## Surface functionalization with ionic liquids

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It is known that some pure hydrophobic ionic liquids can extract metallic species from aqueous solutions. The unique properties of such organic media allow polymerization techniques to convert a liquid organic phase to a solid one. A pyrrolidinium-based polymerized ionic liquid was used to test radioactive indium and thallium behavior by means of solid-liquid extraction. The results obtained allowed us to consider solid-gas extraction systems for extraction of the metals mentioned above. We used commercially available medical In-111 ( $T_{1/2} = 2.8 \text{ d}$ ) and Tl-201 ( $T_{1/2} = 3.0 \text{ d}$ ) radionuclides. First, a procedure to coat an inner surface of a round PTFE tube (250 mm length, 4 mm ID) with a solid polymerized layer was developed (Fig. 1). The polymerized ionic liquid was dissolved in acetone and solution obtained was transferred to the PTFE tube. The coating procedure requires a rotary evaporator application in order to remove the volatile solvent from the tube. Second, the polymerized ionic liquid in acetone was added into the PTFE tube filled with glass beads (either 0.5 or 1 mm diameter) to create a pseudo-monolithic column with open pores. The 0.5 mm column was used in experiments with aqueous solution. The solution with radioactive thallium in its +3 oxidation state was loaded into the column and eluted by means of a peristaltic pump. The extraction efficiency was estimated at a level of 50%.

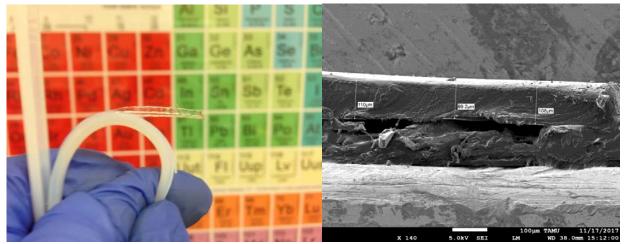
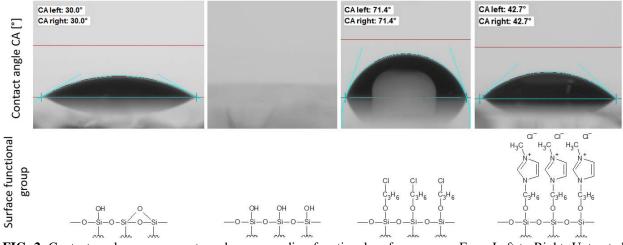


FIG. 1. (Left) The polymer inside the PTFE tube. (Right) SEM thickness measurement of the polymer layer.

In addition, a new step towards advanced Si surface functionalization techniques has been made. Previously developed methods to coat different surfaces with polymerized ionic liquids led to physisorption of the material of interest resulting in a relatively thick layer ( $\sim 6 \text{ mg/cm}^2$ ). A new chemisorption technique allows in principle to minimize the layer thickness and to retain chemically

active centers. The first step includes application of alkoxysilane to convert a hydrophilic glass slide surface to hydrophobic one. This chemical step has been substantially optimized and while literature data suggest to perform the silanization for several hours at elevated temperature, our procedure can result in a surface of interest in less than 30 min at room temperature. The functionalized surface quality has been checked by means of contact angle measurements, atomic force microscopy analysis and adsorption of radioactive thallium in its +3 oxidation state. The results obtained indicate that surface coating was uniform, the contact angle between a drop of pure water and a functionalized surface was in agreement with literature data [1] [2], i.e. the surface is hydrophobic now (Fig. 2). Hence, thallium adsorption dropped down by one order of magnitude. The consequent next step of this work is to attach ionic liquids to previously silanized surfaces.



**FIG. 2**. Contact angle measurements and corresponding functional surface groups. From Left to Right: Untreated surface; cleaned and activated surface; modification with chloro propyl groups; covalently grafted N-methylimidazolium.

- R. Gusain, S. Kokufu, P.S. Bakshi, T. Utsunomiya, T. Ichii, H. Sugimura, and O.P. Khatri, Applied Surface Science 364, 878 (2016).
- [2] D.K. Aswal, S. Lenfant, D. Guerin, J.V. Yakhmi, and D. Vuillaume, Analytica Chimica Acta 568, 84 (2006).