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Article

Ion-exclusion/cation-exchange chromatography using dual-ion-exchange groups for simultaneous determination of inorganic ionic nutrients in fertilizer solution samples for the management of hydroponic culture

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Supplementary Materials

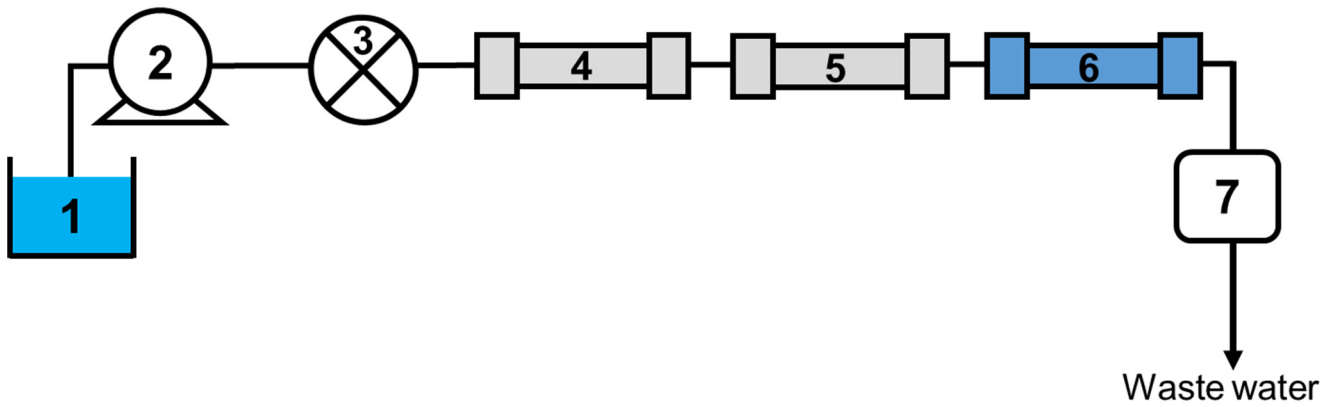

Figure S1 Schematic illustration of the proposed chromatographic system. 1: Eluent bottle, 2: eluent pump, 3: sample injector, 4 and 5: weakly-acidic cation exchange columns, 6: size-exclusion column, 7: conductivity detector (CD).

