# Online Preconcentration of High-Salt Samples Using Pressure-Assisted Field-Amplified Sample Injection in Flow-Gated Capillary Electrophoresis

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Capillary electrophoresis (CE) is a valuable separation method; however, its detection sensitivity is often limited by the small sample volumes injected. Different strategies have been developed to enhance the sensitivity, e.g. on-line sample preconcentration, and/or using sensitive detection such as fluorescence and mass spectrometry. Sample stacking, an effective sample preconcentration strategy, is based on the uneven distribution of electric field across a capillary filled with buffer plugs with different ionic strengths. However, the basic sample stacking method fails for high-salt containing samples. We developed a new technique for flow-gated CE to perform on-line sample preconcentration of high-salt samples such as cerebrospinal fluid (CSF). Initially, the high-salt sample was fluorogenically derivatized with 2,3-Naphthalenedicarboxaldehyde (NDA) in the presence of cyanide. Then, a sample plug was hydrodynamically injected by vacuum on the outlet side of the capillary. Third, a reversed-voltage was applied to conduct field-amplified sample injection while maintaining a counter vacuum to elongate the injection time during the pushback. Finally, a normal-polarity voltage was applied for separations. During the injection procedure, the sample solution was continuously supplied to the cross section of the flow gate via a syringe pump, which ensured the inlet of the capillary was immersed in the sample; and the sample preconcentration might rely on the electrokinetic supercharging principle. Enhancement factors of 50-100 folds at optical conditions were obtained for a series of amino neurotransmitters including γ-aminobutyric acid (GABA), valine, methionine, isoleucine, and phenylalanine, and limits of detection were lowered down to the pico-molar range. Furthermore, this strategy was applied to the determinations of primary amine neurotransmitters in CSF by using the one-point standard addition method enabled by alternative injections of the two samples. The method is expected to be useful for analyzing other high-salt containing samples with such urine and blood plasma.