An Open Tubular Ion Chromatograph

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SUPPORTING INFORMATION

Table S1. OTIC program sequence for sample injection and separation, one cycle

step	Duration Time	SV1	SV2	IV	Pressure	comment
1	1 s	off	Off	load	P_{inj} (typical, 14 psi)	System initialization; apply pressure to the system; Sample has been loaded in IV before running the program
2	1 s	off	Off	injection	P_{inj}	Switch IV to make the sample loop to connect to the eluent line
3	800 ms	on	Off	injection	P_{inj}	Open SV1 to move the undiluted sample zone to the Tee
4	t_{inj} (100-5000 ms)	off	Off	Injection	P_{inj}	Close SV1 for introducing sample into the capillary column
5	3 s	on	Off	Injection	P_{inj}	Open SV1 again for cleaning the remaining sample in the Tee and the line
6	1 s	off	Off	load	P_{sep} (14-100 psi)	Close SV1 and increase the pressure for beginning the separation; trigger data acquisition
7	t_{sep}	off	Off	load	P_{sep}	Separation step. The duration time (t_{sep}) is depended by the duration time of chromatography and column equilibrium.
8	800 ms	off	On	load	P_{inj}	Open SV1 for release tank pressure (when $P_{sep} > P_{inj}$)
9	1 s	off	Off	load	P_{inj}	Return to the initial status for next cycle

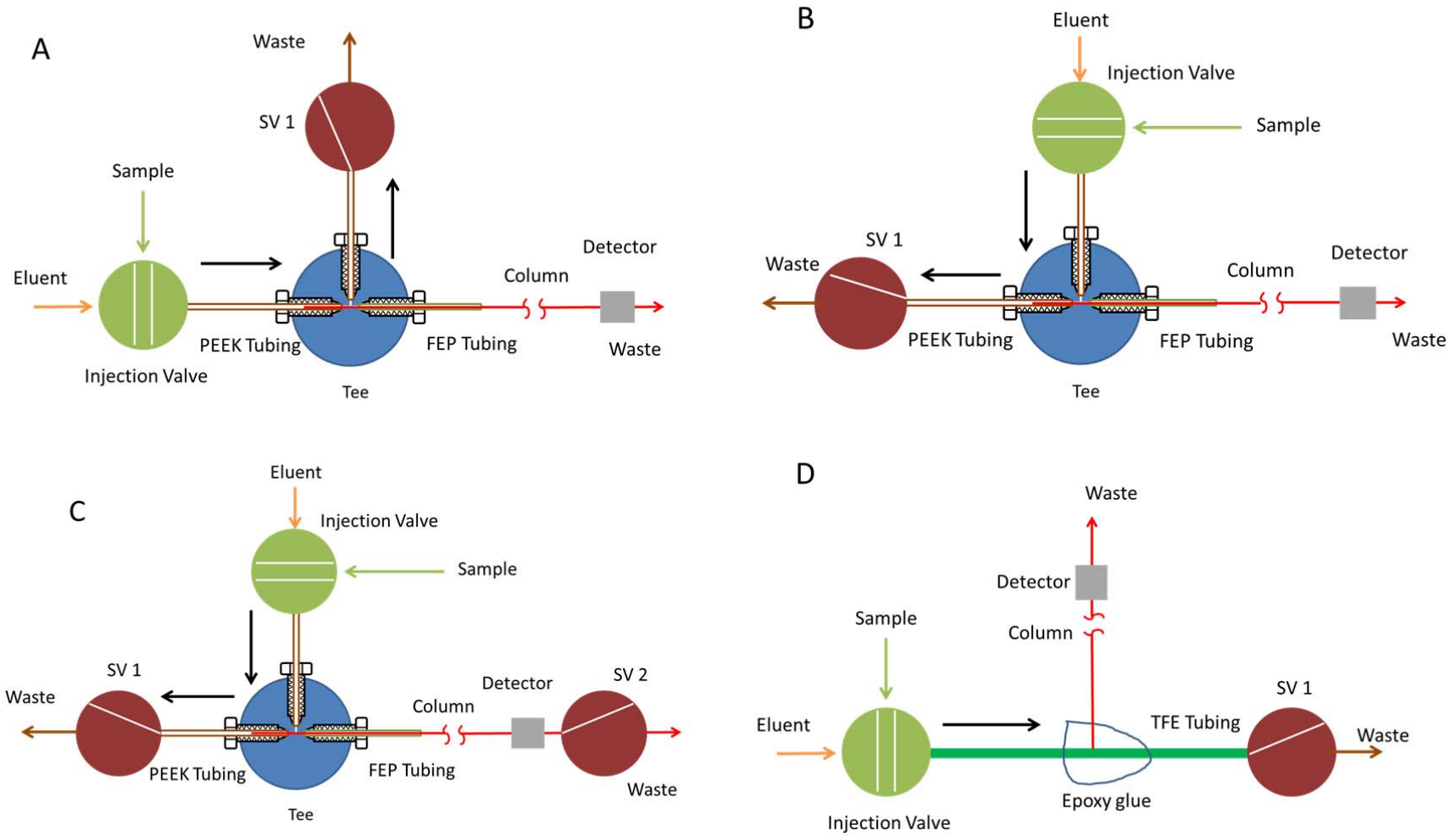

Figure S1. Comparison of autoinjected volumes (V_{aut}) with different configurations (r = 9.8 μm, L= 70 cm, PMMA): **A.** The capillary column is inserted into the eluent inlet tubing through the tee, V_{aut} = 279 pL; **B.** The capillary column is inserted into the eluent outlet tubing, V_{aut} = 38 pL; preferred configuration; used in this work; **C.** The capillary column is inserted into the eluent outlet tubing. The outlet of column was connected to an additional valve (SV2); when the sample is passing through the tee, SV2 was shut off to prevent flow into the column, V_{aut} = 51 pL; **D.** custom tee: hole drilled through a PEEK tube wall, column connected through the hole and epoxy adhesive was used to fix the column, V_{aut} = 149 pL;

