Misbehavior detection and efficient revocation within VANET

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Microfluidics devices applied to radionuclides separation in acidic media for the nuclear fuel cycle

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Abstract

Miniaturization of analytical devices provides new perspectives for safety improvement, intensification, and diversification of processes (reduction of matter shipment, reduction of stored materials, energy savings, reaction conditions that are inaccessible with macroscopic reactors...). This reduced scale satisfies most of the criteria of green analytical chemistry as well as the principle of minimization of hazards associated to radioactive samples, thanks to a major reduction of sample quantities, reactants, wastes, and analysis time, and to automation. An increasing number of specific microsystems or “labs-on-a-chip” have been developed with this ambition, particularly for radionuclides purification and separation steps, and for their analyses in complex and hard-to-handle samples. This article illustrates the development of microsystems for elemental separations in acidic media prior to isotopic or elemental measurements by mass spectrometry or a radiometric analysis method for nuclear-related activities, and underlines the main challenges to take up.

Keywords : solvent extraction ; extraction chromatography ; solid phase extraction ; monolith; functionalization

1. Introduction

The current nuclear reactor fuel consists of a mixture of oxides of uranium and plutonium or uranium oxide. After its stay in reactor, the fuel still contains a significant amount of valuable material which are interesting to recover. Moreover, the nuclear reactions that produced energy have also created other elements, fission products and minor actinides, which make the spent fuel highly radioactive. This is the reason for which the fuel is treated in order to separate material to recycle (uranium, plutonium) from other radioactive elements that constitute waste and condition waste in a safe and inert form. The hydrometallurgical recycling and the storage of the waste need conducting chemical

analyses of the solutions after nuclear fuel dissolution [1-3]. The precise and accurate chemical analysis of nuclear spent fuel (determination of the concentration levels of Uranium, Plutonium and some Fission Products) represents a critical part of materials control and accountancy and plays an essential role in designing future nuclear fuels cycle, reprocessing cycle, after dissolution, and throughout the process for environmental regulatory reasons or non-proliferation monitoring.

To obtain low uncertainties using Thermo-Ionization Mass Spectrometry (TIMS) or Multi-Collection Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS), mono-elemental samples are mandatory. Obtaining pure fractions of each radionuclides remains difficult because nuclear spent fuel samples exhibit an extreme chemical diversity stemming from several schemes of neutron capture, fissions or activation reactions that occur in reactors. This leads to the formation of the so-called transuranium radionuclides (Np, Pu, Am, Cm) as well as a wide variety of fission products constituted of Lanthanides (Nd, Sm, Eu, Gd), alkalines (Cs) and alkaline earth metals (Sr). Then, analysis of radionuclides is done according to operating protocols including the sequence of several separation/purification operations before performing the measurement by liquid scintillation, gamma spectrometry, X spectrometry or inductively coupled plasma mass spectrometry (ICP - MS) in order to remove interferences. Solid phase extraction (SPE) and liquid-liquid extraction (LLE) [4,5], performed in concentrated nitric or hydrochloric acid to form anionic and neutral complexes and stabilize oxidation degrees, pose a significant number of constraints specific to the sample (very irradiating which involves work in glove box, very corrosive), and the required precision. In addition, these separations are difficult to automate, involve the prolonged presence of an experimenter and generate large quantities of waste [6]. Methods dedicated to fast elementary or isotopic analyses, automated, consuming very little solvent, and targeting the desired compounds must be developed to acquire more numerous reliable data at a lower cost. The development of radiochemical separations in acidic media at the micrometric scale is part of the ALARA (As Low As Reasonably Achievable) approach for the reduction of waste and the handling of dangerous chemicals. The major interest of microsystems lies in their ability to integrate a series of operations on a small plate. Operations are faster and the same device brings together several identical processes in parallel. In addition, such a system takes in charge several steps without external intervention between the different stages. Thanks to micro-devices, the volumes of solvents and samples are reduced and operations are linked without human intervention, which limits the losses and contamination of samples.

