

Development of a separative microsystem for radionuclides analysis in nitric acid media on organic monolith

Extended summary – Marion Losno – PhD thesis defended on November 23rd 2017

Spent fuel is reprocessed by dissolution in boiling concentrated nitric acid and then by the separation of uranium, plutonium and non-recoverable waste. Accurate accounting of nuclear material is performed at the entrance of the reprocessing process, after dissolution and throughout the process for environmental regulatory reasons and non-proliferation concerns. Moreover, increased public attention to radioactive waste and potential public health effects of release of radioactive materials to the environment has made accurate and reliable methods for actinide determinations in various environmental and biological samples increasingly important. Hence, the radionuclides analyses have seen an increasing demand.

The analysis of radionuclides which are dissolved in spent fuel samples is carried out according to operating protocols including the sequence of several separation / purification steps before carrying out the measurement to avoid interference and improve measurements accuracy. Current protocols involve separation by solid phase chromatography because they provide an easy way to pre-concentrate and even separate a large number of radionuclides, particularly actinides and selected fission products, from a wide variety of sample matrices, notably UTEVA™, TRU™ and TBP™ columns containing impregnated particulate resins. These protocols are long, irradiating, and difficult to implement in glove box. They produce a significant volume of liquid and solid waste. For instance, only one step of these analyzes currently generates often one hundred milliliters of radioactive effluents which must then be treated.

High-speed methods dedicated to elemental or isotopic analysis of the nuclear domain, consuming only a very small amount of solvent, which can be automated and targeting the desired compounds, must therefore be developed to enable the acquisition of increasingly reliable data at a lower cost. Then, the aim of this PhD work was to propose an innovative alternative to the use of solid-phase extraction columns in radionuclides separation protocols in concentrated nitric medium allowing:

- to reduce waste at the end of the analytical cycle,
- to reduce the implemented radioactivity during the analysis,
- to increase the speed of the analyses,
- an automation to reduce the costs,

while the quality of the separation is maintained.

The development of radiochemical separations at the micrometric scale is part of this approach. The miniaturization of the analytical procedures in the nuclear field is a way forward to reduce both risk and nuisances related to radioactive samples, which are direct functions of involved quantities of samples. The major advantage of the miniaturization is the significant reduction of volume (or quantity) of samples, reagents and waste as well as time of analysis. Microsystems are strong parallel processing tools and present a noteworthy ability to automation. The transfer of solid-phase extraction onto microfluidic format could have been addressed as a simple and direct miniaturization challenge by packing of conventional particles in a trapping zone in microchannel using weirs.

However, two major issues may arise from the packing technology: reproducibility of the packing process and particle immobilization.

Therefore, a second option, inspired from biologic developments, based on the use of photopolymerized monoliths as stationary phases in miniaturized format was chosen. The synthesis of monoliths can easily be conducted *in-situ* and the resulting continuous bed exhibits a bimodal structure with large through-pores for flow and small pores for retention of the analytes. The design of such a system initially required the definition of a specification taking into account the requirements imposed by actinide chemistry in nitric medium but also by technological constraints:

1. ease of microfabrication of the microsystem,
2. compatibility of the constituent material of the microsystem with the integration of the stationary phase and its functionalization,
3. ease and robustness of the integration and functionalization of the stationary phase in microsystem,
4. use of mobile phases of nitric acid several times molar,
5. chemical stability in a concentrated nitric medium (up to $[\text{HNO}_3] = 8 \text{ mol.L}^{-1}$) and mechanical resistance to pressure,
6. versatility of functionalization for adaptation to various separations,
7. high exchange capacity (samples with high concentrations).

A state of the art has been drawn up in order to identify the solutions that best meet these specificities. The requirements 1), 2) and 4) have oriented the choice of the cyclic olefin copolymer as material for the fabrication of the microsystem. The choice to synthesize a porous poly(ethylene glycol methacrylate - co-allyl methacrylate) monolith was led by 3), 4) and 5). Once selected the nature of the stationary phase, the strategy adopted was to develop a "generic" one which can be functionalized with a large variety of extractants and *in-situ* synthesized in the microsystem in order to ease the production of versatile micro-columns.

