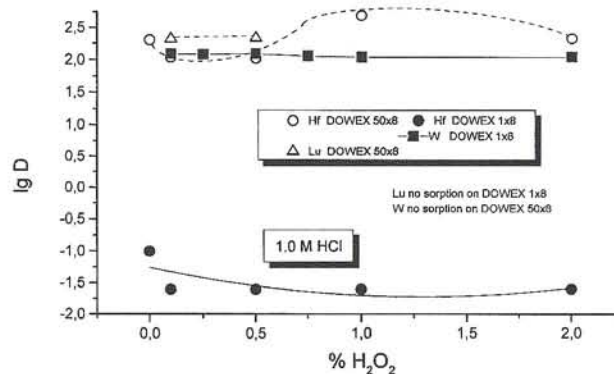


Fig. 4. Distribution coefficients of Lu, Hf, W, Th and U on Dowex 50X8 and Dowex 1X8 as a function of the H₂O₂ concentration at a fixed concentration of 1.0 M HCl.

seaborgium is expected, this procedure can be recommended for the fast on-line separation.

3. Sorption of U

Experience with element 105 showed that extrapolations of chemical properties within a group often fail, at least partially, due to relativistic effects which influence the electronic structure of heavy elements. Element 105, in some cases, does not behave like its lighter homolog Ta, but like Nb or Pa [8, 14, 15]. Until now, there are no serious indications that seaborgium may show similarities to U [16], but the possibility should be taken into consideration. Under the conditions described above, U does not behave similar to group 6 elements but shows strong sorption on the cation exchange resin at a wide range of HCl concentrations at constant H₂O₂ concentration (Fig. 1) and as a function of H₂O₂ concentration in the presence of various HCl concentrations (Figs. 2–4). Therefore, if seaborgium behaves like U, then the HCl/H₂O₂ system is not suitable for fast separation experiments because Sg would remain completely on the cation exchange column. Nevertheless, it can be used in future experiments to distinguish between a W-like or U-like behaviour of Sg. This will require an extra separation step from element 104 if Sg exhibits U-like properties.

4. Structure of the complexes

Hydrogen peroxide compounds of transition metals are well-known. The compositions of the compounds differ widely depending on the amount of metal, pH value, concentration of H₂O₂, state of aggregation and so on. Most of the studies concerning this subject deal with macro amounts of metal, and, therefore, classical physical and chemical methods can be used for determining the structure of the compounds. Furthermore, in many cases, polynuclear complexes are the main products. For our specific conditions – very low metal concentration (<10⁻⁶ M), dilute acid solution and

relatively small amounts of hydrogen peroxide – the information available from literature is rather limited [6].

From literature data [17] lanthanides and trivalent actinides are not expected to interact with H_2O_2 under the conditions described here. They sorb as cations ($\text{M}(\text{H}_2\text{O})_n^{3+}$) on Dowex 50X8 and are not sorbed on the anion exchanger.

Group 4 elements form several complexes with H_2O_2 . In analogy with Ti, for Hf, we expected a structure of the form $[\text{Hf}(\text{O}_2)(\text{H}_2\text{O})_2]^{2+}$ in acid solution [18]. This means that positively charged complexes are formed in good agreement with our results.

It is sorbed both on the cation and the anion exchange resin in our experiments (Fig. 1). Simultaneous presence both of cationic and anionic species would be the most likely explanation of this behaviour. Certain data are not available from literature.

In contrast to Cr, Mo and W form peroxy compounds only in the +6 valence state. Several compounds with varying content of H_2O_2 are known [6]. In weak acid solution, an anionic complex of the structure $[\text{M}(\text{O}_2)_2(\text{O})_2]^{2-}$ dominates [5, 6]. The observed sorption of W on the cation and anion exchange resins is consistent with such a species.

Anionic complexes of U are, in contrast to W and Mo, only formed in alkaline media because uranium compounds of the form $[\text{UO}_2(\text{O}_2)_3]^{4-}$, hydrolyze at low pH [6]. Therefore, we found strong sorption on the cation exchanger.