If numerous microsystems have been developed and are already traded for medical diagnosis [7-9] or chemical synthesis [10, 11] since 2000, few studies deal with very acidic samples like nuclear spent fuels or leach solutions issued from metallurgical processes. Unlike typical microfluidic devices that perform under about neutral pH conditions for biological and environmental applications, devices for radiochemical separations must be chemically compatible with strong mineral acids, and must also contribute negligibly to the trace element analytical blank. Reviews on the use of microfluidic devices

have been published in several fields [12-18]. However, none have highlighted the use of microfluidic devices in very corrosive and complex media. Here, we have reviewed the state-of-the-art of microfluidic tools with a specific focus on the micro-devices used or designed for radionuclides separation in very acidic media.

2. Liquid-liquid extraction of radionuclides in acidic media

Very selective, liquid-liquid extraction is the preferred separation method of nuclear chemistry. Nuclear and pharmaceutical industries allowed its first industrial developments in the 1940s, then the oil and petrochemical industry in the 1955s-1965s. The real boom in the area of the hydrometallurgical allowing recovery of metals in various aqueous solutions (copper, uranium, gallium, rare earth, ...) happened in 1960 [19]. The solvent is made of thinner containing or not an extractant (organic molecule having an affinity for the element to be transferred). If the organic synthesis often uses the solvent extraction by spreading a species from one phase to the other by simple transfer [20, 21], in radiochemistry radioelement extraction is still implementing an extractant. In addition to the diffusion of the element there is a chemical reaction [22]. In this article, only liquid-liquid extraction has been considered.

Since its origins, to save natural resources and given the specific constraints related to radioactive and ionizing radiation, the nuclear industry prioritized raw material economy, recycling and minimization of the final waste, environmental footprint reduction and control of the risks of exposure for workers. This has led to the establishment of the recycling of the fuel, which allows to recover 96 % materials and a minimization of the production of final waste. Now, continuous improvement of these processes is intended to improve their efficiency to decrease the cost, quantities of waste and improving safety around several axes: i) the development of new extractants for selective extraction of uranium ores in order to reduce the environmental impact of mining; ii) the development of new solvents for recycling of fuel which will be more robust, more compact and more efficient; iii) the miniaturization of systems, on the one hand, for the screening of new extractants, obtaining thermodynamic and kinetic data, the optimization of the parameters (temperature, pH, concentrations) of extraction processes and, on the other hand for the analysis of effluents, waste, environmental samples...

Two types of miniaturized systems are identified in the literature regarding the liquid-liquid extraction of radionuclides. The so-called 'chaotic' reactors promote mixing of the phases [23, 24] and allow operation at counter-current of two immiscible phases [25]. By definition, the specific interfacial area of these systems is not known. Their dimensions are rather millimeter and flow rates are tens or even hundreds of mL.h⁻¹ and they found application in the design of process engineering.

Regarding lab on chips, they promote laminarity allowing accurate control of the specific interfacial area. Their dimensions are micrometer and flow rates are less than 10 mL.h^{-1} , which explains their applications are analysis and R & D. Liquid-liquid extraction microsystems provide many advantages such as large interfacial areas [26], short diffusion distance [26-28], high surface/volume ratio [29], process intensification [30] and possible integration of many operations stages on a single compact chip [31-33]. Solvent extraction in microchannels is a contact of two immiscible phases in a microchannel to promote the extraction of an element from one of the two phases towards the other. Only the case of the microsystems is treated in this article.

Two types of flows are implemented in microsystems: parallel flows and segmented flow (a phase is dispersed in the other) (Fig. 1).

Fig. 1. (a) Parallel flows (b) segmented flow.

2.1 Parallel flows

Used for the first time in 2000 for the liquid-liquid micro-extraction (μ -LLE) of iron from an aqueous phase by an ion exchanger in the organic phase by Tokeshi et al. [34], many works have been reported on μ -LLE of actinides, lanthanides or fission products in microsystem for analytical or industrial purposes. In most cases, μ -LLE studies have been carried out in glass microsystems with Y junctions implementing parallel flows because such flow configuration allows deported analysis by collection of the two phases separately and the use of corrosive solvents (Fig. 2).

