Supplemental Information

Figure S1. Images of the BzCl reagent addition junction on all-glass device taken after 10, 30, and 80 min of continuous flow. BzCl was flowed at 0.5 μ L/min (from left) while premixed aCSF/sodium carbonate was flowed 1.5 at μ L/min (from top). Channel dimensions are 75 μ m wide x 85 μ m deep. While a distinct phase boundary can be seen, no precipitation occurred.

Figure S2. Effect of triphosphate chelation on rate of CaCO₃ and MgCO₃ precipitation. (A) Initial image of device at the start of flow. After 120 min the carbonate buffer precipitated more at the junction (B) than carbonate with 100 mM triphosphate (C).

Figure S3. Precipitate formation at laminar interface of BzCl junction after on-chip derivatization of calibration high concentration of 25 compound standard mixture. Reagents were continuously flowed for the 2 hr duration of the experiment.

Figure S4. Best-performing reagent addition devices with respect to mixing. Design A utilizes a sharp turn into serpentine mixers at the junction. Desgin B has a duel-addition junction with each reagent split into parallel channels. Channel dimensions were 75 μ m x 80 μ m (width x depth). Split channels in design B narrow to 37.5 μ m x 80 μ m as they converge on dialysate stream.

Figure S5. Calibration curves representing the range of chemical classes targeted in the method. ACh – unlabeled; Glu, GABA, Asp, Ado, Glucose - singly benzoylated; 5-HT – doubly benzoylated; NE, DA – triply benzoylated. All concentrations shown are in nM except for Glucose (μ M).

Figure S6. *In vivo* microdialysis sampling from the striatum of an anesthetized rat. aCSF with 75 mM K+ was perfused for a pair of 3 min fractions (black arrows) to demonstrate rapid increase in extracellular concentrations and return to baseline.

Figure S7. RIC of 21 analytes overlaid on gradient adjusted for system volume. Left y-axis is relative intensity normalized to the largest analyte signal, tyrosine. The right axis shows the step gradient across the separation window (dotted line). An extra minute of high acetonitrile purging and equilibration is not shown. Concentrations shown span the range between low nM (DA, ACh, 5-HT etc.) and mid μ M (glucose).

Figure S1



Figure S2



Figure S3













Figure S7

