Electronic Supplementary Material (ESI) for Lab on a Chip.

Supporting information for

Experimental Verification of Simultaneous Desalting and Molecular Preconcentration by Ion Concentration Polarization

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Supporting Information 1:
Concentration calculation in 9-branched device (Figure 3(c))

◆ Verification of equation (7) and (8)

Equation (7) and (8) was experimentally verified prior to the main experiment. We conducted an experiment with a device of larger dimension than regular device of this work. With this larger device, direct mass spectrometry measurement was possible by 20 hrs sample collection, c.f. it took 6 months for collecting measurable sample volume with the original device. The comparison results between can calculated by our formula and 20 hrs collection were shown in below table. While the numbers were slightly different (especially the case of outside IDZ) due to unstable formation of ICP layer in the larger device, overall data were concluded to be comparable.

	Normalized c_{Na} by eqn (7) & (8)	**Normalized c_{Na} by 20 hrs collection**
outside IDZ	0.577	0.379
inside IDZ	0.129	0.105
IEZ	1.307	1.335

SI Table 1. Comparison between normalized can calculated by our formula and direct measurement from 20 hrs sample collection.

◆ Quantitative data for Figure 3(c)

step 1) Measuring initial and final concentration of each outlet reservoir by using ICP-MS or ICP-OES

Measured concentration of Li^{+} (analyte electrolyte)		
i^{th} branch	$c_{Li_i}^{initial}$ (mM)	$c_{Li_i}^{final}$ (mM)
1	0.216	1.730
2	0.216	1.298
3	0.108	0.865
4	0.216	0.692
5	0.216	0.865
6	0.216	0.346
7	0.432	0.692
8	0.325	0.519
9	0.541	0.519

Measured concentration of K^{+} (background electrolyte)		
i^{th} branch	$c_{BGE\_i}^{initial}$ (mM)	$c_{BGE\_i}^{final}$ (mM)
1	38.008	32.066
2	38.008	27.943
3	37.931	27.441
4	40.583	31.190
5	40.737	30.037
6	41.755	32.112
7	42.389	31.252
8	40.718	28.763
9	42.063	29.531

step 2) Substituting measured concentration value to eq. (7)

$$c_{\Delta x_i} = \frac{\Delta x_i}{\Delta V_i} = \left(\frac{c_{x_i}^{final} c_{BGE\_i}^{initial} - c_{x_i}^{initial} c_{BGE\_i}^{final}}{c_{BGE\_i}^{initial} - c_{BGE\_i}^{final}} \right), \quad \cdots \quad \text{eq. (7)}$$
$$i = 1,2,\ldots,n.$$

step 3) Finding reassigned concentration of analyte ion (Li^{+}) caused by ICP from eq. (7)

Reassigned concentration of Li^{+}	
i^{th} branch	$c_{\Delta Li_i}$ (mM)
1	9.902
2	4.300
3	2.845
4	2.272
5	2.685
6	0.778
7	1.420
8	0.987
9	0.467
inlet	19.908

Supporting Information 2:
Concentration and number of species calculation in 2-branched device (Figure 4(a) and 4(b))

- **Quantitative data for Figure 4(a) and 4(b)**

step 1) Measuring initial and final concentration of each outlet reservoir by using Ion chromatography

Measured concentration of Li^+, Na^+, Cl^- (analyte electrolyte)			
x	Li^+ (mM)	Na^+ (mM)	Cl^- (mM)
c_x^{inlet}	55.828	63.0757	114.786
$c_{x_i}^{initial}$	0	1.229	109.402
$c_{x_1}^{final}$(outside_IDZ)	7.528	8.891	102.164
$c_{x_2}^{final}$ (inside_IDZ)	1.664	2.740	86.733
$c_{x_3}^{final}$ (IEZ)	14.868	18.933	125.791

Measured concentration of K^+ (background electrolyte)	
x	K^+ (mM)
c_x^{inlet}	0
$c_{BGE\_i}^{initial}$	106.345
$c_{BGE\_1}^{final}$ (outside_IDZ)	78.144
$c_{BGE\_2}^{final}$ (inside_IDZ)	72.383
$c_{BGE\_3}^{final}$ (IEZ)	71.667

step 2) Substituting measured concentration value to eq. (7) and (8)

$$c_{\Delta x_i} = \frac{\Delta x_i}{\Delta V_i} = \left(\frac{c_{x_i}^{final} c_{BGE\_i}^{initial} - c_{x_i}^{initial} c_{BGE\_i}^{final}}{c_{BGE\_i}^{initial} - c_{BGE\_i}^{final}} \right), \quad \cdots \quad \text{eq. (7)}$$

$$i = 1,2,\ldots,n.$$

$$c_{\Delta x_{ca}} = \frac{\Delta x_{ca}}{\Delta V_{ca}} = \left(\frac{c_{x_{ca}}^{final} c_{BGE\_ca}^{initial} - c_{x_{ca}}^{initial} c_{BGE\_ca}^{final}}{c_{BGE\_ca}^{initial} - c_{BGE\_ca}^{final}} \right), \quad \cdots \quad \text{eq. (8)}$$

$$ca = \text{cathode}.$$

step 3) Finding reassigned concentration of analyte ion (Li^+) caused by ICP from eq. (7) and (8).