Fig. 2. (a) Photography of a glass microsystem with Y-Y junctions purchased from IMT^R, the microchannel size: length $L = 8$ cm, width $w = 100$ μm , depth $h = 40$ μm . (b) Photography under the microscope of a biphasic system (organic / aqueous) laminar parallel flows in the microsystem.

From the point of view of radiochemical analysis, parallel flows are advantageous and liquid-liquid extraction coupling with stripping or detection techniques have become possible because the phases can be collected separately at the outlets of the microchannel. The specific interfacial area can reach 6000 m^{-1} [36], but cannot be changed for a given lab on a chip.

Originally, the purpose of the studies in parallel flows were first to show the feasibility of liquid-liquid extraction in microsystem and, second, to highlight the acceleration of the reaction related to the reduction of diffusion distances. This is the case of the studies on the solvent extraction of actinides U(VI), Am(III), and Pu(IV), respectively. Two-phase parallel flows μ -LLE was performed in Y junction glass microsystems for the extraction of uranyl from nitric acid by tributylphosphate (TBP) [37-40]. As of 2005, Hotokezaka et al. [37] performed the extraction of U(VI) diluted in $[\text{HNO}_3] = 3$ mol. L^{-1} by the TBP (pure or diluted to 30% (v/v) in the *n*-dodecane). A yield of 93.8% was reached in 1 second with the organic phase at 30% (v/v) of TBP, and only 0.7 second with pure TBP. The detection of the uranium in the aqueous phase was realized in-situ in the microchannel by thermal lens microscopy. Hellé et al. extracted U(VI) from hydrochloride acid with the anionic extractant tri-*n*-octylmethylammonium (Aliquat 336®) diluted in a *n*-dodecane / 1-decanol mixture [31, 41, 42]. The only study on the extraction of Am(III) from nitric acid by the *n*-octyl phenyl N,N - diisobutyl carbamoylmethyl phosphine oxide (CMPO) diluted in *n*-dodecane was conducted by Ban et al. [43]. They also used a commercial glass made microsystem with Y-junction but with an unbalanced channel profile to ensure parallel phases flow. The equilibrium was achieved within 10 seconds of contact between the 2 phases. Recently, extraction of Pu(IV) was studied by Yamamoto et al. [44] between nitric acid and a 30 % TBP in *n*-dodecane organic phase in stratified flows. These studies highlight that stratified flows solvent extractions in microsystems present the advantage to allow a precise control of the contact times of the two phases, especially short contact times, to lead to high speed and

high performance without any mechanical stirring, mixing or shaking. Moreover, recent technological breakthroughs allow to work with automated microsystems which can be used in parallel processing to increase the throughput or in multiplexed processing of separation/purification steps coupled to a detection system [45, 46]. To take advantage of a combination of micro-unit operations and multiphase flow network, liquid-liquid extraction of the uranium(VI) in HCl media by Aliquat® 336 coupling with stripping in the same microsystem was performed [31].

In the majority of the aforementioned studies, the detection was performed at the outlet of the microchannel by mass spectrometry on each phase recovered pure, so the interface was positioned at the center of the microchannel (Fig. 2-b). To set the interface position, the values of flow rates have to be adjusted considering viscosities values of the two immiscible phases [47]. During solvent extraction, the two phases viscosities are held constant because the extracted element is much less concentrated than the nitric acid or the extractant in the aqueous phase or in the organic phase, respectively. Then, when the radionuclide, is initially present at several tens of g.L^{-1} in the aqueous phase, viscosities values are modified during the extraction process [35] and a change of the position of the interface between the two phases can be expected. This could involve a decrease of the quality of the separation at the outlet of the microsystem [36]. Hence, in 2017, Jasmin et al. [32] studied the extraction of U(VI) present at several tens g.L^{-1} from the nitric acid to the organic one (30% v/v TBP) and showed the influence of the modification of the phases' viscosities on the flow regime. For nuclear or hydrometallurgical applications, this problem has to be considered.

