



## Design of experiments as tools to tailor impregnated polymers specific for radionuclides separation in microsystems



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### ABSTRACT

An experimental design is described for optimization of the microscopic morphology of a methacrylate monolith that was elaborated for chromatographic separation of radionuclides in nitric acid media. This paper presents a systematic study of the synthesis of the polymeric porous monolith poly(ethylene glycol dimethacrylate-co-allyl methacrylate) used as solid-phase support and a post-functionalization of the monolith in microsystem with tributyl phosphate extractant. Polymerization time and chemical composition of the polymerizable mixture that comprises water, 1,4-butanediol, 1-propanol, monomers were chosen as the most relevant experimental factors of the photochemical process. Using the globules area as a significant response of an experimental design, the monolith morphology can be predicted. A new versatile and robust impregnation process was developed in microsystem. The designed micro chromatographic system showed a good resistance in concentrated nitric acid and a great loading capacity compared to commercially available solution (150 mg U versus 75 mgU/g resin).

### 1. Introduction

Growing public health and safety concerns over the use of nuclear technology have made reliable methods for determination of various actinide elements in environmental, biological or nuclear spent fuel samples increasingly important. An essential feature of all of these analytical methods is the preconcentration and purification of the actinides of interest [1], both to isolate them from the large amounts of inactive present substances and to isolate them from radionuclides which may interfere with subsequent measurement. Very often, preconcentration and purification are performed by extraction chromatography [1,2]. In this technique, the stationary phase is a particulate polymeric resin impregnated with an extractant developed for radiochemical separation in very strong acidic media [3,4]. However, these separations are time consuming, difficult to automate and require appropriate shielding level to reduce dose uptake for analyst such as remote handling in hot cells or extreme dilution.

In this context, miniaturization allowed by microfluidics appears to be a valuable alternative to standard procedures since microfluidic tools enable to reduce both volumes of sample and reagents [5–7], analysis time and operators' exposure time avoiding contamination and operator mistakes [8]. Recent technological breakthroughs allow to work with easy to use, disposable and automatable microsystems which can be used in parallel processing to increase the throughput or in multiplexed

processing of separation/purification steps coupled to detection system [9–11]. Nevertheless, while chromatographic lab-on-chips are widely used in biochemistry and medical care diagnostics, their use in the nuclear field has just begun [12,13].

Since their discovery, about two decades ago, monolithic columns have attracted much attention as separation media in chromatography of a large variety of analytes in microsystems or capillaries, including low molecular weight molecules [14–19], metals and radionuclides [12]. Compared with particulate resins used in microsystems [13,20], uniformity of bed with no end frits, higher permeability and ability to design the desired length of polymer are the main advantages of monolithic stationary phase [21]. Among the organic monoliths, methacrylates can be produced by in situ photopolymerization [22] and resistant in very acidic media [12]. Therefore, from several years, we developed a copolymer ethylene glycol dimethacrylate/allyl methacrylate (EDMA-co-AMA). In previous articles [23,24], the robustness of the EDMA-co-EDMA in nitric acid 8 M was demonstrated and a photochemical functionalization method was studied for a given structure in batch. In the present article our objective is to perform a robust polymer with adjustable structure in microsystem, functionalized using impregnation easier to apply than photochemical reaction. As the extractants can present a high viscosity, it is important to manage the structure of the monolith so that the extractant access to the pores of the monoliths. Then, a chemometric approach is proposed for

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optimization of polymerization in order to have a tailor-made control of the monolith morphology. A design experiment is used to optimize the design variable (%wt porogen, %wt monomer, irradiation time) in batch. First, the different polymers were characterized by their globules area and permeability in batch. Second, after the optimization, the transfer of the polymerization was transferred in microsystem and the influence of the structure on the loading capacity in microsystem was studied.

## 2. Materials and methods

### 2.1. Chemicals

Ethylene glycol dimethacrylate (97%, EDMA), allyl methacrylate (98%, AMA), 2,2-dimethoxy-2-phenylacetophenone (> 99%, DMPA), 1,4-butanediol (99%), 1-propanol (99.7%), benzophenone (> 99%, BP), tri-n-butyl phosphate (98%, TBP), methanol (HPLC-grade), ethanol (HPLC-grade) and HNO<sub>3</sub> 65 wt% were purchased from Sigma Aldrich (Isle-D'Abeau, France). Uranyl nitrate hexahydrate (analytical grade) was purchased from Merck (Fontenay sous bois, France). All aqueous solutions were prepared using > 18 MΩ DI water (Direct-Q UV3, Millipore). Microsystem was built with a 381 μm thick film of cyclo olefin copolymer (COC 6013 and COC 6013) pellets purchased from Topas (Polyplastics Co, Germany).

### 2.2. Polymerization procedure

EDMA-co-AMA polymers were prepared by photopolymerization in batch and in microsystems from a polymerization mixtures containing water, 1,4-butanediol, 1-propanol, EDMA, AMA, and DMPA. The amounts of 1,4-butanediol, 1-propanol, EDMA, AMA, were determined by the experimental design (Tables 1 and 2).