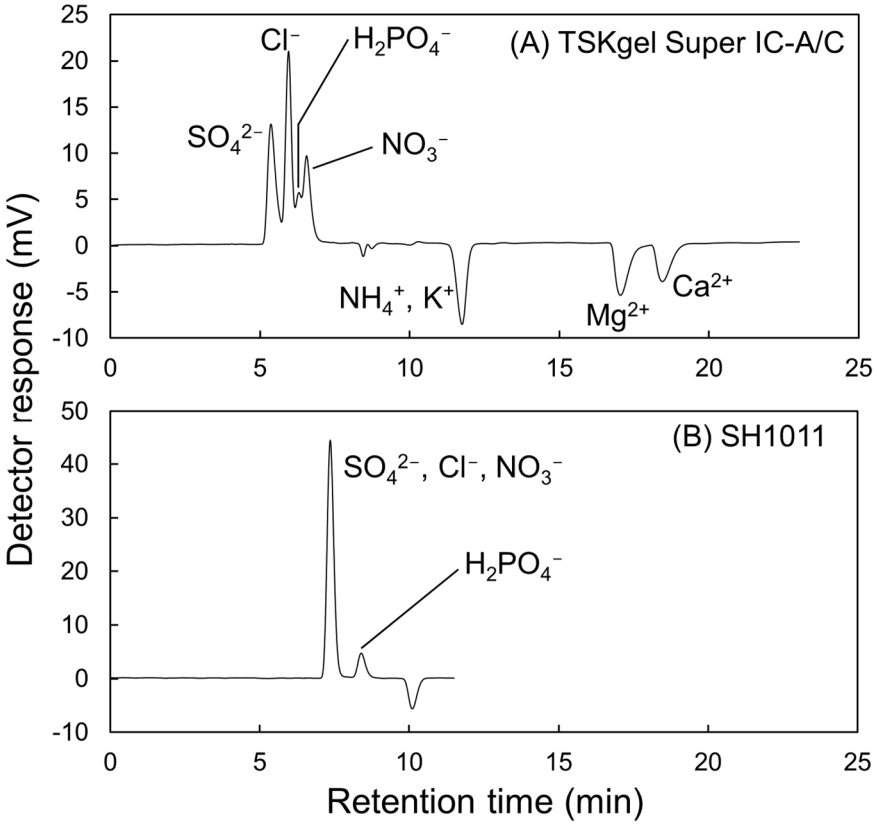

Figure S2 Separation of analyte ions using single ion-exchange group. Separation column (functional group): (A) TSKgel Super IC-A/C (carboxy group), and (B) SUGAR SH1011 (sulfo group); column temperature, 55 °C; injection volume, 5.0 μL; eluent concentration, 5 mM tartaric acid; eluent flow rate, 1.0 mL/min. Injected samples: a mixture of 1.0 mM $MgSO_4$, NaCl, NH_4NO_3, KH_2PO_4, and $CaCl_2$.

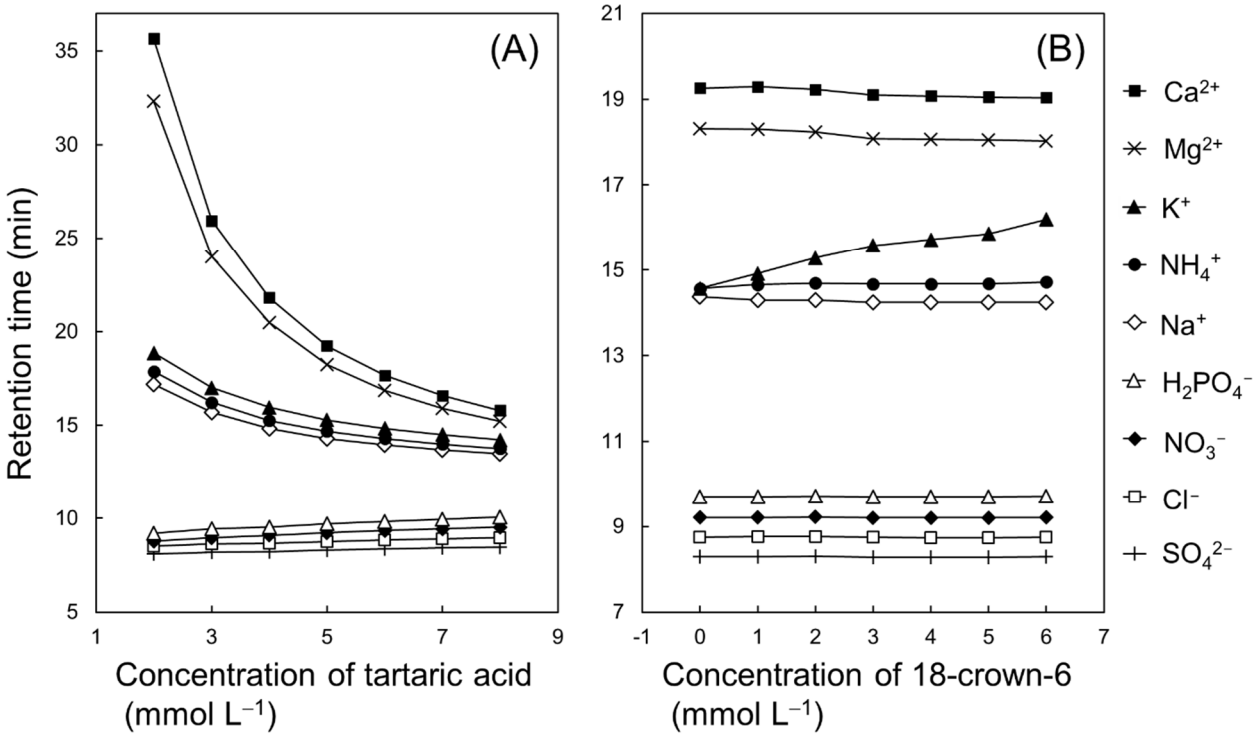

Figure S3 Effect of (A) tartaric acid concentration and (B) 18-crown-6 concentration on the retention time of the analyte ions. The experimental conditions are the same as in Figure S2.