2.2 Segmented flows

In addition to stratified flows, phases can be put in contact by establishing segmented flow in T or flow-focusing junctions (Fig. 3). With segmented flow, specific interfacial area close to 11000 m^{-1} [35, 48] can be obtained. The continuous phase is the organic one if the walls of the microchannel are hydrophobic and the aqueous one if the walls are hydrophilic. On a practical level, the constraint in these flows lies in the need to separate the phases of lab-on-chip output to achieve linkages or measures on each of the phases if the detection does not have a measure in situ.

Fig. 3. Schematic of (a) a T-junction and (b) a flow-focusing junction used to establish segmented flows. In white the continuous phase and in black the segmented phase.

The acquisition of kinetic data is of great interest in the screening of new extractants performed to improve the future fuel reprocessing [49, 50]. Most often, the determination of the chemical reaction coefficients is performed with macroscopic tools which can be classified into two categories: i) tools characterized by a high dispersion of phases, but for which the interfacial area is unknown; ii) tools with controlled interfacial area for which the turbulence and dispersion are weak. Among them, a distinction can be made between tools in which the two immiscible phases are continuous (Lewis cell [51], Nitsch cell [52], rotating diffusion [53] and those in which one phase is dispersed and the other continuous (single drop technique) [54]). These tools have disadvantages. First, they necessitate a significant consumption of reagents that can be costly, the interfacial area is sometimes poorly controlled, and most often cannot be adjusted. The development of a fast and accurate new kinetic data acquisition methodology is an important issue. In order to be effective, the device used must have three key properties: (1) constant and well known specific interfacial area; (2) fast mixing of the two immiscible liquid phases, in order to operate in the kinetic regime, as opposed to the diffusion regime; (3) rapid and high-purity phase settling and separation [55].

In this context segmented flows in microsystems are new tools for kinetics studies [56]. Specific interfacial area can be modulated by changing flow conditions (droplet size can be adjusted [57-59]) and mass transfer is controlled mainly by the movements of internal forced convection to go out in movement. This impacts the mass transfer. Indeed, in microchannels, the velocity field inside the moving drop is not uniform and the renewal of the reagents at the interface is improved [48, 60-66]. Therefore, mass transfer is favored. This is the background for the recent studies of radionuclides extraction in segmented flows. For instance, segmented flows were implemented in Teflon capillaries for the extraction of uranyl from nitric media by Darekar et al. [67, 68] and Tsaoulidis and al. [65,66]. Extraction of U(VI) by TBP in segmented flow nitric media was studied by Tsaoulidis et al. [65, 66] who diluted TBP to 30% (v/v) in ionic liquids, the organic phase being the continuous one. The influence of the residence time on the mass transfer for fixed flow rates was highlighted. Extraction of U(VI) increases with the time of residence. For an aqueous phase such as $[\text{HNO}_3] = 3 \text{ mol.L}^{-1}$, extraction reaches its equilibrium value of 91% in just 14 seconds (compared with 20 minutes in batch). Thereafter, Darekar, et al. [67, 68] studied the influence of the residence time of the drops on the transfer of material.

Nichols et al. [55] determined mass flow rates of 13 lanthanides and yttrium using a Teflon capillary to generate a segmented flow between an aqueous phase (diethylenetriaminepenta acetic acid and ammonium citrate) and an organic phase containing the extractant acid di-(2-ethylhexyl)phosphoric (HDEHP). A system that mimics the TRUEX (TRansUranium EXtraction) [69] liquid-liquid extraction process was studied in a flow-focusing junction by Nemer et al. [70]. The extraction of neodymium (Nd^{3+}) from aqueous droplets to dodecane using the complexant thenoyltrifluoroacetone

(HTTA) and ligand TBP was chosen as a mass-transfer system model. Parameters including diffusion and distribution coefficients were obtained to better understand the contactor behavior.