In batch, the polymerization mixtures were mixed, relieved of gas and photopolymerized with a procedure previously described [24]. A Bio-link BLX cross-linker (VWR International, Strasbourg, France) equipped with five 8W UV tubes emitting at 365 nm was used with a UVX-radiometer (Fisher Scientific, Lyon, France) equipped with a 365-nm sensor (1 cm<sup>2</sup>) to record the total UV-light energy supplied during each polymerization. The resulting monolith was then removed from the test beaker and thoroughly washed with methanol.

In microsystem, the microchannel was first functionalized by the benzophenone method described in literature [25,26]. Then, the monolith was synthesized in the microsystem with the same polymerization mixture as in batch but the microchannel was filled with the polymerization mixture at 1.2 mL·h<sup>-1</sup> during 15 min before UV exposition and 0.6 mL·h<sup>-1</sup> ethanol wash.

### 2.3. Monolith impregnation in microsystem

The microsystem was filled with pure TBP at 0.3 mL·h<sup>-1</sup> during 2 h and then rinsed 7 min with water at 1 mL·h<sup>-1</sup> thanks to a syringe pump KDS Model 100 Series (VWR International, Strasbourg, France).

### 2.4. Scanning electron microscopy (SEM) and pore size measurements

The SEM photographs were used to determine the area of globules.

**Table 1**  
Experimental domain for photopolymerization.

Fixed parameters	1 wt% of DMPA	Monomers/porogen ratio	wt% of 1-propanol
Variable factors	X <sub>1</sub> : wt% of porogen	X <sub>2</sub> : wt% of monomer	X <sub>3</sub> : irradiation time
Level min	0	0	0
Level max	+1	+1	+1

After coating with approximately 40 nm of gold by sputter coating (Cressington Sputter Coater 208 HR, Ted Pella Inc., U.S.) and evaporation (a modified Edwards E14 vacuum coating unit, Edwards High Vacuum, incorporating an automatic tilting and rotation device), microscopic analysis of all samples was carried out in a JEOL JSM 7000F Scanning Electron Microscope (Jeol, Croissy-sur-Seine, France). Final images were recorded for each sample at 1000, 5000, 10,000 times magnification.

### 2.5. Porosity measurements

Porosimetry was measured by mercury intrusion porosimetry (MIP) on an AutoPore IV 9500 Series (Micromeritics, Norcross, U.S.). The samples dried 24 h in the desiccator (fore-vacuum) are immersed in a bath of mercury vacuum. Mercury pressure P<sub>Hg</sub> is applied in increments and the volume of mercury penetrating into the pores is measured at each increment.

### 2.6. Permeability of porous monoliths

A value of permeability K<sub>0</sub> can be inferred from MIP analyses through the theory of Katz and Thompson [27,28] using Eq. (1).

$$K_0 = \varepsilon \frac{1}{89} \frac{D_h}{D_c} (D_h)^2 S(D) \quad (1)$$

With: ε the porosity; 1/89: an experimental coefficient; S(D): volumic fraction of the mercury available pores; D<sub>h</sub>: maximum diameter of hydraulic conductance function (m), D<sub>h</sub>, i.e. the pore diameter for which the fluid moves more easily in the sample; D<sub>c</sub>: the critical diameter of pores, i.e. the diameter for which mercury enters for the first time the sample.

### 2.7. Characterization of the impregnated porous monoliths

#### 2.7.1. Infrared measurements

Fourier-transformed infrared spectroscopy (FT-IR) characterization was carried out on Bruker Equinox 55S with a Golden GateTMSpecac spectrometer with a deuterated triglycerin sulfate detector. Air is measured as background signal. Spectrum was acquired between 5800 and 550 cm<sup>-1</sup> with a 2 cm<sup>-1</sup> resolution, 32 scans through OPUS software. Impregnated monolith was simply put on the germanium crystal without any preparation of the sample.

#### 2.7.2. Loading capacity measurements

Loading capacity of the monolith synthesized and impregnated with TBP measurements were performed directly in the microsystem. Uranyl (VI) was chosen as representative actinide for determination of the loading capacity. First, monolith was conditioned by a 3 M nitric acid solution during 5 min at a flow rate of 1 mL·h<sup>-1</sup>. Then a solution of 15,000 ppm Uranium in 3 M nitric acid was introduced at 0.15 mL·h<sup>-1</sup> during 2 h. The column was rinsed 30 min by 3 M nitric acid at 0.2 mL·h<sup>-1</sup> and remaining Uranium eluted by 0.5 M nitric acid during 1 h at a flow rate of 0.2 mL·h<sup>-1</sup>. All the fractions were analyzed via ICP-MS measurement (7700 × Agilent Technologies) and loading capacity was determined using Eq. (2).

$$C_L = \frac{m_U}{m_{\text{monolith}}} \quad (2)$$

where C<sub>L</sub> is the loading capacity (mg U/g of monolith), m<sub>U</sub> is the mass of uranium(VI) recovered from the elution step (mg) and m<sub>monolith</sub> is the monolith weight (g).

### 2.8. Statistical study

Data analysis of the experimental design was performed with Statistica© 10.0 software software form StatSoft (Tulsa, U.S.).

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