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Microfluidic tools for the liquid-liquid extraction of radionuclides in analytical procedures

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Abstract

The analyses of radionuclides are in great demand and a cost effective technique for the separation of analytes is required. A micro-scale reactor composed of microchannels fabricated in a microchip was chosen to investigate liquid-liquid extraction reactions driven by three different families of metal extractants: neutral, acidic and ion-pair extractants. The extraction conditions in the microfluidic device were considered. These investigations demonstrated that the conventional methodology used for solvent extraction in macro-scale reactors is not directly transposable to micro liquid-liquid extraction systems. However, it is expected that the understanding of the chemical and physical phenomena involved in a reference extraction systems studied in a given selected lab-on-chip will lead us to develop and validate a methodology suitable to miniaturized reactors.

Keywords: Microchannel chip ; Solvent extraction ; Separation ; Radionuclide ; Lab-on-chip

1. Introduction

The analysis of radionuclides present in high and medium level radioactive wastes is carried out according to operating protocols including many separation/purification steps. These steps, essential to obtain a pure fraction containing the radionuclides of interest, are based on the chromatography techniques, liquid-liquid extraction and precipitation/dissolution. Nevertheless, such an analytical procedure is long, complex and difficult to implement

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in hot cells or glove boxes. Indeed these analyses entail both chemical and radiological risks so that the use of solvents must be reduced inducing a modification of the operating procedures.

2. Miniaturization and liquid-liquid extraction

2.1. Contribution of the microfluidics

In the frame of studies aiming to improve these protocols, the microfluidic tools have their own place: they enable to reduce both the volumes of the samples and of the solvents, the analysis time and the operators' exposure time [1]. The feature of microfluidic tools is to group together the different steps which are necessary for the analysis of a sample or for the production of a compound since they combine the functions of injection, purification, pre-concentration, separation, reaction and detection [2]. The integration of these different components on a single chip gives rise to the concepts of µ-TAS (micro Total Analysis System) and then of lab-on-chip. Nevertheless, while lab-on-chips are widely used in biochemistry and medical care diagnostics, their use in the nuclear field is still at its beginning. 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 the detection system [3]. Like biochemistry and medical care diagnostics, radioanalytical chemistry could take advantage of all these characteristics.

2.2. Interests of the µ-liquid-liquid extraction

Most of analytical microsystems involve chromatographic separation, only few ones concern liquid-liquid extraction. If liquid-liquid extraction presents some drawbacks in macro-scale, the technique applied in microsystem shows new features which make it competitive with liquid chromatography. Thanks to miniaturization, coupling liquid-liquid extraction with detection system and with a stripping step is now allowed [4]. On the other hand, in lab-on-chip, specific interfacial area, that is the surface-to-volume ratio, is increased, known and reproducible since it is determined by the geometry of the extraction channel [5]. This is a great advantage with respect to the conventional systems (ARMOLLEX cells, short-time phase contacting cells…).

3. Implementation of the µ-LLE in the nuclear field

3.1. Objectives of the study

This study has two main objectives. The first one deals with the fundamental aspects. Indeed, the microfluidics must allow to exacerbate the interfacial phenomena that makes it a tool of choice to study the interfacial dynamics during the liquid-liquid extraction. The lab-on-chip used in this fundamental part and the methodology developed will be applied to achieve the second objective. The latter consists in analyzing radioactive solutions and thus in separating the radionuclides by liquid-liquid extraction by taking the best advantage of the specificities related to the miniaturization (high specific area, short diffusion path, decrease of volumes and so reduction of chemical and radiological risks…).

3.2. Choice of the microsystem

The liquid-liquid extraction in microsystem with a co-current flow in the case of the analysis of solutions coming from the nuclear field is, currently, practically exclusively studied by the Department of Applied Chemistry of the University of Tokyo [6]. Nevertheless, their developments are about different chemical systems studied in various designs of microsystems. In fact, the chemical systems studied are varied regarding to the

different extractants (tributylphosphate (TBP), carbamoyl phosphine oxide (CMPO)…), the different diluents (n-dodecane, heptane, xylene…) and the different analytes (rare earths, transition metals…) used. In the same way, the design of the microsystems is varied. The shape of the microsystem (H, Y-Y…) varies as well as the geometry of the channels: rectangular or cylindrical section, presence or not of a guide structure, microchannels dimensions (length, width and depth), asymmetry or not… Therefore, it is difficult to compare the performances of different microsystems for a unique chemical extraction system and conversely, to highlight the specific behavior of diverse chemical extraction systems in the same microsystem. Moreover, from a fundamental point of view, only few works have been carried out, today, in order to characterize the relative contributions to the mass transfer of the analytes of diffusion and of the chemical reactions kinetics. That is the reason why we have chosen to study different chemical systems in a given microsystem.