Nirvik et al. [68] performed extraction and stripping in a combined microsystem. μ -LLE experiments were carried out in a T-junction serpentine microchannel and a split-and-recombine microchannel with TBP-nitric acid system. Stripping experiments were carried out in the T-junction serpentine microchannel. The effects of residence time and the organic/aqueous ratio on overall volumetric mass-transfer coefficients were discussed. Flow patterns in microchannels were observed to have more insight into experimental trends. For the same average velocity, the split-and-recombine microchannel was found to give higher overall volumetric mass-transfer coefficients. Overall volumetric mass-transfer coefficients observed for the two microchannels were compared with overall volumetric mass-transfer coefficients reported for conventional extractors.

The extraction of Eu(III) from nitric acid solutions was studied using anionic liquid solution ([CMPO] = 0.2 M–[TBP] = 1.2 M) /1-butyl-3-methylimidazoliumbis[(trifluoromethyl)sulfonyl] amide; ([C4min][NTf₂]) as the extraction phase [71]. The investigations were carried out with the aqueous solution as the dispersed phase. The interfacial area in plug flow and the velocity profiles within the plugs, distribution and mass transfer coefficients were studied.

2.3 Conclusion on solvent extraction in microsystems

As shown with the study of the bibliography (Table 1), in most cases μ -LLE developments have been carried out in glass microsystems with Y junctions implementing parallel flows because such flow configuration allows deported analysis by collection of the two phases separately [26, 76, 77]. However micro-droplets exhibit several properties that justify the use of these systems in research over classical macroscale reactors or miniaturized continuous flow microfluidic systems. Indeed, with segmented flow, recirculation of the compounds within the plugs of the dispersed phase and slugs of the continuous phase is responsible for a huge improvement in the global mass transfer [60]. The transport of the compounds within their respective phases is operated both by diffusion and advection. So, segmented flows may be used to retrieve or acquire kinetic data for various extracting molecules.

Table 1 : Synthesis of the literature review of extraction of nuclear systems studied in microsystems

Extracted analyte	Parallel flows	Segmented flow	
		Organic continuous phase	Aqueous continuous phase

U(VI) in nitric acid extracted by TBP	[37, 67, 68]	[65-67]	[68]
U(VI) in hydrochloric acid extracted by Aliquat 336	[42]		
Am(III) in nitric acid extracted by CMPO	[43]		
Pu(IV) in nitric acid extracted by TBP	[44]		
Nd	[48, 72]	[70]	
Tm, Gd, Dy, Y par le PC-88A	[33, 73, 74]		
Eu in nitric acid extracted by DMDBTDMA	[31, 41, 42]		
Eu in nitric acid extracted by CMPO		[71]	
Lanthanides and Am stripping		[55, 75]	

3. Solid phase extraction (SPE)

Liquid chromatography for the separation of elements is currently used in radiochemistry for elemental and isotopic analyses protocols. The protocols on extraction chromatographic resins are widely implemented on radioactive samples for purified actinides or others elements like lanthanides [78-83]. Common methods for actinide matrix removal use chromatographic resin beds that are several milliliters in volume. The difficulty of the miniaturization of solid phase extraction in microsystem lies in the integration of the stationary phase in microchannel. Indeed, the stationary phase should allow the retention of the solutes, presenting a maximum exchange capacity and, often, be resistant to concentrated acids used in radiochemistry. Moreover, a sufficient resolution to obtained purified fraction of each radionuclide is needed. For radiochemical application in acidic media, two routes were considered: filling of the microchannels by particles [62] or a stationary phase synthesized in - situ [6, 84, 85].

3.1 Particulate stationary phase in microchannel

Two companies have addressed the manufacture of chromatographic microsystems as a simple scale-down technology transfer, from the usual chromatographic columns (inner diameter of 4.6 mm) to microchannels of hundreds of microns or less, integrating particulate stationary phases. Agilent Technologies has developed a "top-down" approach by integrating the injection loop and the separation column into a microsystem in polyimide [86]. This device helped to significantly improve the robustness of the instrumentation, its ease of use and the reduction of the risk of leaks. In terms of performance, the integration of part of the injector in the microsystem minimizes external dispersion phenomena and improves separation [86, 87]. Eksigent society has adopted the same approach for its chip [88]. However, these two commercial chips found application in the field of biology.