The PhD work focused on four axes:

- I. the fabrication of the microsystem in COC and the modification of the microchannels internal surface characteristics to be compatible with the anchorage of the monolith,
- II. the development of a customizable generic stationary phase in acrylate copolymer,
- III. the development of a versatile functionalization methodology in microsystem,
- IV. the demonstration of the feasibility of a separation.

Before the implementation of the stationary monolithic phase in the microsystem, a new method of *in situ* modification of the COC microfluidic channel was implemented. Indeed, the monolith needs to be firmly anchored at the surface of the wall to avoid any leaks of the mobile phase. Leaks could lead to the deformation of the separation profile and avoid the separation of the species. One of the challenges was to anchor on a COC surface because COC was first chosen because of its low reactivity with chemicals to not interact with mobile phase. The anchoring method was developed following an experimental design and the functionalization of the surface was checked by contact angle measurement. The advantage of the method is the use of the same reagent as compounds of the monolith. It prevents any unexpected interactions between the COC channel modification and the

synthesized monolith. The international deposited patent confirms the innovative aspect of the developed method [1].

Since the optimization of a new morphology of monolith is empirical and time consuming, a design experiment was realized to establish a relation between the experimental conditions and globules area and permeability. The chemometric approach is often used for the optimization of molecularly imprinted polymers, but it is very unusual for other organic polymers. The stationary phase is a monolithic organic phase polymethacrylate. The *in situ* synthesis was optimized by use of a mixture design that resulted in a predictive model (correlation coefficient of $R^2_{\text{adjusted}} = 0.96$). The morphology of the monolith checked by scanning electron microscopy and Hg porosity measurements allowed to determine the permeability of the material thanks to the Katz and Thomson model. This reasoned approach provided the synthesis of a stationary phase with specific adjustable nodules diameter and permeability area. This was verified for three diameter values of the nodules (1, 1.5 and 2 μm). The study of the stationary phase at different scales has revealed an influence of the dimensions of the microchannel on the diameter of the nodules, in particular the width of the microchannel and the diameter of the nodules are linked by a 2nd order polynomial relation. Thanks to the model resulting from the mixture design and to this polynomial relation, it is possible to synthesize a monolith with an adjustable structure in a microsystem [2, 3, 4, and 5].

At that point, a customizable generic stationary phase was synthesizable. The development of the functionalization method could be started. In order to be able to adapt the functionalization to the separation of interest, the versatile method of impregnation was chosen. At macroscopic scale, impregnation of inert particulate resin is a common way to functionalize stationary phases used for separation or pre-concentration of chemical elements. Unfortunately, this protocol is not compatible with an implementation in microsystem because of contraction of monolith in dry environment and difficulties to dry the whole stationary phase in the channel. Wet impregnation protocols were then developed for elemental separation purposes. In all cases the molecule of interest was dissolved in an organic solvent but experiments carried out during the PhD showed that this step avoids any extractant fixation because it is eluted through the washing aqueous mobile phase. Wet impregnation was tested to functionalize the monolith in microsystem by tributyl phosphate (TBP) without the drying step but no extractant was found on the monolith surface.

Then, an innovative impregnation methodology was developed in microsystem for the polymethacrylate monolith [6]. The feasibility was first demonstrated with tributyl phosphate (TBP), a model extractant of the fuel cycle, then for two additional extractants of interest in the nuclear field (the diamyl amylophosphonate (DAAP) and a TBP/ CMPO mixture). The effective impregnation of the stationary phase was checked by Fourier transform infrared spectroscopy with attenuated total reflectance measurements. The functionalization is both adaptable and robust 24 h in $[\text{HNO}_3] = 8 \text{ M}$. The exchange capacities obtained are of the order of 150 mgU / g of monolith for TBP and up to 280 mgU / g of monolith for the DAAP in microsystem. In each case, the exchange capacity values are almost twice as high as those of the commercial equivalent chromatographic extraction columns.