5. Sorption of W in HCl/ H_2O_2 /HF containing media

For the separation of group 6 elements from group 4 elements 0.05–0.1 M HCl solution containing HF concentrations up to 10^{-3} M can be used as described in [1]. For higher HF concentration desorption of HF and Zr from the cation exchange resin was observed due to formation of fluoride complexes. Similarly, the $\lg D$ values decrease when the HCl concentration is increased. Therefore, the HCl and HF concentrations can only be varied in the ranges 0.05–0.1 M HCl and 10^{-4} – 10^{-3} M HF as reported in [1]. Unfortunately, a partial sorption of W on the cation exchanger observed in the batch experiments [1] leads to a relatively high elution volume in column experiments with the ARCA apparatus [22]. Adding H_2O_2 to these solutions does not effect the sorption behaviour of lanthanides and group 4 elements because their peroxy complexes are weaker than the respective fluoride complexes [21]. However, for W it is the opposite. The peroxy complexes are much stronger than the fluoride complexes [21], and this gives the possibility to decrease the partial sorption of W on the cation exchanger.

Using concentrations of 10^{-3} M and 10^{-4} M HF plus 0.1–0.5 vol.% H_2O_2 , we determined the distribution coefficients of W on Dowex 50X8 and Dowex 1X8 as a function of the HCl concentration. The

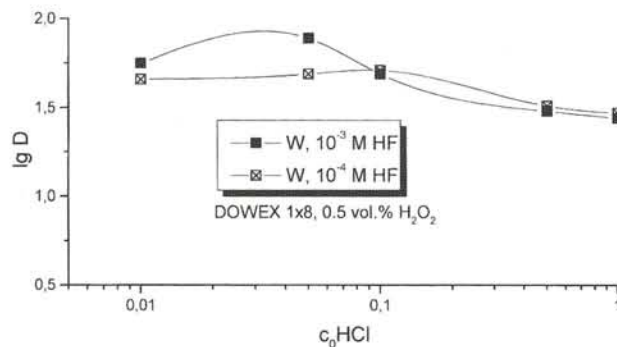


Fig. 5. Distribution coefficients of W on Dowex 1X8 as a function of the HCl concentration at 0.5 vol.% H_2O_2 and 1.0×10^{-4} M HF, 1.0×10^{-3} M HF, respectively.

sorption behaviour of W did not appreciably change in the interval of 0.1–0.5 vol.% hydrogen peroxide. The results on Dowex 1X8 obtained with 0.5 vol.% H_2O_2 are plotted as an example in Fig. 5. Sorption on Dowex 50X8 was not observed at all. The $\lg D$ values on the anion exchanger are nearly independent of HCl concentration and only slightly lower than in the experiments without HF (Fig. 1). So, by adding H_2O_2 to the HCl/HF solutions used in [1], the partial sorption of W on the cation exchanger can be suppressed and, in this way, a considerably lower elution volume should be needed in experiments with the ARCA apparatus.

Conclusions

1. a) Ion exchange on Dowex 50X8 from solutions containing 0.1–1.0 M HCl and 0.5–2.0 vol.% H_2O_2 is proposed as a suitable chemical system for the separation of tungsten from hafnium, thorium and the lanthanides. This system can be applied in fast on-line experiments for the separation of seaborgium using the ARCA II apparatus. A detailed description of the separation scheme of this setup can be found in [2].
b) Uranium shows a completely different sorption behaviour on Dowex 50X8 in comparison to that of tungsten. It is sorbed on the cation exchange resin with high distribution coefficients from solutions in the concentrations interval of 0.1–1.0 M HCl and 0.5–2.0 vol.% H_2O_2 .

2. This chemical system can only be applied for the separation of seaborgium from element 104 and heavy actinides if a tungsten-like behaviour of seaborgium is expected. However, it can be used to distinguish between W-like or U-like properties of Sg.

3. Adding 0.1–0.5 vol.% H_2O_2 to solutions of 0.05–0.1 M HCl/ 10^{-3} – 10^{-4} M HF suppresses the partial sorption of W on Dowex 50X8 described in [1]. This system should improve the method for the separation of seaborgium in applications with the ARCA apparatus by lowering the elution volume needed in comparison to the use of HCl/HF solutions without hydrogen peroxide.

4. Ion exchange on Dowex 1X8 from solutions containing 0.1–1.0 HCl and 0.5–2.0 vol.% H₂O₂ is an alternative chemical system for the separation of tungsten from hafnium, thorium and the lanthanides.

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