

## Ph.D. defense

Institut de Chimie Séparative de Marcoule / CEA Marcoule  
(UMR 5257, CEA, CNRS, Université Montpellier, ENSCM)

**ELIZABETH MAKOMBE**

will present her Ph.D. dissertation

### Actinide(VI) and actinide(IV) extraction by malonamides

The defense will take place on **Monday, March 13, 2023 at 10:30 AM**

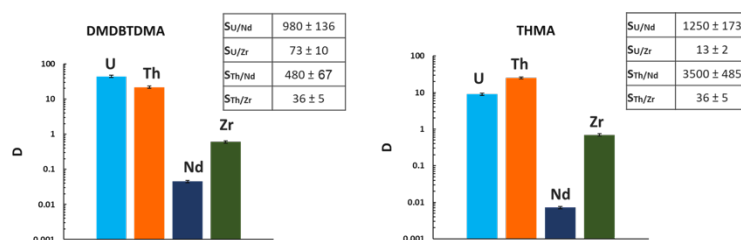
in the ICSM Auditorium

This research work aims to study the extractive properties of malonamides for the extraction of uranium(VI) and plutonium(IV) from nitric aqueous phases, and their separation without the use of redox chemistry as in the case of the current PUREX process. Malonamides have been widely studied for the separation of minor actinides, however, these molecules are also good extractants of uranium(VI) and plutonium(IV).

The extractive properties of malonamides regarding uranium(VI), thorium(IV) and plutonium(IV) were investigated by comparing two structural isomers, DMDBTDMA (*N,N'*-dimethyl-*N,N'*-dibutyl tetradecyl malonamide) and THMA (*N,N,N',N'*-tetrahexyl malonamide). The influence of the diluent was studied by comparing n-heptane and toluene. Both malonamides allow an efficient co-extraction of actinides at high concentrations of nitric acid (3 to 5 mol/L) and An(VI)/An(IV) separation at a lower acidity (1 mol/L). The An(VI)/An(IV) selectivity is better with DMDBTDMA which has a higher affinity for uranium(VI) than THMA. Molecular and supramolecular characterization of the species in organic solutions has been carried out. For the two malonamides, an increase in the concentration of uranium in the organic phase led to the supramolecular organization of the organic solution. DFT calculations suggest that the complex  $[UO_2(NO_3)_2L]$  (L being malonamide) formed with DMDBTDMA is more stable than that formed with THMA. This would explain the greater affinity of DMDBTDMA for uranium(VI).

The extraction of thorium(IV) is highly influenced by the molecular topology of the ligand molecule. The differences in extraction behavior observed could be linked to differences in the nature of Th-malonamide interactions: Th-THMA complexes appear to be classical molecular complexes while Th-DMDBTDMA complexes are suspected to be more complex supramolecular species.

Th(IV) and Pu(IV) present differences in the extraction behavior, which could be due to different speciation in the organic phase: DFT calculations as well as the slope method suggest higher ligand stoichiometries for Th(IV) than for Pu(IV).



**Keywords:** Solvent extraction; Malonamides; Uranium(VI); Thorium(IV); Plutonium(IV)

