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"Pseudostationary Ion-Exchanger" Sweeping as an Online Enrichment Technique in the Determination of Nucleosides in Urine via Micellar Electrokinetic Chromatography

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ABSTRACT: The presented study aims to develop a new online enrichment strategy ["pseudostationary ion-exchanger" (PSIE) sweeping] for the analysis of highly hydrophilic nucleosides in urine samples with a special focus on the fundamental aspects regarding the enrichment process itself. In the first method, we employ the ionic liquid (IL)-type surfactant 1-tetradecyl-3-methylimidazolium bromide (C_{14}MImBr) as micelle forming agent under alkaline pH conditions. It is shown that maximum enrichment efficiency can be obtained by keeping the retention factors very high within the sample zone and very low within the background electrolyte (BGE) while maintaining a sufficient resolution for the studied analytes. With this method, detection limits as low as 0.1 µg mL^{-1} are obtained for all analytes studied. For the nucleosides, adenosine and cytidine, a second method is developed using sodium dodecyl sulfate (SDS) as micelle forming agent under acidic pH conditions. In addition, we investigate the effect of replacing ionic buffering constituents with a zwitterionic/isoelectric buffering compound (aspartic acid) with regard to separation and enrichment efficiency. With the second method, the achieved limits of detection are as low as 0.1 µg mL^{-1} for Ado and 0.2 µg mL^{-1} for Cyd. The applicability of the two complementary methods to the analysis of the nucleosides under investigation is shown for blank and spiked human urine samples after their extraction using the commercially available phenylboronate affinity gel.