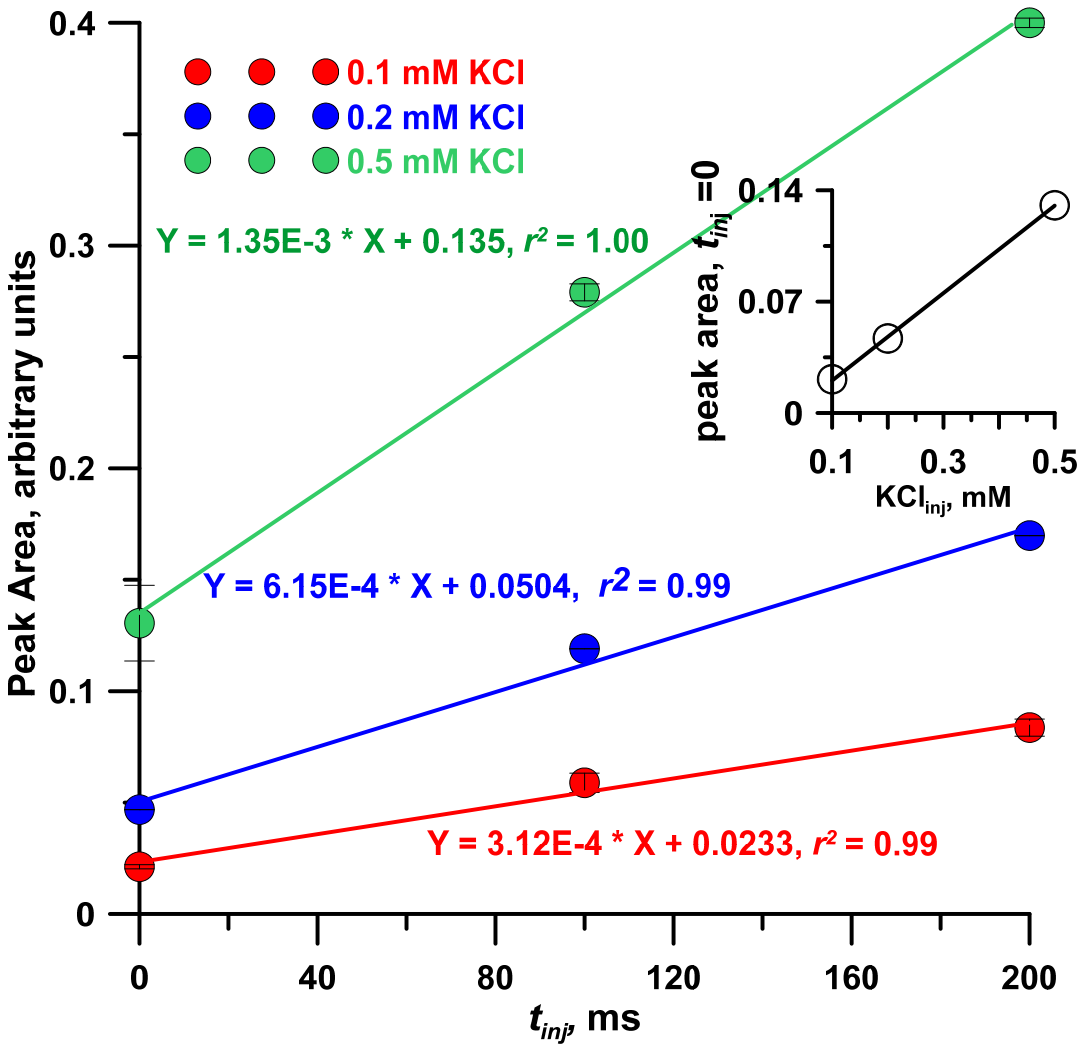

Figure S2. The Peak Area of Cl^- at different injection time (n=3). Conditions: Triplicate injection, 1 mM NaBz eluent, r =9.8 μm, L = 70 cm, P_{Elu} 30 psi, 63 nL/min.

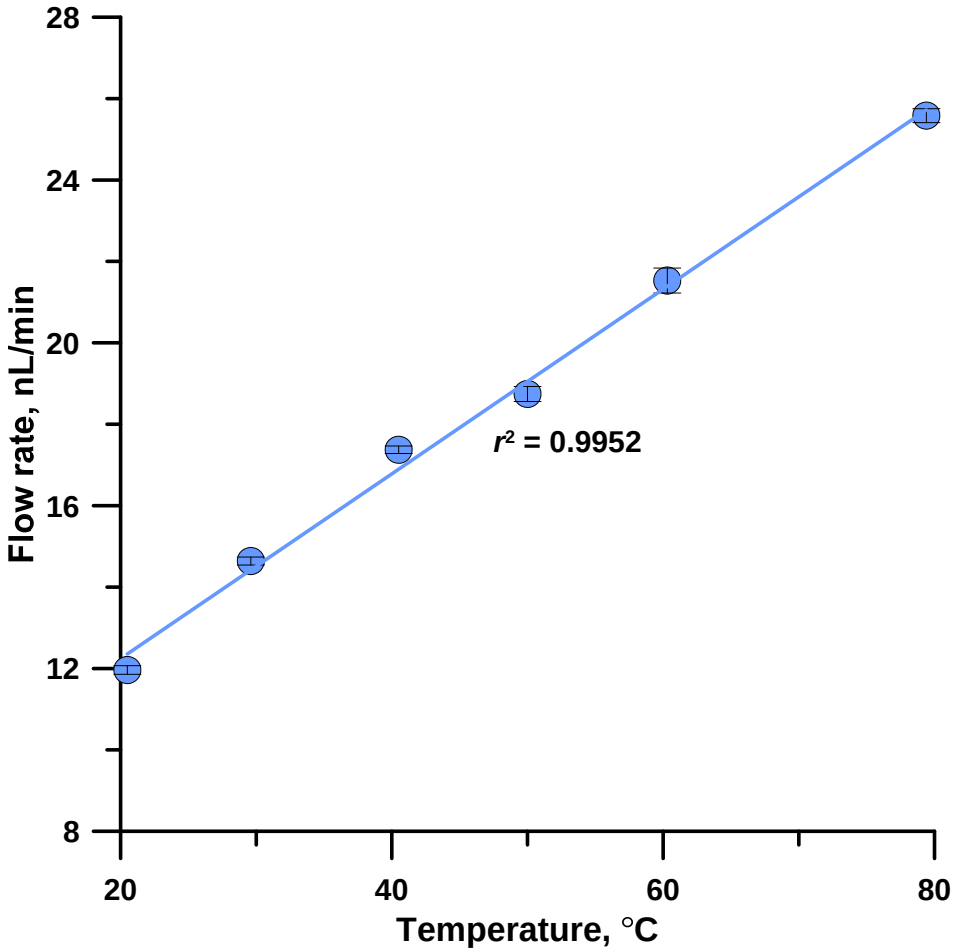

Figure S3. Silica capillary, r = 5 μm, L= 55 cm. 2 mM sodium benzoate, pressure fixed at 55 psi. Flow rates were measured gravimetrically.

