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Chromatographic studies of Rf (element 104) with tributylphosphate (TBP)

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Abstract

The extraction behaviour of Rutherfordium (element 104, Rf), carrier-free Zirconium, and Hafnium in the system HCl–TBP (tributylphosphate) was examined. The 65-s α-emitting isotope ^{261}Rf was produced via the reaction ^{248}Cm(^{18}O,5*n*). The recoil products were transported with a He(KCl) jet to the Automated Rapid Chemistry Apparatus (ARCA) where 1140 separations were performed. In contrast to previous data showing a seemingly low extraction of Hf and Rf we find much higher distribution coefficients. The extraction increases in the order Hf<Rf<Zr. © 1998 Elsevier Science S.A.

Keywords: Tributylphosphate; ARCA; Extraction

1. Introduction

The solution chemistry of Rf (element 104) started with pioneering work of R.J. Silva and coworkers [1]. They eluted Rf together with the other group 4 elements Zr and Hf from a cation exchange resin with 0.1 M ammonium α-hydroxyisobutyrate at pH=4 while the actinides were strongly absorbed. E.K. Hulet et al. [2] showed that anionic chloride complexes of Rf are extracted from 12 M HCl like its lighter homologues into a quarternary amine held on an inert support. K.R. Czerwinski et al. [3,4] examined extraction of Rf into 0.25 M TBP (tributylphosphate) in benzene as a function of HCl, chloride, and hydrogen ion concentrations between 8 M and 12 M. Similar studies were carried out with Zr, Hf, Th, and Pu. In the experiments where the chloride and hydrogen ion concentrations were varied, Rf extraction differed from that of the group 4 elements and behaved like Pu(IV). The following work by C.D. Kacher et al. [5] showed discrepancies to Czerwinski's work with regard to the behaviour of Hf. From 8 M HCl, only about 25% of Hf was extracted in Czerwinski's work, whereas in [5], about 85% was extracted under the same conditions. The explanation for this discrepancy was that the data from [3,4] were based on online data taken at the cyclotron, where the activity was collected on teflon discs. It was found that Hf sorbs onto teflon which probably accounts for the seemingly lower extraction. Since only the organic phase was measured, the missing activity was automatically assigned to the aqueous phase not taking into account possible losses by adsorption.

Though the authors of [5] realized the adsorption effects for Hf, they did not perform new experiments for Rf, but took the data from [3,4] to compare with their Hf and Zr data, not taking into account that Rf may have been adsorbed to the teflon surface like Hf. Then the order of extraction seemed to be Rf<Hf<Zr. In view of the somewhat unsatisfactory situation with the data in [3–5] we decided to conduct independent experiments with Zr, Hf, and Rf to check the TBP extraction behaviour of all three elements.

2. Experimental

The carrier-free radionuclides ^{98}Zr (from fission), ^{169}Hf (from the reaction of ^{18}O with ^{nat}Gd), and ^{261}Rf (from the ^{248}Cm(^{18}O,5*n*) reaction) were used for online experiments at the Mainz TRIGA reactor and at the PSI cyclotron. It was the first time that an actinide target was irradiated at a Swiss accelerator. The Cm target consisted of 450 μg/cm^2

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of ^{248}Cm plated as the nitrate onto 2.34 mg/cm^2 of Be and converted to the oxide by heating. Special precautions were undertaken to prevent contaminations of the target with heavy elements because even nanograms of Pb, Au, or Pt in the targets will produce lots of disturbing α-emitters like At, Fr, or ^{213}Po from the decay of ^{213}Bi with a decay energy close to that of ^{261}Rf. Therefore, instead of using a Pt electrode, a Rh anode was used for electroplating. The $^{18}O^{5+}$ beam was entering the target with 101.4 MeV. Typical beam intensities were up to 1.5 electrical μA. The reaction products recoiling out of the target were stopped in He gas (about 1.5 bar) which had been loaded with KCl aerosols produced by sublimation from the surface of KCl powder at 640°C. The activities were swept out of the recoil chamber with 1.6 l/min of He gas through a stainless steel capillary (2.0 mm inner diameter) to the collection site of ARCA. In the collection position the aerosols exited through a nozzle and were deposited by inertial impaction on the top slider of ARCA.

The microcomputer-controlled Automated Rapid Chemistry Apparatus (ARCA) [6] is a miniaturized liquid chromatography system. It is designed to carry out fast and repetitive separations in a chemically inert system. It allows group separations of elements within a few seconds. The 40 microchromatographic columns (1.6 mm diameter, 8 mm height) were filled with undiluted TBP on an inert support (Voltalef 30–80 μm, weight ratio TBP:Voltalef= 1:5). After a collecting time of 90 s, the reaction products were loaded onto the column in 12 M HCl. Subsequently, a Hf fraction was eluted in 200 μl of 8 M HCl. This fraction contained 75% of the Hf, and no Zr; see Fig. 1. Thereafter a Zr fraction was stripped from the column with 167 μl of 2 M HCl. This fraction contains the remainder of the Hf, and >93% of the Zr. For a faster and smoother evaporation of the effluents, as compared with our previous techniques, where little droplets were collected, we continuously sprayed the eluent through a 60-μm nozzle onto heated Ta discs mounted on an electrically heated turntable. After the evaporation under the flow of hot He gas and additional heating by infrared light focused into the liquid, the samples were placed on one of eight 450-mm^2 PIPS detectors. The energy of each α-particle or spontaneous fission event was stored in list mode together with the time after the start of counting and the detector designation.