To the best of our knowledge, to date, no commercial microsystem dedicated to the separation of metals or radionuclides has been developed and only one study implementing particulate stationary phase in microchannel was reported. Gao et al. [89] designed 100- μL and 20- μL solid-phase separation columns in microfluidic devices built in thermoplastic polyvinyl chloride (PVC, Fig. 4). The microcolumns, packed by centrifugation with specific resins, provide efficient actinide matrix removal from trace element impurities. Commercially-available anion exchange and chromatographic resins were chosen to separate traces impurities from concentrated thorium or uranium matrices in strong nitric acid solutions, while trace impurities passed through quantitatively for analysis by inductively coupled plasma - optical emission spectroscopy (ICP-OES). Actinides were subsequently recovered using dilute hydrochloric acid solution. The filling of the micro-columns was performed with the open system and phases particulate were held in place thanks to the presence of sintered at both ends of microcolonnes. Flow rates ranged from 20 to 100 $\mu\text{L}.\text{min}^{-1}$.

Fig. 4. Assembled 20- μL solid-phase extraction microfluidic device, filled with AG MP-1 resin (column 1) and UTEVA resin (column 2). Scale is illustrated using a US dime coin (17.9 mm diameter) [89].

3.2 Monolithic stationary phase synthesized in-situ in microchannel

Monolithic stationary phases in chromatography and electrochromatography emerged in the early 1990s [90, 91]. These materials gained popularity because they are formed from a single piece of porous material that includes large flow through pores enabling separations at high flow rates achieved at low back pressures. Organic monoliths can be easily prepared within the confines of a microchannel (mold) by photo-initiated polymerization of a mixture of monomers (functional and crosslinker), porogenic solvents, and a free radical initiator. Organic monoliths combine a good mechanical resistance by covalent anchored to the walls of the microchannels, good control of porosity and permeability, and wide possibilities of chemical functions. Reviews [91-94] demonstrated that organic polymer-based monoliths for off-line SPE can be prepared in formats including the conventional syringe cartridges, pipette tips, stir bars, and spin columns. For on-line SPE, however, the in-tube or microchip formats are mandatory, and include nuts and ferrules for fitting the column to the analyzers and flow-through detectors. Then, monolithic columns for extraction of metal ions from environmental water and biological matrices (human hair, urine, and serum) were prepared by functionalizing the stationary phase with complexing functionalities [95].

The strong acidity of the mobile phases used in radiochemistry leads to the use of organic monoliths for their chemical resistance.

Inspired from the study of Lafleur et al. [96] who have elaborated a monolithic microcolumn inserted into a centrifuge microsystem for the separation and analysis of V, Pb, Cu and Co in water to drink, Bruchet et al. [6] developed an original design of microfluidic platform integrating four rectangular microchips made of thermoplastic (cyclo olefin copolymer COC). The microchips, dedicated to anion-exchange chromatographic separations, integrated a localized monolithic stationary phase as well as injection and collection reservoirs (Fig. 5). For a simplified simulated nuclear spent fuel sample composed of non-radioactive isotopes of Eu and U in usual proportion for Uranium Oxide nuclear spent fuel, analytical results were consistent with the conventional procedure (extraction yield for Europium of about 97 %). The use of the centrifugal microfluidic platform allowed to reduce the volume of liquid needed by a factor 250. Thanks to their unique “easy-to-use” features, centrifugal microfluidic platforms are potential successful candidates for the downscaling of chromatographic separation of radioactive samples (automation, multiplexing, easy integration in glove-boxes environment and low cost of maintenance). A quaternary ammonium was covalently bound to the monolith thanks a thermal reaction. However, the functionalization was not robust in nitric acid media and the functionalization procedure was suitable only for the grafting of tertiary or secondary amines.