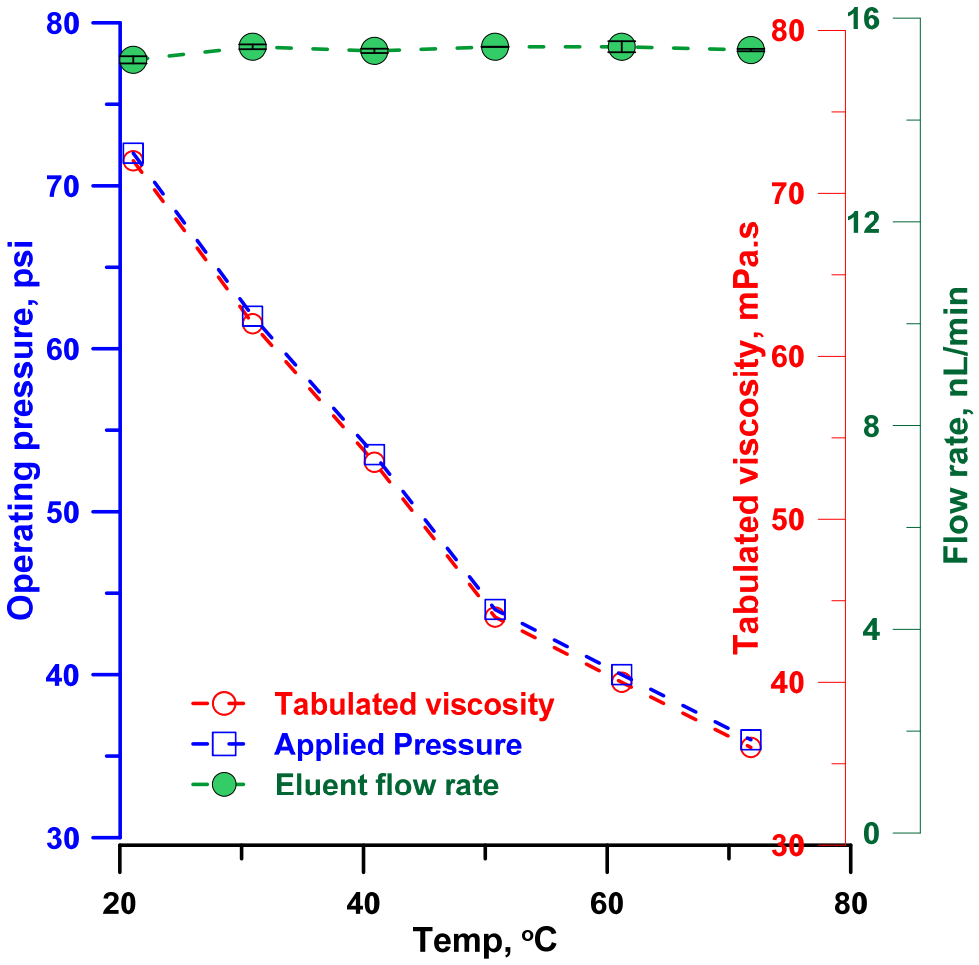

Figure S4. Maintaining constant flow rate by varying applied pressure as temperature varies**.** Silica capillary, *r* = 5 μm, *L*= 55 cm, 2 mM Na-Benzoate. Flow rate measured gravimetrically.

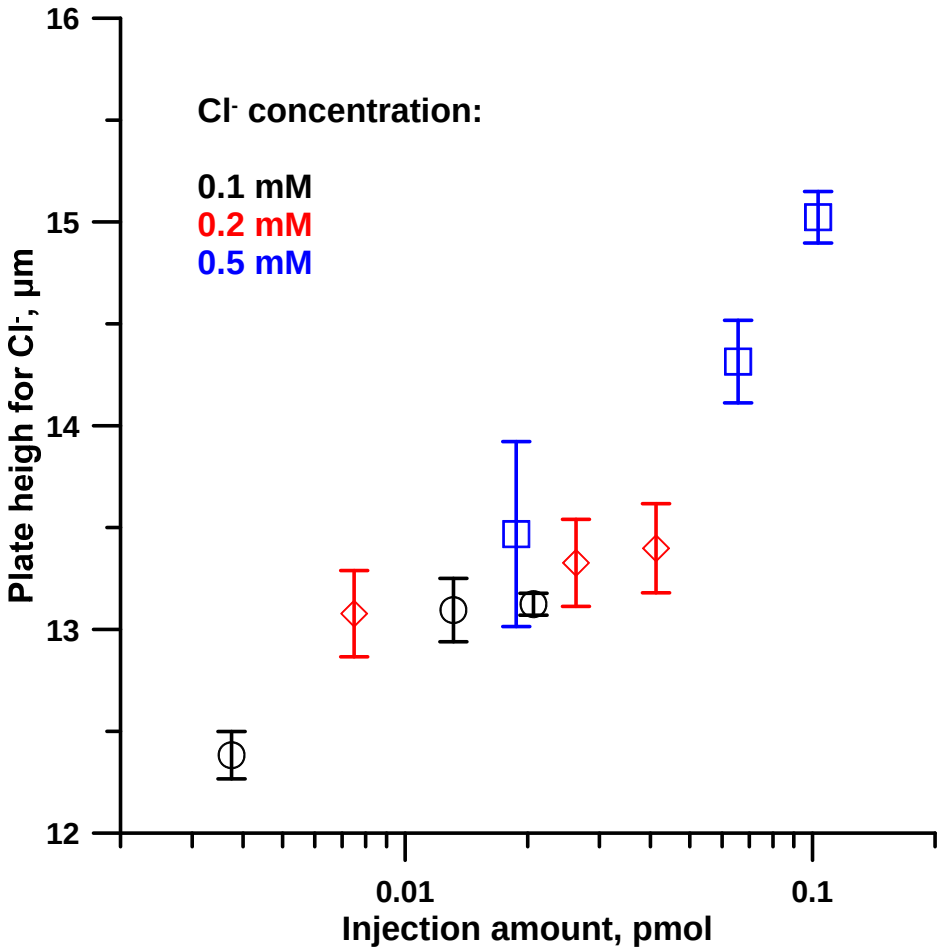

Figure S5. Plate height of Cl^- as a function of amount injected. 0.1, 0.2 or 0.3 mM KCl was injected for 0 (autoinjection), 100 or 200 ms at 14 psi. Triplicate injection, 1 mM NaBz eluent, r = 9.8 µm, L = 70 cm, P_{Elu} = 30 psi, 63 nL/min