To establish separation protocols of radionuclides by solid phase extraction in microsystems, affinity of the microcolumn for radionuclides was determined for each acidity. The values of the partition coefficients of the impregnated monoliths were determined for U(VI), Th(IV), Eu(III) and Nd(III) for the 3 extractants (as well as for Pu (IV) in the case of impregnated monoliths by TBP) and compared

with commercial equivalent chromatographic extraction columns in the concentration range of 0 to 8 M nitric acid. The realization of the impregnation at different scales has once again shown the influence of the dimensions of the microchannel on the exchange capacity. It seems that miniaturization improves the impregnation. Then, knowing the adsorption behavior of radionuclides in nitric acid, the choice of the conditioning, loading and eluting phases was achieved. The separation of U(VI), Th(IV) and Eu(III) was then carried out using only nitric acid at different concentrations as mobile phases.

The reduction of the quantities of radioactive samples (tens of mL) needed for the analysis of radionuclides is a major objective. In this context, an innovative alternative to the use of solid-phase extraction columns in radionuclides separation protocols in concentrated nitric medium was proposed and realized. Two prototype microsystems, functionalized by TBP, were developed and tested to separate the elements Eu, Th, and U in concentrated nitric acid medium (0.1-5 M) :

- a microsystem can be used in conjunction with a measurement technique (column volume = 36 μL),
- a centrifugal microsystem is adapted to the parallelization and automation of separations on a platform of the lab-on-a-disk type (column volume = 12.5 μL).

This innovative development shows performance comparable to those of conventional methods of separation on resin with a reduction of the samples volume by a factor up to 300 while the quality of the separation is maintained. The ability of the polymer to resist to concentrated nitric acid, a corrosive medium but necessary to keep the radionuclides in solution, is no more a technological lock. Moreover, in order to adjust the microcolumn to other separations of interests, both the stationary phase and the functionalization are customizable.

This study constitutes an original development issued from the union of analytical chemistry, radiochemistry, microfluidics and inspired by “omics” technologies. The overall development of the stationary phase as described in the microsystem has been enhanced by the publication of 2 international patents [1, 6], 5 peer-reviewed papers [2, 3, 4, 5 and 7] and 2 presentations at an international level. The PhD work was highlighted in 2108 by the Jean Bourgeois award attributed by the French Society of Nuclear Energy (SFEN).

This PhD work was carried out at the Laboratory of Analytical, nuclear, isotopic and elemental separations (LANIE) of CEA Saclay in partnership with the MMBM team (Macromolecules and Microsystems in Biology and Medicine) of the Institut Curie at IPGG (Pierre-Gilles Institute of Gennes).

The PhD work showed interesting results that could have an impact in terms of effluents generation and integrated dose for the operators thanks to the lower volumes needed. The reduction of the volume by a factor 100 or 300 could be of great interest for industrial application in the laboratory. This is the reason why the developed system could be used at an industrial scale in nuclear laboratories in case of confirmation of the encouraging results of the PhD.

[1] WO2019008278A1 patent, January 2019, M. Losno, C. Mariet

[2] Losno, M. *et al* (2016), *Micromachines*, 7(3), 45.

- [3] Losno, M. *et al* (2016), *Procedia Chemistry*, 21, 446-452.
- [4] Losno, M. *et al* (2018), *Reactive and fonctionnal polymers*, 127, 48-54.
- [5] Losno, M. *et al* (2018), *Talanta*, 185, 586-591.
- [6] WO2018197789A1 patent, November 2018, M. Losno, C. Mariet, R. Brennetot
- [7] Mariet C., Losno M. *et al* (2019), *Micro an Nano Engineering*, 3, 7-14.