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STEP

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TITLE: The extraction of zirconium and hafnium by tri-n-octylamine from metal fluoride solutions

SOURCE: Ekstraktsiya; teoriya, primeneniye, apparatura, no. 2, Ed. by A.P. Zefirov and M.M. Senyavin. Moscow, Gosatomizdat, 1962, 141 - 153

TEXT: The extraction of Zr and Hf from K_2MF_6 (where M = Zr, Hf) by a solution of pure tri-n-octylamine (TOA) in benzene is discussed. TOA will extract Zr and Hf only from weak acid solutions since more acid solutions tend to form $R_3N.HX$ (where X = HSO_4, Cl, NO_3). Highest values for the distribution coefficients, D_{Zr} and D_{Hf}, were obtained with 0.2 M H_2SO_4 while HNO_3 leads to the lowest D_M values. With H_2SO_4,

Card 1/2

$D_{Hf} > D_{Zr}$ but with HNO_3 Zr is preferentially extracted. The influence of additions was also studied. The values of D_M decrease as the concentration of the addition in the aqueous phase increases. With small additions of KCL of KF $D_{Hf} > D_{Zr}$ but at higher concentrations ($> 8g/l$ for KCl - $\succ 1\%$ for KF) $D_{Zr} > D_{Hf}$. Addition of K_2SO_4 make $D_{Zr} > D_{Hf}$ but with NH_4NO_3 $D_{Hf} > D_{Zr}$. Extraction from K_2ZrF_6 (10 g/l) acidified with 0.2 M $(COOH)_2$ by 5% benzene solution of TOA gives D_{Zr} = 47 and D_{Hf} = 10. Both D values decrease as the molarity of the acid is decreased. The extraction mechanism is summarized by: $2(R_3NH)HSO_{4org.} + K_2ZrF_{6aq.} \rightleftharpoons (R_3NH)_2ZrF_{6org.} + 2KHSO_{4aq.}$. Evidence for this mechanism is discussed in detail.

There are 12 figures and 6 tables.

Card 2/2