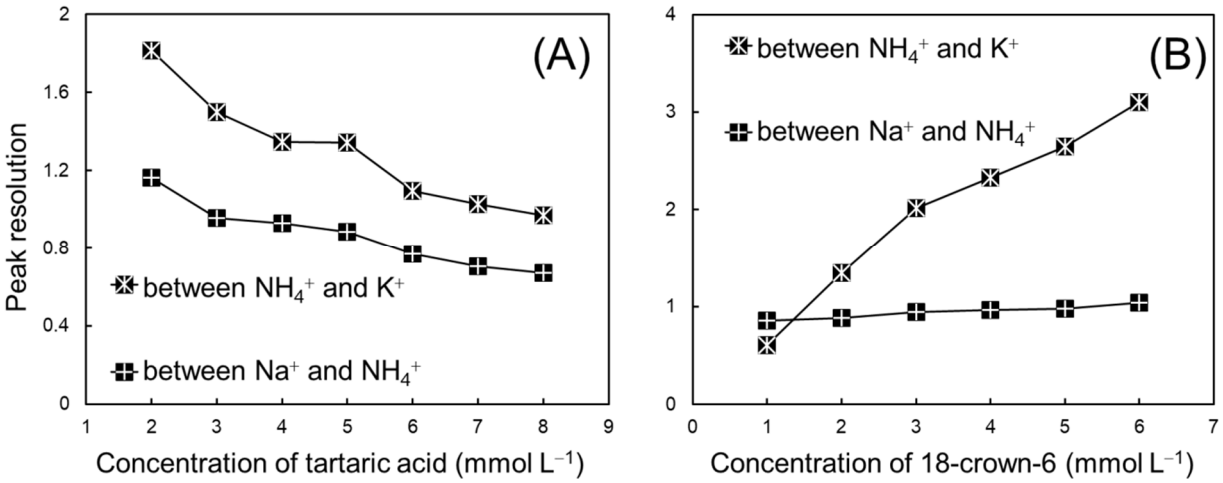

Figure S4 Effect of (A) tartaric acid concentration, and (B) 18-crown-6 concentration on the resolution of Na^+, NH_4^+, and K^+. The experimental conditions are the same as in Figure S3.

