Electronic Supplementary Information

Table S1 Applications for iodine speciation analysis using HPLC (or IC) hyphenated with ICP-MS

Mode	Separation column	Mobile phase & flow rate	ICP-MS insrument	Analytes (Retention time, min)	Detection limit (μg L^{-1})	Sample analyzed	Ref.
AEC	G3154A/101 (150 mm×4.6 mm, 10 μm)	20 mM NH_4NO_3 (pH 5.6), 1.0 mL min^{-1}	Agilent 7500c Injection: 50 μL	IO_3^-(2.0), I^-(8.8)	Unkown	Microalgae	1
AEC	ICS-A23 (75 mm× 4.6 mm)	30 mM NH_4NO_3 (pH 8.0), 0.8 mL min^{-1}	Agilent 7500a Injection: 1 mL	IO_3^-(2.2), I^-(8.8)	IO_3^-(0.008), I^-(0.012)	Marine aerosol	2
AEC	IonPac AS 19 (250 mm×4 mm, 7.5 μm)	45 mM KOH, 1.0 mL min^{-1}	Agilent 7500ce Injection: 25 μL	IO_3^-(2.6), I^-(5.2)	Unkown	Edible salt	3
AEC	ICS-A23 (75 mm× 4.6 mm)	30 mM $(NH_4)_2CO_3$ (pH 8.0), 0.8 mL min^{-1}	Agilent 7500a Injection: 1 mL	IO_3^-(2.2), I^-(9.0)	IO_3^-(0.008), I^-(0.012)	Drinking water	4
AEC	ICS-A23 (75 mm× 4.6 mm)	50 mM $(NH_4)_2CO_3$ (pH 8.0), 0.8 mL min^{-1}	Agilent 7500a Injection: 1 mL	IO_3^-(2.1), I^-(8.7)	IO_3^-(0.008), I^-(0.012)	Atmospheric aerosol	5
AEC	ICS-A23 (75 mm× 4.6 mm)	30 mM $(NH_4)_2CO_3$ (pH 9.4), 0.8 mL min^{-1}	Agilent 7500a Injection: 1 mL	IO_3^-(1.7), I^-(8.8)	IO_3^-(0.025), I^-(0.025)	Groundwater	6
AEC	ICS-A23 (75 mm× 4.6 mm)	30 mM $(NH_4)_2CO_3$ (pH 9.4), 0.8 mL min^{-1}	Agilent 7500a Injection: 1 mL	IO_3^-(1.7), I^-(8.8)	IO_3^-(0.035), I^-(0.025)	Underground water	7
AEC	AS11-HC (4.0 mm×250 mm)	A: H_2O; B: 200 mM NH_4NO_3, 1.0 mL min^{-1} Gradient: 0-3 min, 15%B; 3-8min, 15%B→50%B; 8-26min, 50%B→100%B; 26-36min, 100%B; 36-41min, 100%B→15%B; 41-43min, 15%B.	Elan DRC-e Injection: 100 μL	IO_3^-(2.6), I^-(5.3), MIAA(9.7), CIAA(15.2), DIAA(23.4)	IO_3^-(0.1), I^-(0.1), MIAA(0.1), CIAA(0.2), DIAA(0.2)	Drinking water, groundwater, surface water, and swimming pool water	8
AEC	PRP-X100 (150 mm×4.1 mm, 10 μm)	A: 15 mM NH_4NO_3 (pH 10.0), B: 100 mM NH_4NO_3 (pH 10.0), 1.5 mL min^{-1} Gradient: 0-1.5 min, 100%A; 1.5-3.5 min, 100%A→100%B; 3.5-9 min, 100%B	Elan 6100 DRC Injection: 200 μL	IO_3^-(2.3), I^-(7.2)	IO_3^-(0.001), I^-(0.002)	Tap water, urine, seaweed and milk powder	9
AEC	G3268A (30 mm×4.6 mm, 5 μm)	60 mM $(NH_4)_2CO_3$ (pH 9.4), 1.0 mL min^{-1}	Agilent HP4500 Injection: 20 μL	IO_3^-(1.6), I^-(4.1)	IO_3^-(0.1), I^-(0.5)	Marine aerosol	10