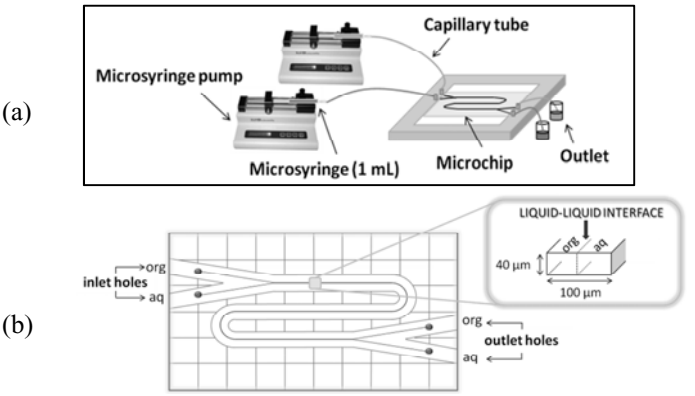

Fig. 1. (a) An experimental setup for extraction experiment; (b) A schematic illustration of glass microchannel chip with a focus on a part of the microchannel

The apparatus used is shown in Fig 1. The microsystem has a double-Y shape, is constituted of a symmetric extraction channel and does not present a guide structure. This microchannel has an extraction length of 8 cm, a width of 100 µm and a depth of 40 µm. The aqueous and organic solutions in microsyringes are pushed out at a fixed flow rate using microsyringe pumps (KDScientific). To ensure that no leak occurs at the inlets and at the outlets of the microchannels, we chose a tried and tested glass microsystem manufactured and commercialized by the Institute of Microchemical Technology (IMT, Japan). This criterion is fundamental in the frame of the analysis of radioactive solutions. The choice of the material has been realized in the same way. Indeed, this material must be resistant to the solvents (dodecane for instance) as well as to the acids (highly concentrated nitric and hydrochloric acid solutions) used during the radiochemical separations.

3.3. Choice of the chemical systems

In this microsystem, we propose to study liquid-liquid extraction of Eu for three chemical systems corresponding to the three main extractants families: neutral, acidic and ion-pair extractants. In this way, it will be possible to highlight the chemical behavior differences in the microsystem of reference and thus to exacerbate their features.

3.3.1. Neutral extractants

Malonamides, diglycolamides and some organophosphorus extractants belong to this category. Regarding the latter, only rare data are available because either no kinetic problems were encountered or the extractants was developed too recently. However, the dimethyl-N1,N3-dibutyl-2-tetradecyl malonamide (DMDBTDMA) has

been the subject, at the macro-scale, of numerous studies, mainly thermodynamic in nature but some kinetic studies are also available in the literature up to date. Thus, Toulemonde [7] and Dal Don [8] have measured kinetic constants for the extraction of U, Am, and lanthanides by the DMDBTDMA in n-dodecane with a constant interfacial area cell (ARMOLLEX cell). Thus, the chemical system constituted by the DMDBTDMA in n-dodecane was chosen like the reference system to validate the microfluidic tool in comparison with the results obtained in the ARMOLLEX apparatus.

3.3.2. Acidic extractants

The di-2-ethylhexylphosphoric acid (HDEHP) is one of the most studied reagent among the acidic extractants. The interest for this compound lies in its use in the TALSPEAK process (diluted in dodecane) for the separation trivalent actinides/trivalent lanthanides [9]. There are some kinetic studies for the mass transfer carried out with the HDEHP regarding the extraction of Zn, Ni, Co as well as rare earths and transplutonium elements. For these reasons, we propose to keep the HDEHP as an acidic extractant model.

3.3.3. Ion-pair extractants

The molecules often used in hydrometallurgy for the implementation of a liquid-liquid extraction reaction by formation of ions pairs are the protonated trioctylamine (contained in Alamine 336), the methyl-trioctylammonium chloride (contained in Aliquat 336) and the 2-oxo-1-phenylhydrazinolate of ammonium more commonly named Cupferron. Though the literature is abundant regarding the extraction of U and rare earths for this family, we do not have found study on the extraction kinetics apart from the one of the chromium, probably because the extraction kinetics are fast and thus do not cause any problem in analysis. So we have chosen the system Aliquat 336 in dodecane.

3.4. Methodology of the study

Firstly, it will be necessary to develop and validate a methodology in the selected microsystem. We will compare the results obtained for the chemical system Eu/DMDBTDMA/dodecane in macro-scale and in lab-on-chip. Once the microfluidic tool is validated for this reference from the thermodynamic and kinetic points of view, the study of the interface will be investigated *via* different techniques (physico-chemical characterization, addition of surfactants, variation of the interfacial area…).. Through the miniaturization, we wish to render preponderant interface reactions with respect to volume reactions and thus to determine the precise role of the interface in the extraction process.

