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Microsystems for Anion Exchange Separation of Radionuclides in
Nitric Acid Media

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Abstract

An efficient and reproducible photopolymerized poly(ethylene glycol methacrylate methacrylate-co- allyl methacrylate) monolith was synthesized and a photografting process based on the ene-thiol click-chemistry has been performed to give anion exchange properties to the monolith. Since their introduction in the early 1990s polymethacrylate monoliths have emerged as a powerful alternative for microscale separations or sample treatment. Their relatively simple implementation in columns with small internal diameters makes them particularly attractive for the new chromatographic challenges of complex matrices analysis and on-chip separations. Despite their relatively poor ion-exchange capacity due to their highly porous structure, their use as anion exchangers is of large interest for nuclear analysis as numerous separations are based on this process. This paper presents a systematic study of the synthesis of the polymeric porous monolith and the versatile and robust functionalization method developed for the specific strong acidic media used in radiochemical procedures. The robustness of the stationary phase was tested in concentrated nitric acid.

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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

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containing the radionuclides of interest, are based on chromatographic techniques, liquid-liquid extraction and precipitation/dissolution which are long, complex and difficult to implement in hot cells or glove boxes. 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 volumes of reagents, the analysis time and the operators' exposure time¹. 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 detection². 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 system³. Like biochemistry and medical care diagnostics, radioanalytical chemistry could take advantage of all these characteristics.

1. Ion exchange chromatography in the nuclear field and miniaturization

Extraction chromatographic materials like analytical grade ion exchange resins are commonly used for the sample preparation needs of the radiochemists and geochemists. These resins were developed at Argonne National Laboratory in the 1990s⁴. Since the complexation of the uranyl UO_2^{2+} by nitrate in concentrated HNO_3 leads to the formation of complexes of the form $[\text{UO}_2(\text{NO}_3)_x]^{(2-x)}$ ($1 \leq x \leq 3$), anion exchange chromatography is commonly used to separate uranium (VI) from other radionuclides [5-8]. Anionic complexes of U are formed in nitric acid for a concentration exceeding 4 mol.L^{-1} ⁵ whereas Eu(III) formed cationic complexes. Thus, the functionalization by an anion exchanger will enable the separation of the two components in $[\text{HNO}_3] > 4 \text{ mol.L}^{-1}$. In a first step U(VI) will be fixed in the stationary phase and the Eu(III) will be eluted. Then U(VI) will be eluted in diluted HNO_3 . Strong anion exchange resins used contain quaternary ammonium groups⁵⁻⁸. Numerous analytical microsystems involve electrochromatographic separation. The main advantage of this method is that the electroosmotic pumping gives birth to a flat flow profile that reduces the phenomenon of widening of bands, the separation is thus more efficient which is not negligible when decreasing the lengths of separation. Today, in the nuclear field, the bibliography mention no micro capillary electrochromatographic system designed for analysis of radioisotopes. Only Vio et al.⁶ have demonstrated the potential of the electrophoretic techniques for the miniaturized separation of lanthanide. However, this technique is not consistent with the use of the privileged concentrated nitric acid media used in radiochemistry. Although some examples of chromatographic separations of metals in microsystems were found in the literature¹⁰⁻¹³, very little was on the separation of radionuclides⁷. The potentialities of centrifugal microfluidic platforms for chromatographic anion-exchange separations was demonstrated in a previous work with high extraction yield for U and Eu⁷. However this separation was achieved in hydrochloric acid medium because the anion exchange monolithic stationary phase was not compatible with the concentrated nitric medium.

The aim here is to develop a new versatile functionalization method of a monolithic stationary phase compatible with concentrated nitric acid and that could be integrated in the microchannel of a cyclo olefin copolymer (COC) microsystem. The stationary phase has to present a high chemical stability and to be easily synthesized and functionalized in a microsystem. So, first, a photo-polymerized polymethacrylate monolith was developed. Second, a thiol-ene click-reaction chosen as versatile photo-functionalization method was selected. Then the robustness of the functionalized stationary phase was tested in $[\text{HNO}_3] \geq 5 \text{ mol.L}^{-1}$.

2. Materials and Methods

2.1. Materials

Ethylene glycol methacrylate (97%, EDMA), allyl methacrylate (98 %, AMA), 2,2-dimethoxy-2-phenylacetophenone (> 99 %, DMPA), 1,4-butanediol (99 %), 1-propanol (99,7 %), methanol (HPLC-grade), thiosalicylic acid (Fig. 1 (a)), (97 %), 2-phenylethanethiol (98 %) (Fig. 1 (b)), (11-mercaptoundecyl)-N,N,N-trimethylammonium (≥ 90 %, ammonium thiol) (Fig. 1 (c)), HNO_3 65 % (wt) were purchased from Sigma Aldrich (Isle-D'Abeau, France). All aqueous solutions were prepared using $>18 \text{ M}\Omega$ deionized water (Direct-Q UV3, Millipore).

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