

# PILOTING SEPARATION IN LIQUID-LIQUID SYSTEMS

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One of the challenges for separative chemistry remains the control of flows of metal mixtures of variable composition. The primary intent is generally to separate everything, and the processes currently proposed are sequential. This strategy has its limits in the area of recycling because processes become too complex and generate too many effluents. In some cases, there is an interest in working on mixtures, without going till ultimate separation. We propose to approach this point by the development of multi-phase, adaptive systems, allowing to generate flows of controlled composition.

The LHYS has developed an expertise in the understanding of how a metal ion usually not soluble in an organic phase can be maintained into it by using classical extractants. We elucidated the impact of the interactions which take place at the molecular level, ie. chemical bonding and electrostatic interactions, and low energy second order interaction (H bonding, polarisation, dipole...) on several separation issues.<sup>1</sup>

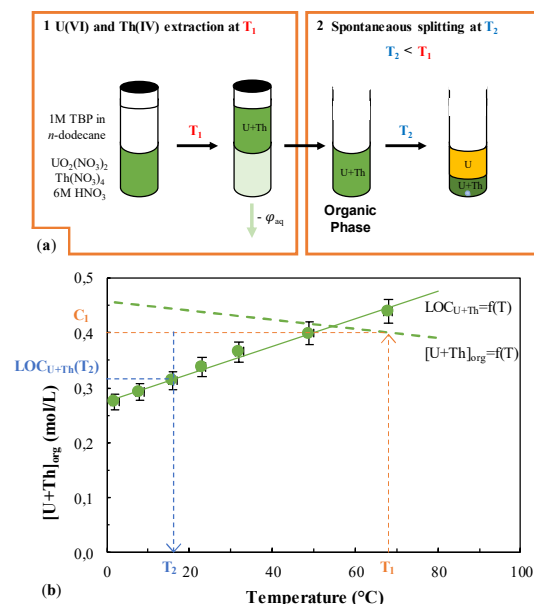


Figure 1: Principle of a. U-Th separation through organic phase self-splitting and b. piloting of the process using variation of Limiting Organic Concentration (LOC) according to temperature (T)

Amongst the approaches envisioned, the spontaneous phase splitting of an organic phase containing U and Th upon cooling was employed to design a non-proliferat-

ing nuclear fuel reprocessing scheme employing classical tributyl phosphate (TBP) extractant (Fig. 1):<sup>2</sup> A first biphasic system is obtained after extraction of both U and Th at high temperature ( $T_1$ , 70 °C). The two phases are separated, then the organic phase loaded with U and Th is cooled below a critical temperature (about 50 °C) where it segregates between a heavy and a light organic phase. Two fluxes are thus obtained: the first contains almost all of the Th in the presence of U in a controlled ratio, the second contains surplus U. The U/Th ratio in the heavy phase is controlled by the final temperature of the system (between 1 °C and 20 °C).

In another approach, completely different from the classical method where a single molecule is designed to extract metal cations under specific conditions, dynamic covalent chemistry has been exploited as a tool for inducing the generation of the extractant species. In collaboration with the LCS (ISIS), the LHYS team has implemented an adaptive dynamic covalent library to the liquid-liquid extraction of copper(II) nitrate: A dynamic library of acylhydrazones constituents self-build and distribute through both phases of the system (Fig. 2).<sup>3</sup>

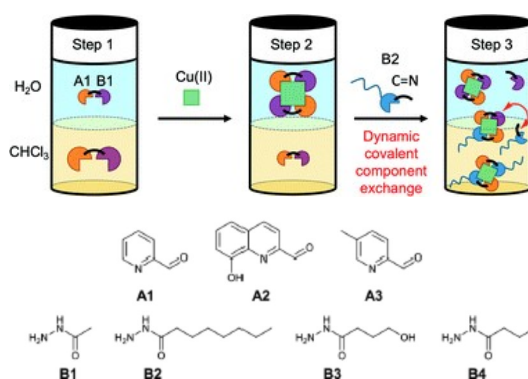


Figure 2: Principle of dynamic covalent chemistry in biphasic systems and reference library of aldehyde A1-A3 and hydrazone B1-B4 components

This work laid the foundation of a new liquid-liquid metal extraction-separation approach which opens the possibility of developing a system responding to several metal extraction-separation problems. The strategy is currently under further investigation at the LHYS in the frame of the PhD thesis of R. Moneuse. Latter work is dedicated to the study of dynamic acylhydrazones based biphasic systems encompassing metalating cations such as Cu(II), Fe(III) and Pd(II).

<sup>1</sup> D. Bourgeois, A. El Maangar, S. Dourdain, "Importance of weak interactions in the formulation of organic phases for efficient liquid/liquid extraction of metals", *Current opinion in colloid & interface science*, 2020, 46, 36-51.

<sup>2</sup> J. Durain, D. Bourgeois, M. Bertrand, D. Meyer, "Short Alternative Route for Nuclear Fuel Reprocessing Based on Organic Phase Self-Splitting", *Molecules*, 2021, 26, 6234.

<sup>3</sup> A. Chevalier, A. Osypenko, J.M. Lehn and D. Meyer, - "Phase transfer of metal cations by induced dynamic carrier agents: biphasic extraction based on dynamic covalent chemistry" *Chem. Sci.*, 2020, 11, 11468.