Reassigned concentration			
x	Li^+ (mM)	Na^+ (mM)	Cl^- (mM)
$c_{\Delta x_1}$(outside_IDZ)	34.542	36.385	76.192
$c_{\Delta x_2}$ (inside_IDZ)	7.634	8.164	5.388
$c_{\Delta x_3}$ (IEZ)	68.219	82.461	0

Normalized concentration			
x	Li^+	Na^+	Cl^-
$\frac{c_{\Delta x_1}}{c_x^{inlet}}$	0.619	0.577	0.664
$\frac{c_{\Delta x_2}}{c_x^{inlet}}$	0.137	0.129	0.047
$\frac{c_{\Delta x_3}}{c_x^{inlet}}$	1.222	1.307	0

step 4) Finding formula for normalized number of analyte ions

We can calculate normalized volume change in outlet reservoirs from eq.(3).

$$\frac{V_i}{\Delta V_i} = \frac{c_{BGE\_i}^{final}}{c_{BGE\_i}^{initial} - c_{BGE\_i}^{final}} \quad \cdots \quad \text{eq. (3)}$$

Normalized volume change in i^{th} reservoir can be expressed as

the division of i^{th} volume change (ΔV_i) and total volume change ($\sum_k \Delta V_k$).

Then, normalized number of analyte ion ($N_{\Delta x_i}$) can be expressed as

the product of normalized concentration ($\frac{c_{\Delta x_i}}{c_{x_i}^{inlet}}$) and normalized volume change ($\frac{\frac{\Delta V_i}{V_i}}{\sum_k \frac{\Delta V_k}{V_k}}$).

$$N_{\Delta x_i} = \frac{c_{\Delta x_i}}{c_{x_i}^{inlet}} \times \frac{\frac{\Delta V_i}{V_i}}{\sum_k \frac{\Delta V_k}{V_k}} \quad \cdots \quad \text{eq. (SI.1)}$$

step 5) Calculating values of normalized number of analyte ions in i^{th} branch

	Normalized volume change	**Normalized number of Li^+**	**Normalized number of Na^+**	**Normalized number of Cl^-**
i^{th} branch	$\frac{\frac{\Delta V_i}{V_i}}{\sum_k \frac{\Delta V_k}{V_k}}$	$N_{\Delta Li_i}$	$N_{\Delta Na_i}$	$N_{\Delta Cl_i}$
1 (outside_IDZ)	0.435	0.291	0.271	0.312
2 (inside_IDZ)	0.565	0.064	0.061	0.022
3 (IEZ)	0	0.644	0.668	0

Supporting Information 3:
Concentration in 2-branched device (Figure 5(c))

◆ Quantitative data for Figure 5(c)

step 1) Measuring initial and final concentration of each outlet reservoir by using ICP-MS or ICP-OES

Measured concentration of Na^+(analyte electrolyte)	
x	Na^+ (mM)
c_x^{inlet}	326.276
$c_{x_i}^{initial}$	0.288
$c_{x_1}^{final}$(outside_IDZ)	29.828
$c_{x_2}^{final}$ (inside_IDZ)	9.333
$c_{x_3}^{final}$ (IEZ)	153.426

Measured concentration of K^+ (background electrolyte)	
x	K^+ (mM)
c_x^{inlet}	0
$c_{BGE\_i}^{initial}$	94.289
$c_{BGE\_1}^{final}$(outside_IDZ)	84.098
$c_{BGE\_2}^{final}$(inside_IDZ)	74.275
$c_{BGE\_3}^{final}$(IEZ)	74.659

step 2) Substituting measured concentration value to eq. (7) and (8)

$$c_{\Delta x_i} = \frac{\Delta x_i}{\Delta V_i} = \left(\frac{c_{x_i}^{final} c_{BGE\_i}^{initial} - c_{x_i}^{initial} c_{BGE\_i}^{final}}{c_{BGE\_i}^{initial} - c_{BGE\_i}^{final}} \right), \quad \cdots \quad \text{eq. (7)}$$

$i = 1, 2, \ldots, n.$

$$c_{\Delta x_{ca}} = \frac{\Delta x_{ca}}{\Delta V_{ca}} = \left(\frac{c_{x_{ca}}^{final} c_{BGE\_ca}^{initial} - c_{x_{ca}}^{initial} c_{BGE\_ca}^{final}}{c_{BGE\_ca}^{initial} - c_{BGE\_ca}^{final}} \right), \quad \cdots \quad \text{eq. (8)}$$

$ca = \text{cathode.}$

step 3) Finding reassigned concentration of analyte ion (Li^+) caused by ICP from eq. (7)

Reassigned concentration	
x	Na^+ (mM)
$c_{\Delta x_1}$(outside_IDZ)	187.206
$c_{\Delta x_2}$ (inside_IDZ)	35.535
$c_{\Delta x_3}$ (IEZ)	337.538

Normalized concentration	
x	Na^+
$\frac{c_{\Delta x_1}}{c_x^{inlet}}$ (outside_IDZ)	0.574
$\frac{c_{\Delta x_2}}{c_x^{inlet}}$ (inside_IDZ)	0.110
$\frac{c_{\Delta x_3}}{c_x^{inlet}}$ (IEZ)	1.035