

Speciation of Plutonium in Nitrate Media: Effect of Fluorides

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The CEA DAM operates actinides recycling processes in nitrofluorhydric media. In this context, understanding and controlling the complexes formed by plutonium in these media is of critical importance for optimising existing processes and designing novel and efficient process schemes. This study aims to investigate the coordination chemistry and formation of these complexes (speciation) in nitrate media and in the presence of fluoride ions.

For the Pu(IV) oxidation state and varying nitric acid concentrations from 5 to 12 M, three species are identified via visible-near infrared absorbance spectroscopy: the dinitrato complex $\text{Pu}(\text{NO}_3)_2^{2+}$ predominates at 5 M while the hexanitrato species $\text{Pu}(\text{NO}_3)_6^{2-}$ is major at 12 M; and a tetranitrato complex $\text{Pu}(\text{NO}_3)_4(\text{aq})$ coexists between with both the latter [1, 2].

This speciation study deals with the determination of the complexation constants (β) of these complexes. After studying Pu(IV) in nitric acid alone, the influence of other species, such as fluoride ions, is also examined. At a concentration of 12 M nitric acid, the addition of fluoride results in a decrease in the intensity of the characteristic band at 491 nm of the plutonium hexanitrato complex $\text{Pu}(\text{NO}_3)_6^{2-}$ leading to the appearance of a band at 476 nm (Figure 1). Spectral decomposition reveals a signal that may correspond to a mixed complex $\text{PuF}_x(\text{NO}_3)_y^{(4-y-x)}$, where $x = 1$ or 2.

Preliminary results highlight the significant impact of fluoride ions in the coordination chemistry of Pu(IV). The formation of several mixed plutonium/nitrate/fluoride complexes is observed and is currently under investigation and characterisation. Taking into account these species into the chemistry of current or future processes could provide substantial benefits, including the optimization of fluorine usage through controlled, on-demand addition.

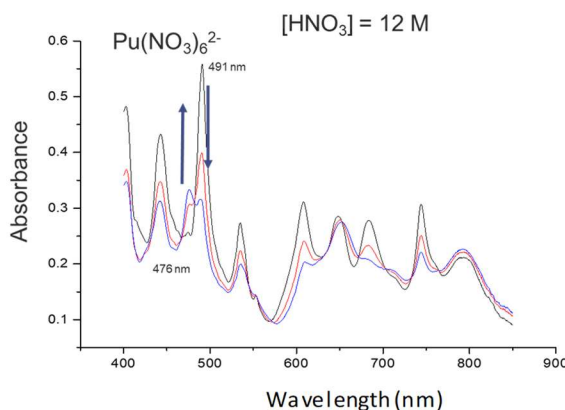


Figure 1. Absorption spectrum of a Pu(IV) hexanitrato complex in 12 M nitric acid (black: $[\text{F}^-] = 0$ M) and spectral evolution upon fluoride addition (red: $[\text{F}^-] = 0.03$ M; violet: $[\text{F}^-] = 0.06$ M).

[1] Altmaier, M., Gaona et al. Aqueous Solution and Coordination Chemistry of Plutonium (2019). In D. L. Clark et al. (Eds.), "Plutonium Handbook". American Nuclear Society: La Grange Park, Illinois 60526, USA, [2] G. Bailly et al., Journal of Radioanalytical and Nuclear Chemistry (2022) 331: 1267-1273