NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U.S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.
The extraction of zirconium and hafnium by tri-octylamine from metal fluoride solutions

The extraction of Zr and Hf from $K_2M_F_6$ (where $M = \text{Zr, Hf}$) by a solution of pure tri-octylamine (TOA) in benzene is discussed. TOA will extract Zr and Hf only from weak acid solutions since more acid solutions tend to form $R_3NX$ (where $X = \text{HSO}_4^-, \text{Cl}, \text{NO}_3^-$). Highest values for the distribution coefficients, $D_{\text{Zr}}$ and $D_{\text{Hf}}$, were obtained with $0.2 \text{M H}_2\text{SO}_4$ while $\text{HNO}_3$ leads to the lowest $D$ values. With $\text{H}_2\text{SO}_4$, $D_{\text{Hf}} > D_{\text{Zr}}$ but with $\text{HNO}_3$, Zr is preferentially extracted. The influence of additions was also studied. The values of $D$ decrease as the concentration of the addition in the aqueous phase increases. With small additions of KCl of KF $D_{\text{Hf}} > D_{\text{Zr}}$ but at higher concentrations (> 8g/l for KCl - > 1% for KF) $D_{\text{Zr}} > D_{\text{Hf}}$. Addition of $\text{K}_2\text{SO}_4$ makes $D_{\text{Zr}} > D_{\text{Hf}}$ but with NH$_4$NO$_3$, $D_{\text{Hf}} > D_{\text{Zr}}$. Extraction from $\text{K}_2\text{ZrF}_6$ (10 g/l) acidified with 0.2 M (COOH)$_2$ by 5% benzene solution of TOA gives $D_{\text{Zr}} = 47$ and $D_{\text{Hf}} = 10$. Both $D$ values decrease as the molarity of the acid is decreased. The extraction mechanism is summarised by: $2(R_3\text{NH})\text{HSO}_4$$_{\text{org.}} + \text{K}_2\text{ZrF}_6$$_{\text{aq.}} \leftrightharpoons (R_3\text{NH})_2\text{ZrF}_6$$_{\text{org.}} + \text{2KHSO}_4$$_{\text{aq.}}$. Evidence for this mechanism is discussed in detail.

There are 12 figures and 6 tables.