

PREPARATION OF METHACRYLATE POROUS MONOLITHS WITH OXIDIZED SINGLE-WALLED CARBON NANOHORNS INTO SPIN COLUMNS FOR THE EXTRACTION OF NONSTEROIDAL ANTI-INFLAMMATORY DRUGS FROM URINE SAMPLES

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Since the first synthesis of monolithic polymers at the end of the 20th century, organic monoliths derived from methacrylates, acrylamides, and styrenes have been successfully applied as stationary phases in chromatography,¹ and as sorbents in sample treatment techniques but to a lesser extent.² Monolithic solids have been used in different microextraction formats such as spin columns. Monolithic silica spin column was first introduced by Namera and Saito in 2008.³ The monolithic solid is packed in the bottom of the column unit without using frits, and then solvents are passed through the sorbent phase by centrifugation. Thus, it is one of the most advantageous formats due to its simple extraction procedure, and the need of low sample and eluate volumes.

Sample preparation has been the focus of intense research in order to improve the isolation and preconcentration steps of the analytical procedures. Current trends in this context involve the simplification and miniaturization of separation techniques in both solid and liquid phase formats. The success of these tendencies depends on the efficiency of the extracting medium. To achieve more specific interaction of the analytes with the polymeric networks, nanomaterials including graphene, carbon nanotubes, and carbon nanohorns, have been combined with monolithic materials to prepare novel stationary phases or sorbents with enhanced performance.⁴

In this study, a hybrid monolithic phase based on a combination of methacrylate monomers and oxidized SWNHs (o-SWNHs) has been synthesized into a spin column device employing a UV-polymerization approach. To ensure covalent attachment of the monolith to the inner wall of the polypropylene device, a surface modification was first carried out with grafted chains of ethylene dimethacrylate (EDMA). Then, variables dealing with the covalent attachment of the hybrid monolith to polypropylene beds of the spin column device as well as variables related to the polymerization reaction were deeply studied. In addition, the resulting hybrid monolithic polymers were also characterized by scanning electron microscopy (SEM) and nitrogen intrusion porosimetry. The monolithic material was used for the extraction of NSAIDs from urine samples prior to HPLC-UV analysis.

¹ Carrasco-Correa, E. J.; Vela-Soria, F.; Ballesteros, O.; Ramis-Ramos, G.; Herrero-Martínez, J. *M. J. Chromatogr. A*, **2015**, 1379, 65.

² Fresco-Cala, B.; Cárdenas, S.; Valcárcel, M. *Microchim. Acta*, **2016**, 183, 465.

³ Namera, A.; Nakamoto, A.; Nishida, M.; Saito, T.; Kishiyama, I.; Miyazaki, S.; Yahata, M.; Yashiki, M.; Nagao, M. *J. Chromatogr. A*, **2008**, 1208, 71.

⁴ Fresco-Cala, B.; Cárdenas, S.; Valcárcel, M. *J. Chromatogr. A*, **2016**, 1468, 55.