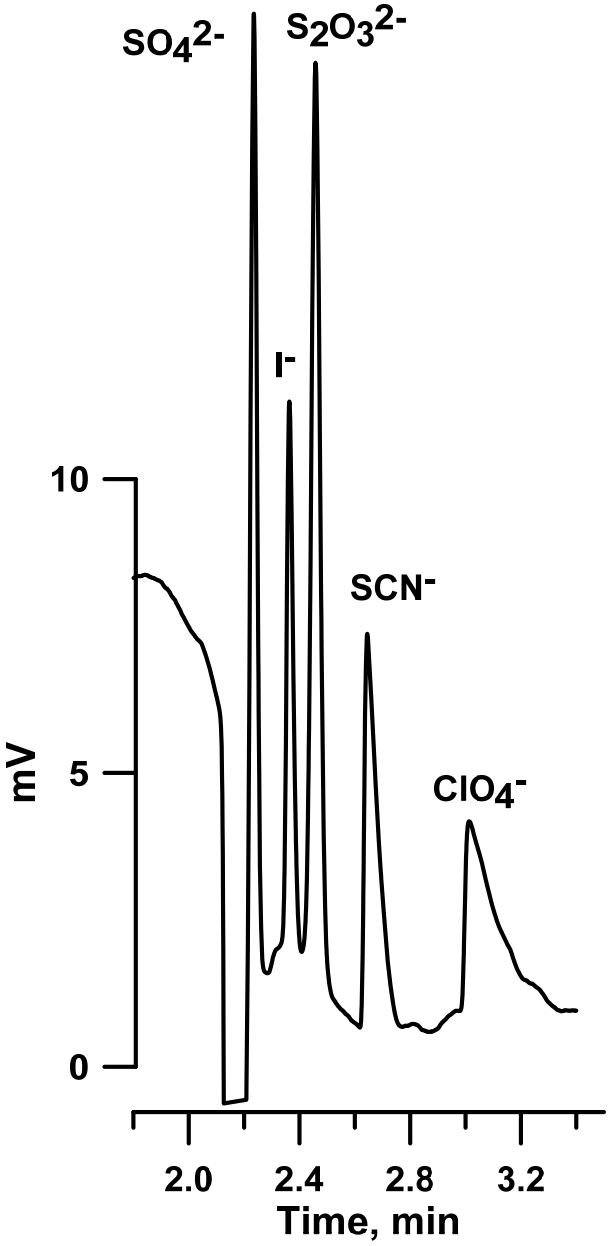

Figure S6. Chromatogram of strongly retained anions. r = 9.8 μm, L = 70 cm; Eluent, 2 mM phthalate, pH= 7.4; samples, 200 μM SO_4^-, I^-, $S_2O_3^-$; 500 μM ClO_4^-, SCN^-; injection volume 100 pL; P_{Elu} =45 psi, linear velocity 0.54 cm/s (96 nL/min).

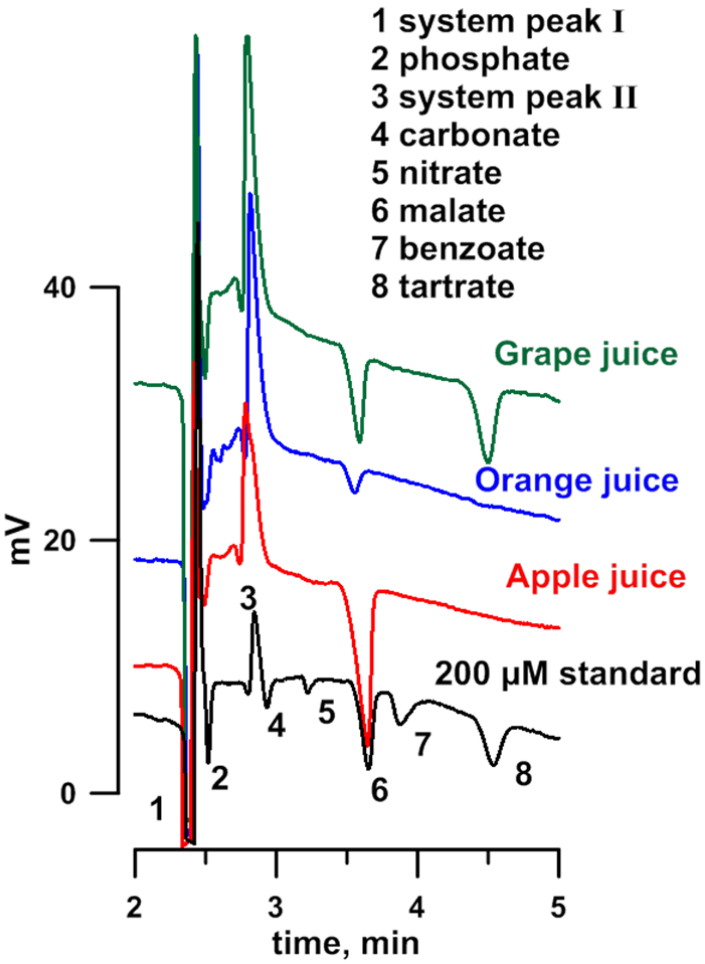

Figure S7. Chromatograms of separation typical organic acids in fruit juice samples. Conditions: (r =8.5 µm, L = 59 cm long; injection volume, 1.8 nL; Eluent, 1 mM Na_2SO_4 + 1mM NH_4OAc, pH = 5.0 (adjusted with HOAc); P_{Elu} =40 psi, linear velocity 0.40 cm/s (26 nL/min). standard concentrations: 200 µM each analyte. Citrate takes too long under these conditions and is better eluted with a phthalate eluent.

Table S2. Inorganic and organic anions concentration in samples

	Chloride	Nitrate	malate	tartrate	citrate
Grape juice	4.226±0.023	0.256±0.012	1.190±0.080	18.42±1.34	0.545±0.152
Apple juice	0.891±0.020	0.252±0.015	24.58±0.74	ND	ND
Orange juice	1.378±0.037	ND	0.066±0.007	ND	13.48±0.48
Mineral water	0.146±0.006	0.076±0.003	3.050±0.285	ND	ND

Concentrations given in mM, uncertainties represent ±1 SD (n=3).
Inorganic anions were determined with a benzoate eluent, citrate was determined with a phthalate eluent, other organic acids were determined with a acetate buffered sulfate eluent (see Figure S7).