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Mode	Separation column	Mobile phase & flow rate	ICP-MS insrument	Analytes (Retention time, min)	Detection limit (μg L^{-1})	Sample analyzed	Ref.
AEC	Dionex AS16 (250 mm×4.0 mm, 9 μm)	35 mM NaOH, 0.9 mL min^{-1}	Perkin Elmer Injection: unkown	IO_3^-(4.0), I^-(12.7)	IO_3^-(0.01), I^-(0.02)	Rain, snow and aerosol	11
AEC	Dionex AS16 (250 mm×4.0 mm, 9 μm)	35 mM NaOH, 0.9 mL min^{-1}	Perkin Elmer Injection: unkown	IO_3^-(4.3), I^-(9.3)	IO_3^-(0.04), I^-(0.04)	Snow	12
AEC	Dionex AS16 (250 mm×4.0 mm, 9 μm)	35 mM NaOH, 0.9 mL min^{-1}	Perkin Elmer Injection: unkown	IO_3^-(4.3), I^-(9.4)	IO_3^-(0.01), I^-(0.02)	Snow	13
AEC	Dionex AS16 (250 mm×4.0 mm, 9 μm)	35 mM NaOH, 0.9 mL min^{-1}	Perkin Elmer Injection: unkown	IO_3^-(3.7), I^-(9.8)	IO_3^-(0.01), I^-(0.02)	Rain	13
AEC	ICS-A23 (75 mm× 4.6 mm)	30 mM $(NH_4)_2CO_3$ (pH 9.4), 0.8-1.0 mL min^{-1}	Yokogawa PMS-2000, Agilent HP4500 or 7500 Injection: 50-200 μL	IO_3^-(1.8), I^-(7.1)	IO_3^- and I^-(0.1-1.0)	Rain, riverwater, brine, soil	14
AEC	IonPac AS 11 (250 mm×2.0 mm, 13 μm)	5 mM NaOH, 0.3 mL min^{-1}	Agilent 7500ce Injection: 20 μL	IO_3^-(1.9), I^-(6.7)	IO_3^-(0.12), I^-(0.2)	Seaweed	15
AEC	Self-made PS/DVB-type (100 mm×4 mm)	30 mM NH_4NO_3 (pH 7.1), 1.0 mL min^{-1}	Thermo VG PQ2+ Injection: 585 μL	IO_3^-(1.9), I^-(10.9)	IO_3^-(0.045), I^-(0.15)	Standard mixture solution	16
AEC	ICS-A23 (75 mm× 4.6 mm)	30 mM $(NH_4)_2CO_3$ (pH 9.2), 1.0 mL min^{-1}	Agilent HP4500 Injection: 500 μL	IO_3^-(2.2), I^-(7.5)	IO_3^-(0.034), I^-(0.051)	Raw and ozonized water	17
AEC	IonPac AG 11 (50 mm×4.0 mm, 13 μm)	8 mM $(NH_4)_2CO_3$, 1.5 mL min^{-1}	Thermo X series Injection: 20 μL	IO_3^-(0.8), I^-(2.6)	IO_3^-(0.015), I^-(0.081)	Edible salt	18
AEC	IonPac AS 7 (250 mm×4.0 mm)	175 mM NH_4NO_3 (pH 3.8) in 15% Methanol Gradient: 0-8 min, 0.5 mL min^{-1}; 8-9 min, 0.5→1.5 mL min^{-1}; 9-17 min, 1.5 mL min^{-1}; 17-18 min, 1.5→0.5 mL min^{-1}; 18-20 min, 0.5 mL min^{-1}	Thermo X series Injection: 50 μL	IO_3^-(3.1), MIT(4.9), DIT(7.1), I^-(14.6)	IO_3^-(0.09), MIT(0.06), DIT(0.09), I^-(0.08)	Seaweed	19
AEC	G3154A/101 (150 mm×4.6 mm, 10 μm)	20 mM NH_4NO_3 (pH 5.6), 1.0 mL min^{-1}	Agilent 7500c Injection: 10 μL	IO_3^-(2.4), I^-(12.8)	IO_3^-(1.5), I^-(2.0)	Seawater	20
RPC	Shiseido C_{18} SG120 (35 mm×4.6 mm, 5 μm)	A: 100 mM $(NH_4)_2HPO_4$ -0.1%H_3PO_4 (pH 7.3) in 10% MeOH for I^-, MIT and DIT; B: 100 mM $(NH_4)_2HPO_4$ -0.1%H_3PO_4 (pH 7.3) in 50% MeOH for T3,rT3 and T4. 1.0 mL min^{-1}	Seiko SPQ-6100 Injection: 20 μL	I^-(1.5), MIT(2.7), DIT(9.3) I^-+MIT+DIT(1.6), T3(4.1), rT3(6.4), T4(8.6)	I^-(1.7), MIT(2.2), DIT(3.5) T3(4.2), rT3(6.0), T4(6.5)	Enzymatic digest of bovine thyroglobulin	21