Fig. 5. Design of the microchips: C1 ion-exchange column, C2 restriction channel, C3 vent channel, R1 injection reservoir, R2 collection reservoir and chromatographic connection, R3 vent and chromatographic connection, E1 entry port and E2 vent port of the injection reservoir. The centrifugal platform is presented in [6].

To take advantage of the versatility and robustness in nitric media of chromatographic microsystems filled with a stationary particle phase while having the quality of filling of microsystems with a monolithic stationary phase, Losno et al. [84, 85] developed a new porous poly(ethylene glycol methacrylate - co-allyl methacrylate) monolithic microcolumn. A new way of functionalization based on impregnation with extractants customized for radionuclides separation in nitric acid media was devised in a simple microsystem P1 and in a centrifugal microsystem. The versatility of the functionalization was demonstrated by the impregnation of TBP, CMPO and TBP mixture or diamylamyl phosphonate (DAAP). Distribution coefficients were determined in microsystems for Eu, Th, U, Pu in nitric acid from 0 to 8 mol.L⁻¹.

The separation of Eu, Th and U was performed in the simple microsystem functionalized with TBP with only 30 μ L of reagents compared to mL used in classical SPE with flow rates set at 2 μ L min⁻¹. Compared to the protocol carried out for classic SPE [97], there is a significant reduction in volumes handled (Table 2). The procedures of Gao et al. [89] is faster (about 30 minutes) than the one made on TBP impregnated monolith, but possible parallelization of separation in centrifugal microsystem allows to compensate for this difference.

Table 2 : Performance comparison of different SPE systems of radionuclides in acidic media

Separation	Separative	Column	Sample	Time	Media	Reference
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	column	volume (μL)	volume (μL)	(min)		
U /Pu / Am, Eu, Ce	Commercial column TBP/CMPO	2000	2500	90	HNO_3 , HCl and oxalic acid	[97]
Eu /Th, U	Microsystem P1 TBP	36	72	256	HNO_3	[85]
Eu /Th, U	Centrifugal microsystem TBP	2.75	5.5	90	HNO_3	[85]
Pu / transition metals, non metals	AG-MP1 et UTEVA TM Particulate stationary phase in microchannel	100	200	25	HNO_3 puis HCl	[89]
U / transition metals, non metals	UTEVA TM Particulate stationary phase in microchannel	20	20	28	HNO_3 puis HCl	[89]
U / Eu	Anionic exchanger centrifugal microsystem	2.5	5	65	HCl	[6]

Compared to the classic SPE, a microsystem of extraction chromatographic incorporating a monolithic stationary phase dimensioned based on the detection limit of the measurement technique allows to make separations with volumes samples less than 100 μL and at flow rates lower than 100 $\mu\text{L}.\text{min}^{-1}$. Thanks to this tool, much less effluent will be generated by analysis that demand continually believes and the cost of waste management in nuclear laboratories will be reduced.

4. Conclusion

In 2011, George M. Whitesides noted microfluidics, and the concept of the lab-on-a-chip, have had a spectacularly successful 15-year run of science and technology [98]. He asked “what comes next?” Henceforth, this review is indicative of the rise of the development of lab on chips dedicated to radiochemistry. In the nuclear field, chemical and physico-chemical analysis and screening of new extractant now consider environmental issues in the development of a technique or a method of analysis. At every stage of an analytical process, the questions focus on:

- the reduction of volumes of reagents, solvents and samples;
- the reduction of waste production;
- the reduction of the consumption of energy, water, gas...
- the increase of speed and accuracy of the analytical response.

To meet current and future needs, the preferred development areas relate to:

- i) the implementation of parallelizable and automatized sample preparation methods. Microfluidic tools already significantly reduce analytical effluent generated by the methods currently used in

laboratories. However, their parallelism and their automation must still be subject to developments requiring the collaboration of chemists, control engineers, programmers.

(iii) the development of MicroTAS (miniaturized total analytical system). In radiochemistry, developed microsystems are coupled to spectrometers of laboratories for elemental or isotopic analyses. Now, the effort should focus on integration of the measure directly in the lab on a chip. It will lead to a drastic decrease of the volumes of samples and reagents.

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