Table S3. Analytical parameters for the separation of inorganic anions and organic anions [a]

	Linear range (μM)	R	RSD [b] (%)	LOD_1 [c] (μM)	LOD_2 [d] (μM)
F^-	10-400	0.9972	4.92	2.6	1.8
Cl^-	5-250	0.9980	3.37	1.4	0.8
NO_2^-	5-250	0.9985	4.82	1.9	1.0
Br^-	5-250	0.9994	3.22	1.5	0.7
NO_3^-	5-250	0.9993	3.00	2.3	1.0
SO_4^{2-}	10-400	0.9997	0.68	-	3.3
$H_2PO_4^-$	40-400	0.9979	7.46	-	11.1
Malate	40-400	0.9994	3.53	-	12.6
Benzoate	100-400	0.9971	7.33	-	28.5
Tartrate	70-400	0.9994	4.38	-	21.9
Citrate	100-400	0.9969	5.07	-	32.0

a) Eluent for F^-, Cl^-, NO_2^-, Br^- and NO_3^-: 1 mM benzoate;
Eluent for $H_2PO_4^-$, malate, benzoate, tartrate: 1 mM Na_2SO_4 and 1 mM NH_4Ac, pH = 5.0 (adjusted with HAc);
Eluent for SO_4^{2-} and citrate: 2 mM phthalate with pH 7.0 (adjusted with LiOH);
b) n = 3; sample concentration: 200 μM; Injected sample volume: 1.2 nL;
c) S/N = 3 criterion verified at each stated LOD; injected sample volume: 0.5 nL;
d) Injected sample volume: 1.2 nL

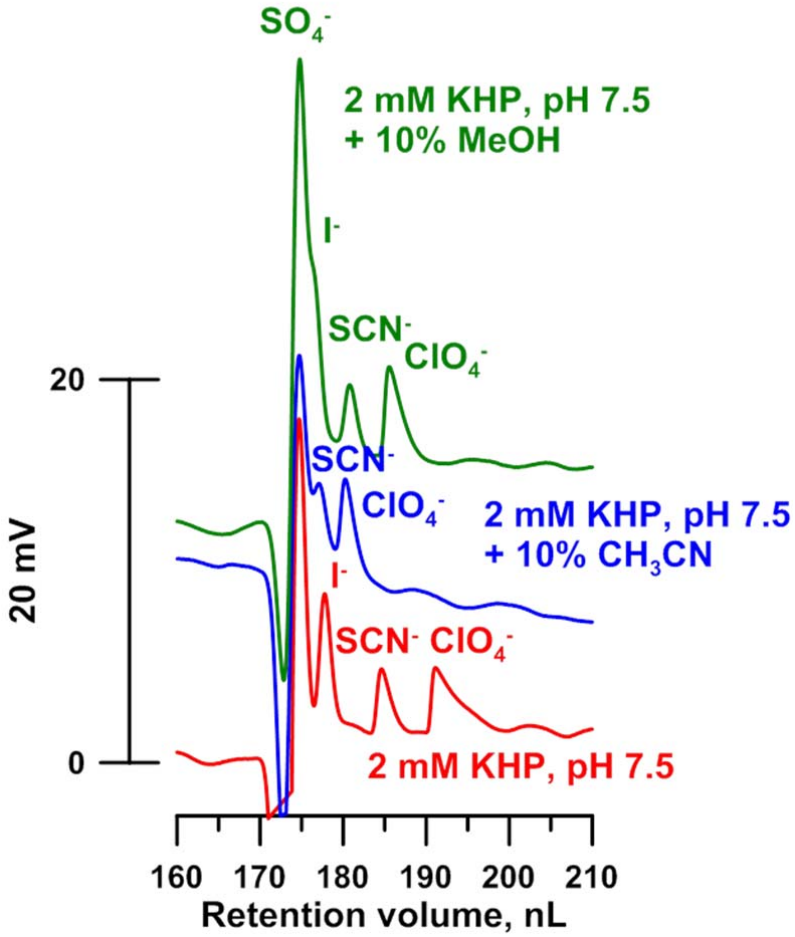

Figure S8. PMMA, r = 9.8 μm, L_{eff} = 58 cm. Flow rate: 48 nL/min. 500 μM each I^-, SCN^-; 1 mM each SO_4^{2-}, ClO_4^-, 0.2 nL injection. Perchlorate asymmetry at 10% height changed from 8.1 to 3.4 to 2.0 in going from pure water to 10% methanol to 10% acetonitrile.

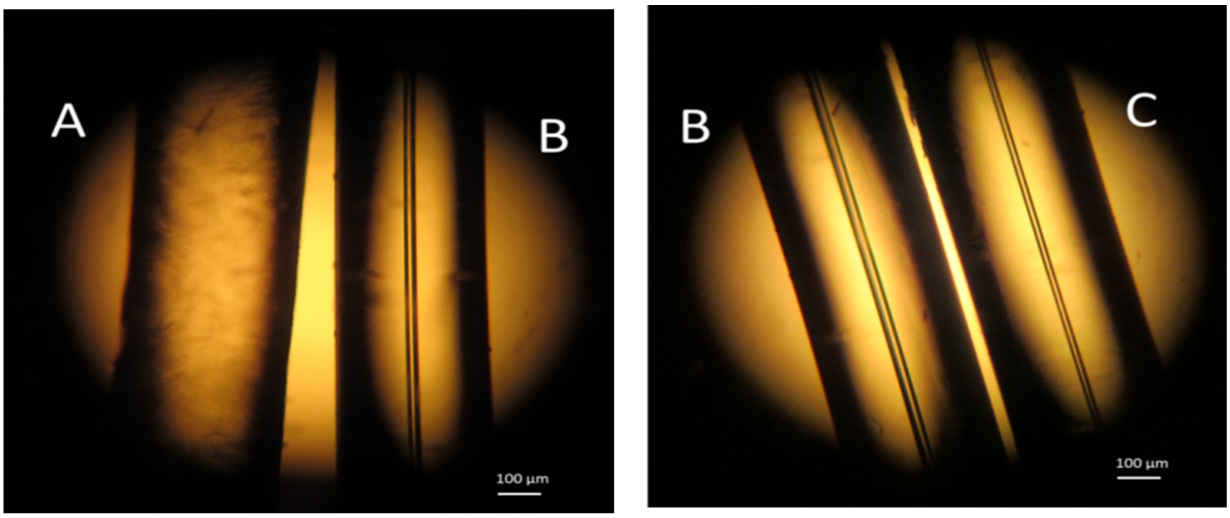

Figure S9. A): immersed into 50% (v/v) acetonitrile solution for 10 h; B) original PMMA capillary, without treatment with acetonitrile; C) the channel passed by 30% (v/v) acetonitrile solution for 2 h.