The delay between the end of irradiation and the start of counting was typically 40 s for the first fraction and 64 s for the second sample. Measuring times in the cycle were typically 350 s; in some cases during column changes, some samples were measured for longer times in order to determine the background.

3. Results

The overall yield determined with ^{169}Hf, including losses from the gas jet and evaporation step, was 38%.

In the α-energy range 8.0 MeV to 8.65 MeV, 30 α-decays attributed to ^{261}Rf and its daughter ^{257}No were recorded, among those 5 mother–daughter correlations. Monte Carlo simulations of the random correlation rate showed that these are true correlations. From the distribution of the α-events between the Hf-fraction and the Zr-fraction we can calculate the distribution coefficient for Rf in the system 8 M HCl–TBP as $K_d = 150\pm^{64}_{46}$ the corresponding values for Hf, and Zr are 65, and 1180, respectively. So the extraction increases in the order Hf< Rf<Zr (Fig. 2).

4. Conclusion

Our experiments strongly support the explanation that in [3] Rf was adsorbed like Hf on the teflon surface. Consequently, the absolute values for the percentage of extraction for Rf and Hf were grossly underestimated due to missing activity. The extraction sequence observed in

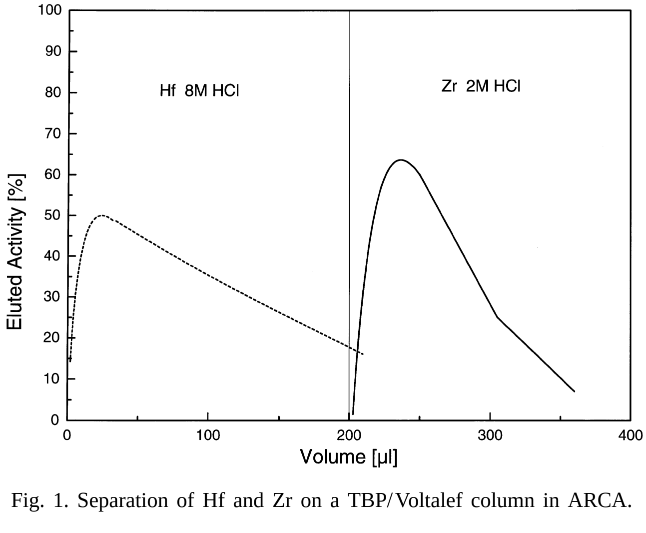

Fig. 1. Separation of Hf and Zr on a TBP/Voltalef column in ARCA.

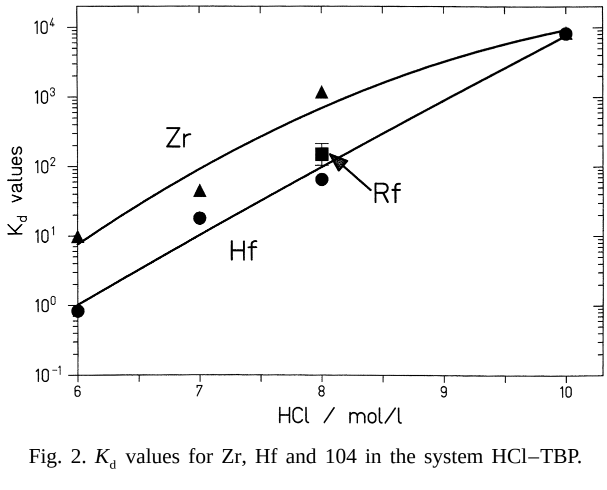

Fig. 2. K_d values for Zr, Hf and 104 in the system HCl–TBP.

the present work, Zr>Rf>Hf, is in agreement with the trend Nb>Ha>Ta found for group 5 elements as a result of theoretical considerations [7] in which the competition between hydrolysis and the complex formation (and extraction) has been explicitly taken into account: $M(OH)_xCl_{6-x} + xHCl \Leftrightarrow MCl_6^- + xH_2O$. The sequence for Nb, Ta and Ha was determined by predominant changes in the electrostatic part of the interaction energy metal–ligand when OH^- groups are replaced by Cl^-. For group 4, the analogous equilibrium is: $M(OH)_xCl_{4-x} + xHCl \Leftrightarrow MCl_4 + xH_2O$. To predict the equilibrium constant for this reaction, one has to consider the difference in the total energies of the (partially) hydrolyzed species on the left-hand side that are not extracted and of the extractable MCl_4. Knowing a close analogy between groups 4 and 5 (the same trend in effective charges in going down the groups) and supposing that the Coulomb interaction will define the process, the trend in the group 4 complex formation will be Zr>Rf>Hf. Since the complex formation defines the extraction process, the same trend should be observed for the K_d values, which has been found in the present experiments. The tendency for the hydrolysis of the group 4 chloro complexes (a reverse process of the complex formation) is then Hf>Rf>Zr [7].

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