The same methodology will be applied for the kinetic study involving acidic and ion-pair extractants.

3.5. Choice of the flow type

There are numerous types of flow in microsystem with different features: dispersed flow and continuous counter-current or co-current flows (Fig 2.). In the dispersed flows, a phase is dispersed into another (organic in aqueous or vice-versa) which leads to the formation of droplets or slugs [10]. These flows have a high specific interfacial area favoring a faster extraction but some practical difficulties exist. The first one lies in the separation of the two phases after extraction. Indeed, this separation necessitates an additional step, in batch, which therefore cancels the benefit of the liquid-liquid extraction in microsystem. Secondly, the precise determination of the specific interfacial area is difficult in the case of droplets or slugs. Another drawback of this kind of flow is the complexity of modeling the extraction kinetics with respect to a system where the flows would be parallel and continuous.

The parallel continuous flows are obtained in the case of co-current and counter-current flows. The counter-current flow is scarcely used in microsystem for several reasons [11]. Firstly, the interface stability is difficult to maintain and necessitates a surface modification. This process should enable to render hydrophobic the part of the channel dedicated to the organic phase and thus to confine the aqueous and organic phases in the hydrophilic and hydrophobic parts of the channel, respectively. Moreover, the instability of the interface with counter-current flow leads to a limitation of the range of flow rates being able to be used even if a surface functionalization has been carried out. These drawbacks intrinsic to dispersed and counter-current flows lead us to choose co-current flow for performing µ-LLE.

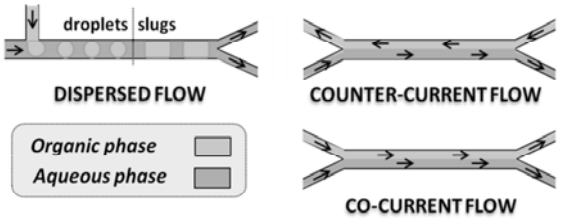

Fig. 2. Conceptual schemes of dispersed, counter-current and co-current flows in microfluidics

3.6. Choice of the hydrodynamic parameters

Although the hydrodynamic conditions influence the extraction efficiency, the reaction kinetics and the diffusion during the mass transfer, the choice of the most relevant hydrodynamic parameters stays difficult. The flow rates (or linear velocities), Reynolds number (often used in batch but very few in microsystems) or contact times of the two phases are typical parameters used in the literature.

The study of the extraction efficiency, of the analyte concentration or of the distribution ratio as a function of the flow rates of both aqueous and organic phases presents some difficulties in microsystem. Because the viscosity is a predominant force at the micrometric scale, it is impossible to change a composition of a phase without changing the viscosity and then the flow rate. Also, this involves a modification of the position of the interface in the microchannel.

The second hydrodynamic parameter used, widespread, is the contact time between the two phases during the extraction in microsystem. The simplest expression of this contact time is given by Ooe et al. and is deduced from the total volume of the extraction channel and the faster flow rate used [12]. Nevertheless, Ban et al. propose another method to calculate the contact time and they express it with the following relation [13]:

$$t_o = \frac{w_o * d_o * l}{f_o}$$

where w_o, d_o, l refer to the width, the depth and the length of the extraction channel and f_o denotes the flow rate of the organic phase. This expression of the contact time takes into account the flow rates used and the specific width of the phase considered which depends itself of the flow rates and of the viscosities of the two phases. Thus, it seems that this calculation method of the contact time is the most adapted to the micrometric scale.

Aware of these experimental specificities of the study, we have chosen to fix the viscosities by the imposed concentrations of the solutions whereas the flow rates will be chosen in order to keep constant the position of the interface. For this, the flow rate of the organic phase will be adapted to obtain the height of the interface previously chosen while the aqueous flow rate will be fixed since this phase is impoverished (during the extraction) and its properties vary little.

4. Conclusion

The nuclear field needs to miniaturize its analytical systems in order to improve their performances while reducing the chemical and radiological risks. Among the systems to improve, the liquid-liquid extraction presents significant advantages to be used at the miniaturized scale. Before the achievement of the optimization of the analyses by liquid-liquid extraction in microsystem, it is necessary to understand the interfacial dynamics and the reaction kinetics for different chemical systems in a reference microsystem. For this, the continuous co-current flow has been chosen and the hydrodynamic parameter selected is the contact time between the two phases. When these kinetic and interfacial studies will be carried out, the optimization of the analyses will be possible and it will be interesting to compare the experimental results with those obtained by molecular dynamics.

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