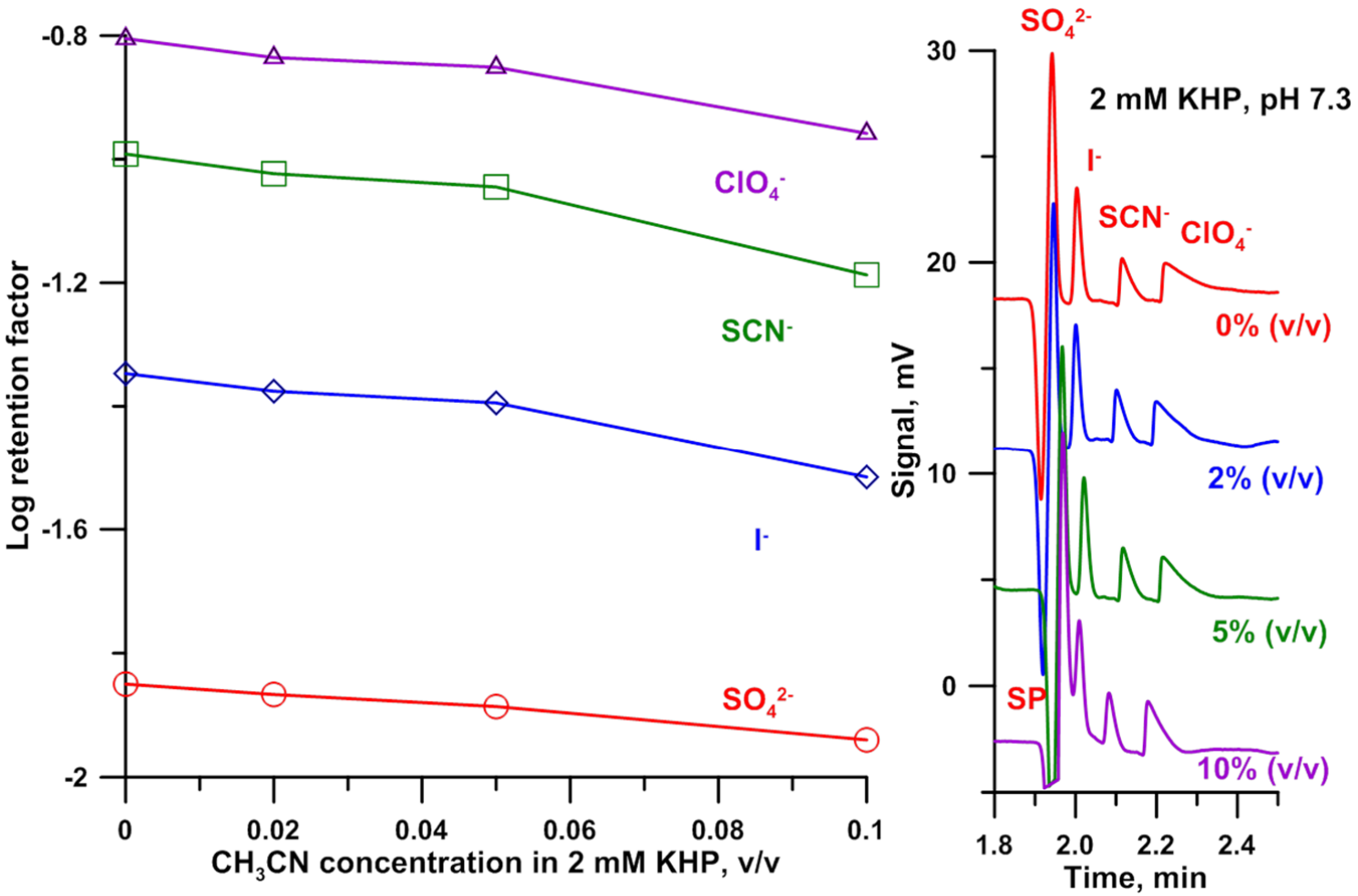

Figure S10. Variations in acetonitrile content in an acetonitrile containing phthalate eluent 2 mM phthalate at pH 7.3 plus acetonitrile as indicated; r = 7.2 μm, L = 47 cm, PMMA, injection volume,0.25 nL; P_{Elu} 48 psi; linear velocity 0.40 cm/s (44 nL/min). I^- and SCN^- at 0.5 mM, $SO_4^{2-}$and ClO_4^-at 1 mM.

