
SELECTIVE EXTRACTION AND ANALYSIS BY CHIP LC-MS OF COCAINE AND ITS METABOLITE FROM URINE

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The growing interest on chip technology has led to many developments in this field. A chip integrating an enrichment column, and a nano-LC column, with a nanopump and a micropump respectively, coupled on-line to a nanoelectrospray tip for MS detection, is now available. This automated and miniaturized device has been already successfully applied to oligosaccharides analysis in milk [1], to proteomic analysis [2], even to biomarker discovery [3].

Our objective was the application of such a device to the analysis of small molecules in complex matrices. Cocaine and its main metabolite benzoylecgonine were chosen as model molecules. Two different chips characterized by different size of enrichment columns, of separation channels and porosity were compared.

After the optimization of separation conditions, the enrichment step was improved by studying analyte breakthrough as a function of the injected sample volume, its content in organic solvent, and as a function of the flush volume, i.e. the volume of solution required to transfer the analytes from the autosampler to the enrichment column. The performance of the method was evaluated on pure media and the method was applied to spiked urine samples.

Despite the good performance of the system in terms of limit of quantification, the performance of the method was improved by adding a clean-up step based on the use of molecularly imprinted polymer (MIP). To better fit to the miniaturized device, two approaches were considered for the synthesis of this MIP: bulk polymerization and precipitation polymerization. The MIP supports were evaluated for both the selective extraction of cocaine and the elimination of interferences before chip LC-MS analysis. All of these results may lead to an on-chip molecularly imprinted polymer solid phase extraction procedure.

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[2] Yin, H.; Killeen, K.; Brennen, R.; Sobek, D.; Werlich, M.; van der Goor, T. *Anal. Chem.* 2005, 77, 527-533

[3] Fortier, M.; Bonneil, E.; Goodley, P.; Thibault, P., *Anal. Chem.* 2005, 77, 1631-1641