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Mode	Separation column	Mobile phase & flow rate	ICP-MS insrument	Analytes (Retention time, min)	Detection limit (μg L^{-1})	Sample analyzed	Ref.
RPC	Asahipak GS-220 7C (100 mm×7.5 mm)	50 mM malonic acid - 37.5 mM TMAH (pH 6.9), 1.0 mL min^{-1}	Thermo Element 2 Injection: 20 μL	IO_3^-(2.6), I^-(5.3)	IO_3^-(0.02), I^-(0.03)	Seawater	22
RPC	Alltima C_{18} (150 mm×4.6 mm, 5 μm)	A: 10 mM Tris-HCl (pH 7.3); B: 10 mM Tris-HCl (pH 7.3) in 50% MeOH. 0.5 mL min^{-1} Gradient: 0-5 min, 100%A→45%B; 5-8 min, 45%B→85%B; 8-10 min, 85%B→100%B; 10-40 min, 100%B	Agilent 7500ce Injection: 50 μL	I^-(2.9), MIT(9.8), DIT(12.1)	Unkown	Seaweed	15
RPC	Capcell-C_{18} (35 mm×4.6 mm, 7.5 μm)	A: 10 mM Tris-HCl (pH 7.3) in 1% MeOH; B: 10 mM Tris-HCl (pH 7.6) in 50% MeOH. 0.85 mL min^{-1} Gradient: 0-1 min, 100%A; 1-2 min, 20%B; 2-5 min, 20%B→45%B; 5-7 min, 45%B→85%B; 7-11 min, 85%B→100%B; 11-26 min, 100%B	Elan 5000 Injection: 100 μL	I^-(1.1), DIT(4.3), MIT(4.6), rT3(18.8), T3(19.9), T4(24.5)	Unkown	Human serum	23
RPC	Capcell-C_{18} (35 mm×4.6 mm, 7.5 μm)	A: 10 mM Tris-HCl (pH 7.3) in 1% MeOH; B: 10 mM Tris-HCl (pH 7.6) in 50% MeOH. 0.85 mL min^{-1} Gradient: 0-1 min, 100%A; 1-2 min, 20%B; 2-6 min, 20%B→45%B; 6-8 min, 45%B→85%B; 8-12 min, 85%B→100%B; 12-26 min, 100%B	Elan 5000 Injection: 100 μL	I^-(1.2), DIT(4.2), MIT(4.8), rT3(18.7), T3(20.8), T4(24.4)	I^-(0.08), DIT(0.1), MIT(0.08), rT3(1.2), T3(1.5), T4(0.8)	Urine	24
RPC	Capcell-C_{18} (35 mm×4.6 mm, 7.5 μm)	A: 10 mM Tris-HCl (pH 7.3) in 1% MeOH; B: 10 mM Tris-HCl (pH 7.6) in 50% MeOH. 0.75 mL min^{-1} Gradient: 0-1 min, 100%A; 1-2 min, 20%B; 2-5 min, 20%B→45%B; 5-7 min, 45%B→85%B; 7-11 min, 85%B→100%B; 11-26 min, 100%B	Elan 5000 Injection: 100 μL	I^-(1.2), DIT(4.2), MIT(4.8), rT3(18.7), T3(20.8), T4(24.4)	I^-(0.08), DIT(0.1), MIT(0.08), rT3(1.2), T3(1.5), T4(0.8)	Zebrafish	25
RPC	Zorbax XDB-C_8 (150 mm×4.6 mm)	A: 0.2% m/m CH_3COOH (pH 2.7); B: 0.2% m/m CH_3COOH (pH 2.3) in MeOH. 0.85 mL min^{-1} Gradient: 0-3 min, 100%A; 3-3.5 min, 100%A→90%A; 3.5-6 min, 10%B; 6-6.5 min, 10%B→20%B; 6.5-8 min, 20%B; 8-8.5 min, 20%B→40%B; 8.5-14 min, 40%B; 14-15 min, 40%B→0%B; 15-23 min, 100%A	Thermo X series Injection: 50 μL	I^-+IO_3^-(3.9), MIT(14.5), DIT(17.9)	I^-+IO_3^-(0.058), MIT(0.035), DIT(0.025)	Seaweed	19
SEC	Superdex-75 (300 mm×10 mm, 13 μm)	30 mM Tris-HCl (pH 7.0), 0.75 mL min^{-1}	Agilent 7500c Injection: 50 μL	TG(10.6), T3(28.8), I^-(39.2)	Unkown	Microalgae	1

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Mode	Separation column	Mobile phase & flow rate	ICP-MS insrument	Analytes (Retention time, min)	Detection limit (μg L^{-1})	Sample analyzed	Ref.
SEC	TSK G3000PW (300 mm×7.5 mm, 10 μm)	50 mM $(NH_4)_2CO_3$ (pH 9.4), 0.8 mL min^{-1}	Agilent 7500a Injection: 25 μL	IO_3^-(10.6), I^-(17.4)	Unkown	Atmospheric aerosol	5
SEC	TSK G3000PW (300 mm×7.5 mm, 10 μm)	30 mM $(NH_4)_2CO_3$ (pH 9.4), 0.8 mL min^{-1}	Agilent 7500a Injection: 25 μL	IO_3^-(10.3), I^-(15.5)	Unkown	Groundwater	6
SEC	Superdex-75/200 (300 mm×10 mm, 13 μm)	30 mM Tris-HCl (pH 7.0). 0.75 mL min^{-1}	Elan 6000 Injection: 100 μL	TG(10.3), T3(28.4), I^-(36.1)	TG(1.0), T3(1.0), I^-(1.0)	milk	26

Abbreviations: monoiodoacetic acid (MIAA); chloroiodoacetic acid (CIAA); diiodoacetic acid (DIAA); 3-iodotyrosine (MIT); 3, 5-diiodotyrosine (DIT); tri-iodothyronine (T3); reversed tri-iodothyronine (rT3); tetra-iodothyronine (T4); thyroglobuline (TG); anion exchange chromatography (AEC); reversed phase chromatography (RPC); size exclusion chromatography (SEC); tetramethylammonium hydroxide (TMAH).

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