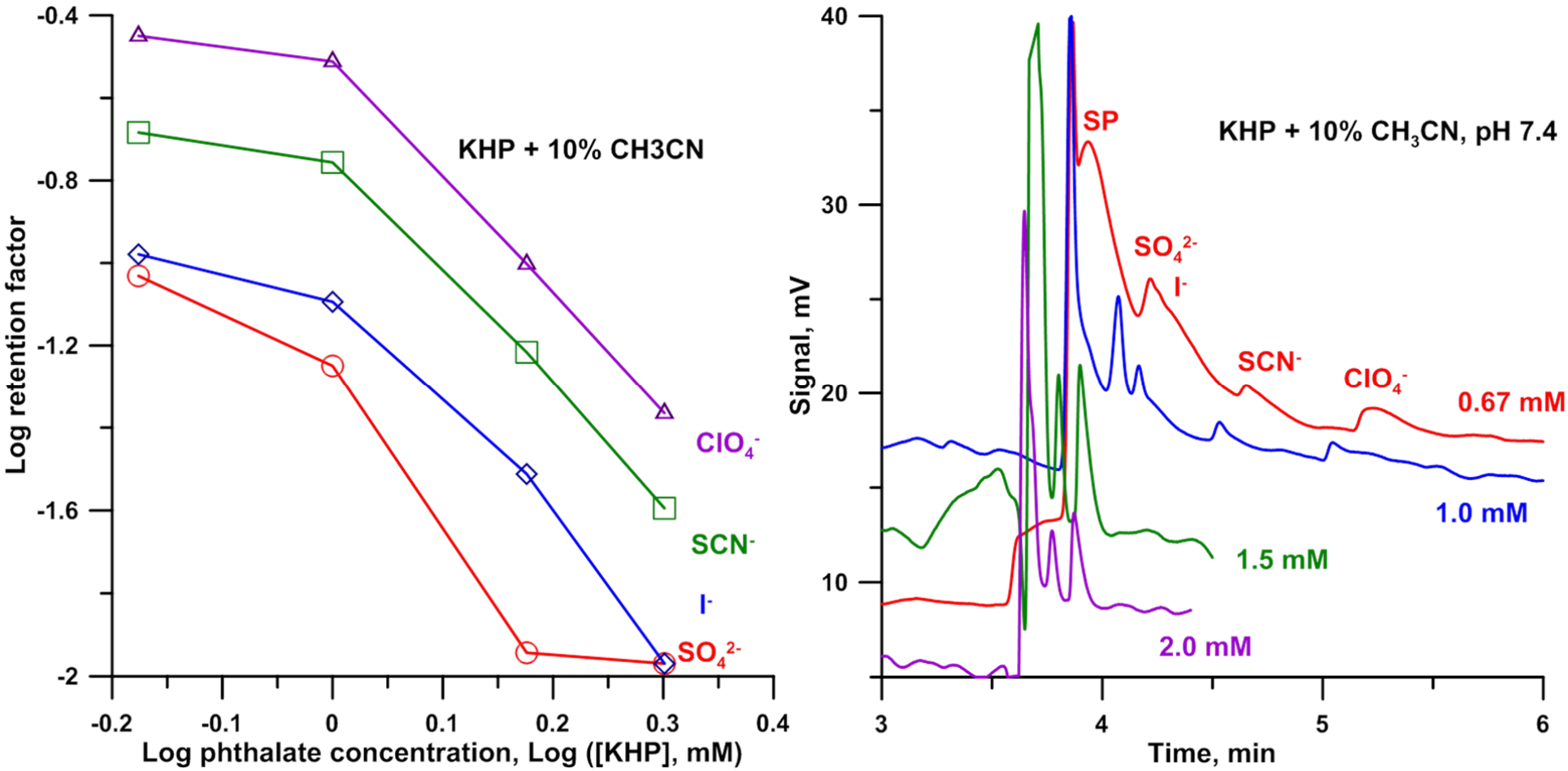

Figure S11. Variations in phthalate content in a phthalate eluent (pH 7.4) containing 10%v/v acetonitrile r = 7.2 μm, L = 68 cm, PMMA, injection volume,0.2 nL; P_{Elu} 48 psi, linear velocity 0.32 cm/s (31 nL/min); I^- and SCN^- at 0.5 mM, $SO_4^{2-}$and ClO_4^-at 1 mM.

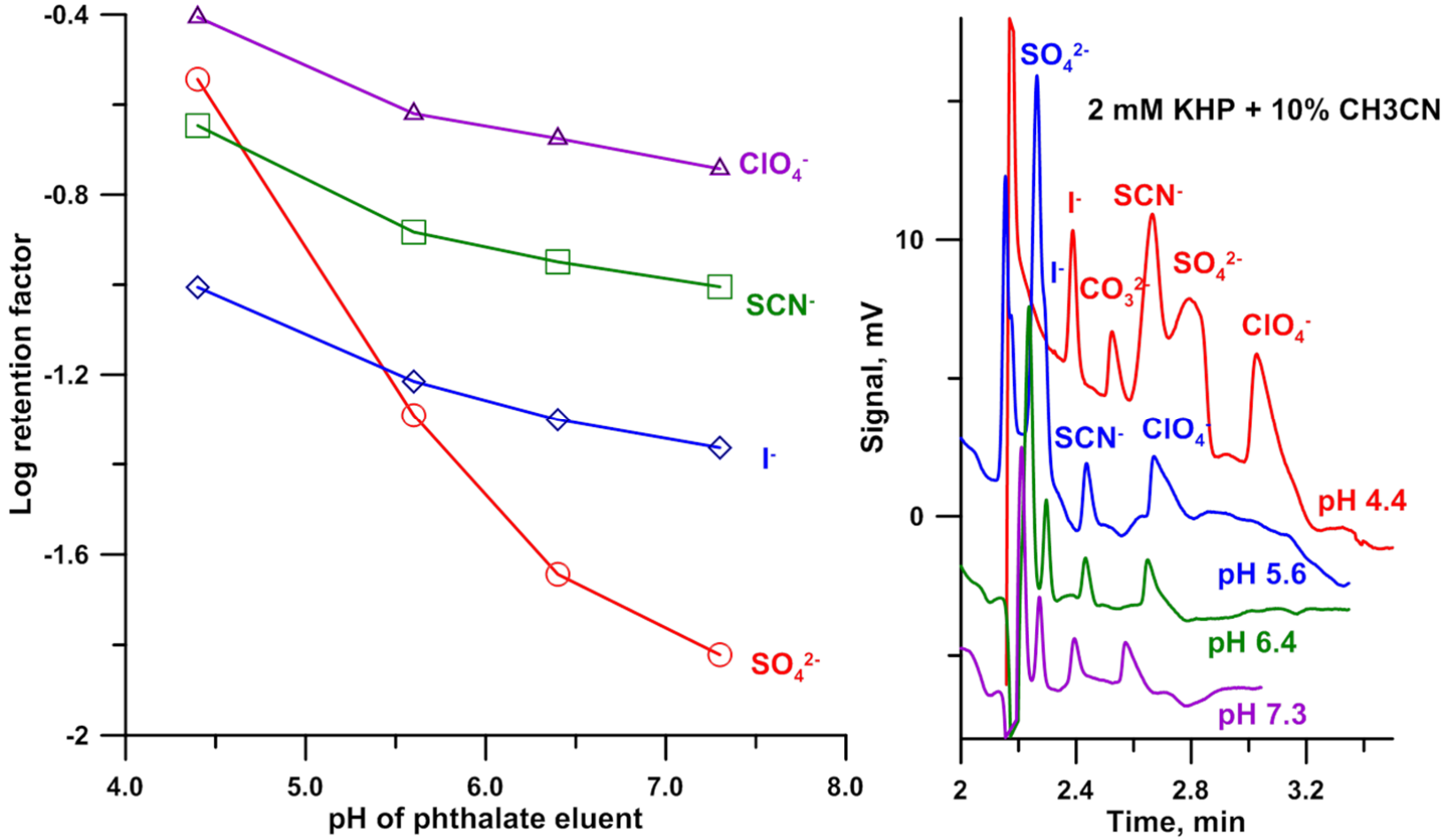

Figure S12. Variations in pH in a 2 mM phthalate eluent containing 10%v/v acetonitrile r =7.2 μm, L = 54 cm, PMMA, injection volume, 0.25 nL; P_{elu} 48 psi, linear velocity 0.40 cm/s (38 nL/min); I^- and SCN^- at 0.5 mM, SO_4^{2-} and ClO_4^- at 1 mM.