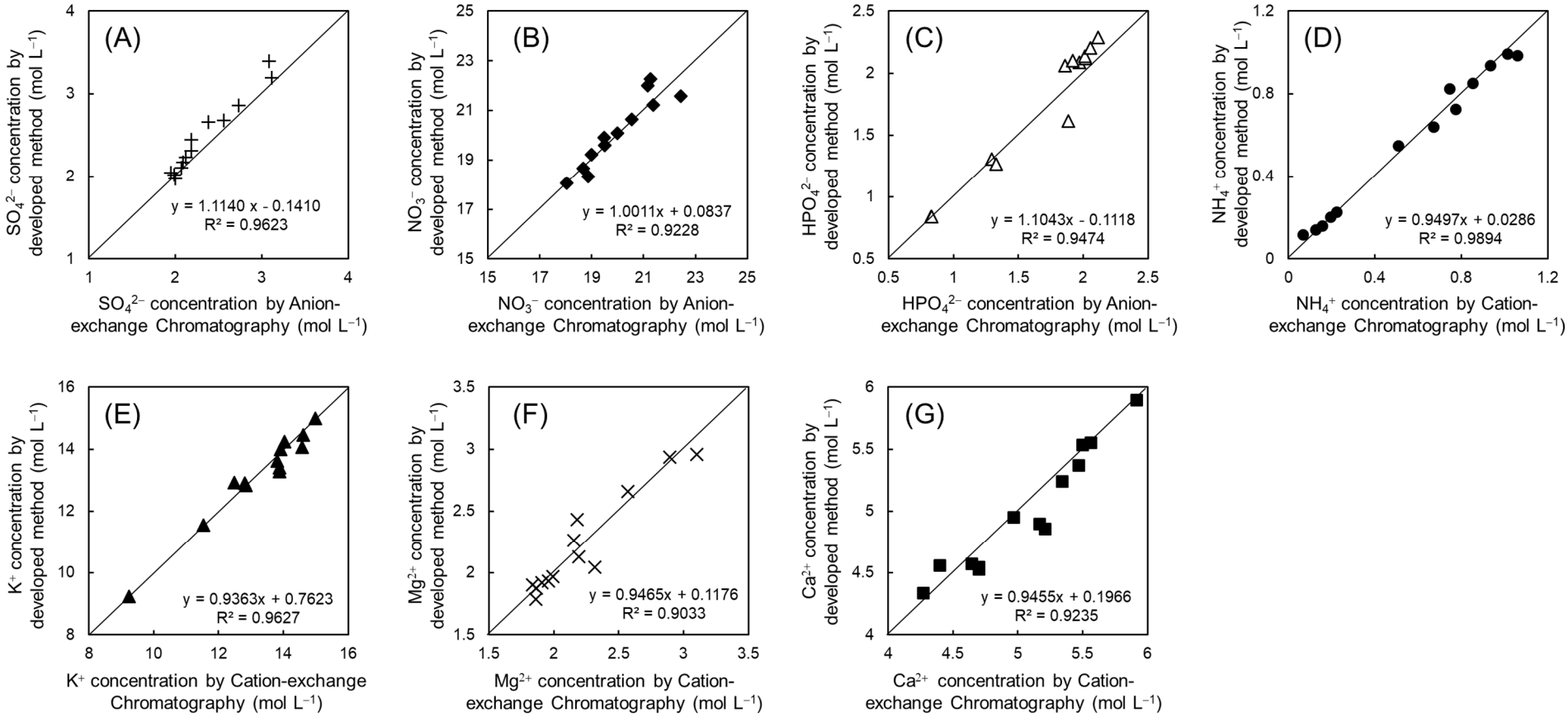

Figure S5 Comparison of the analyte ion concentration obtained from the developed method and the conventional ion-exchange chromatographic method. Analytes: (A) SO_4^{2-}, (B) NO_3^-, (C) $H_2PO_4^-$, (D) NH_4^+, (E) K^+, (F) Mg^{2+}, (G) Ca^{2+}. The experimental conditions were the same as those in Figure 2.

Table S1 Analyte performance under optimal conditions.

Analyte	Retention time, min	RSD, % (n = 5)			LoD, µM (S/N = 3.3)	LoQ, µM (S/N = 10)	Linearity range, mM	Correlation coefficient, R^2	Additional recovery, %
		Retention time	Peak area	Peak height					
SO_4^{2-}	8.27	0.0494	0.243	0.318	7.89	23.9	0.125–1.00	0.9996	104
Cl^-	8.78	0.0465	0.174	0.289	17.3	52.3	0.375–3.00	0.9999	97.6
NO_3^-	9.17	0.0563	0.324	0.353	10.6	32.0	0.125–1.00	0.9998	105
$H_2PO_4^-$	9.72	0.0420	0.709	0.533	22.6	68.4	0.125–1.00	0.9999	96.7
Na^+	14.3	0.0857	2.59	1.93	86.3	262	0.125–1.00	0.9995	101
NH_4^+	14.7	0.0277	2.50	1.72	84.3	255	0.125–1.00	0.9997	102
K^+	15.6	0.0262	0.840	0.856	25.7	77.8	0.125–1.00	0.9999	98.1
Mg^{2+}	18.1	0.0699	2.20	2.75	66.7	202	0.125–1.00	0.9999	105
Ca^{2+}	19.1	0.0838	1.53	2.63	51.5	156	0.125–1.00	0.9981	98.5

The experimental conditions are the same as in Figure 2.

Table S2 Analytical results for 12 fertilizer solution samples collected during the hydroponic cultivation.

	Analyte concentration (mol)											
Date of hydroponic cultivation	0	4	7	9	11	14	16	18	21	23	25	28
Water volume	4.00	3.53	3.39	3.29	3.17	3.00	2.82	2.56	2.04	1.72	3.12	2.24
Height of edible part	0.00	1.29	2.01	2.62	2.70	5.67	6.73	7.71	9.61	10.5	12.3	14.0
SO_4^{2-}	7.79	7.02	7.02	6.87	6.72	6.56	6.17	6.10	5.58	5.30	7.98	6.97
Cl^-	N.D.*	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
NO_3^-	73.3	65.9	66.1	64.1	63.4	61.6	60.3	57.4	43.4	36.4	59.3	40.4
$H_2PO_4^-$	7.74	6.56	6.68	6.31	6.39	6.04	5.80	5.41	2.64	1.42	4.14	1.86
Na^+	N.D.*	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
NH_4^+	3.42	3.02	2.53	3.49	2.46	2.02	1.44	0.577	0.320	0.337	0.401	0.152
K^+	48.9	45.3	47.6	45.7	43.8	41.7	41.1	37.4	30.6	23.9	36.0	20.7
Mg^{2+}	8.29	6.58	6.46	6.45	6.32	6.95	6.18	5.51	5.24	5.34	6.80	6.49
Ca^{2+}	18.1	15.5	15.9	15.3	16.5	15.5	14.0	13.7	11.2	9.4	17.4	13.3

*N.D., not detected

The experimental conditions are the same as those in Figure 3.