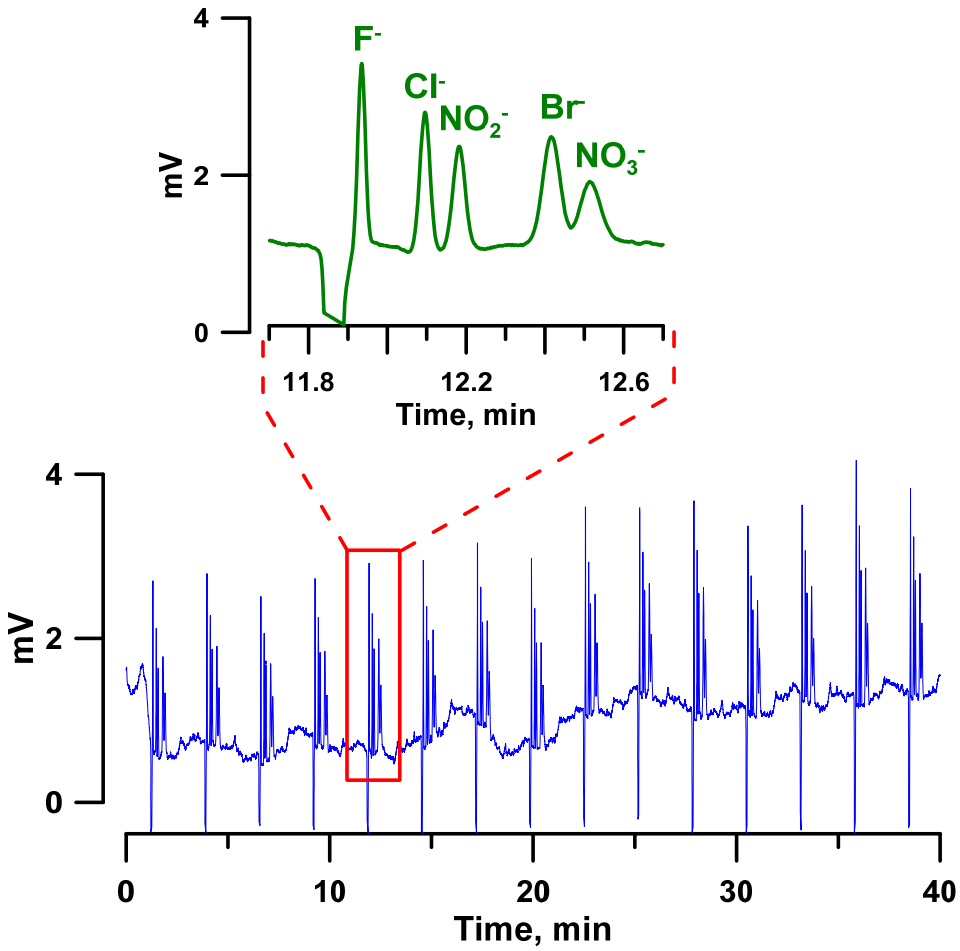

Figure S13. Fast separation (1 min window) of five ions. r = 9.8 μm, L = 80 cm, PMMA , injection volume, 0.48 nL; samples, 200 μM F-; 100 μM of Cl^-, NO_2^-, Br^-, NO_3^-; P_{Elu} =100 psi, linear velocity 1.07 cm/s (191 nL/min).

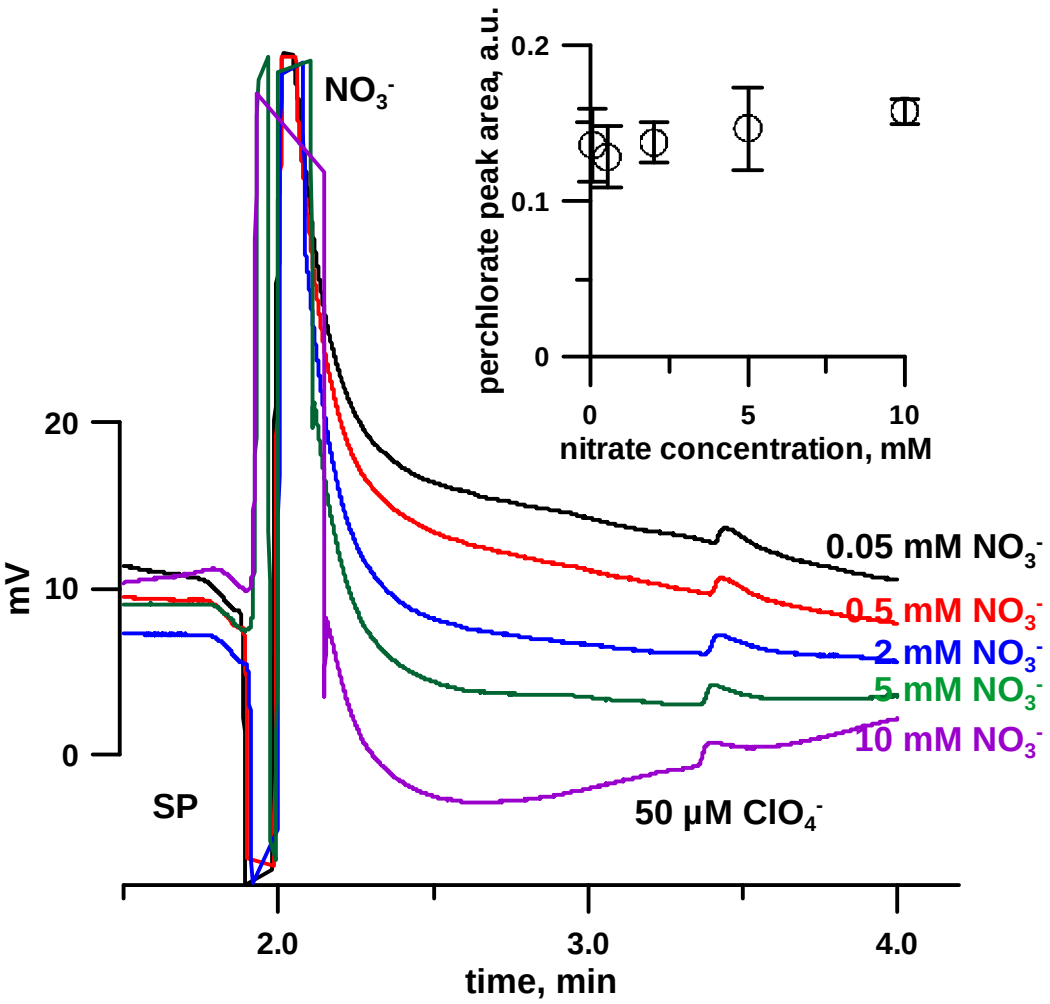

Figure S14. Chromatograms for the separation and quantitation of ClO_4^- in the presence of varying amounts of NO_3^- (up to 200x). The inset shows the constancy of the ClO_4^- peak area. r = 7.3 μm, L = 40 cm, PMMA, 50 μM ClO_4^- in presence of 50 -10,000 μM NO_3^-; 2 mM potassium phthalate (pH 7.4) with 10% (v/v) acetonitrile. Injection volume, 4.11 nL; P_{Elu} =40 psi, linear velocity 0.32 cm/s (32 nL/min).

Baseline Correction procedure. As experiments were done without temperature control and electrical properties such as conductance are highly temperature dependent, at high sensitivities baseline drift was significant. As the periods for a chromatogram were short the drifts were mostly linear (not always) and we simply assumed the baseline drifted linearly from the start (before any peaks) to the end (after complete elution of all analytes). This was then subtracted from the raw data.