Supporting information

Sensitive online speciation analysis of arsenic in biological samples by ambient mass spectrometry

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Supporting Information

Table of Contents

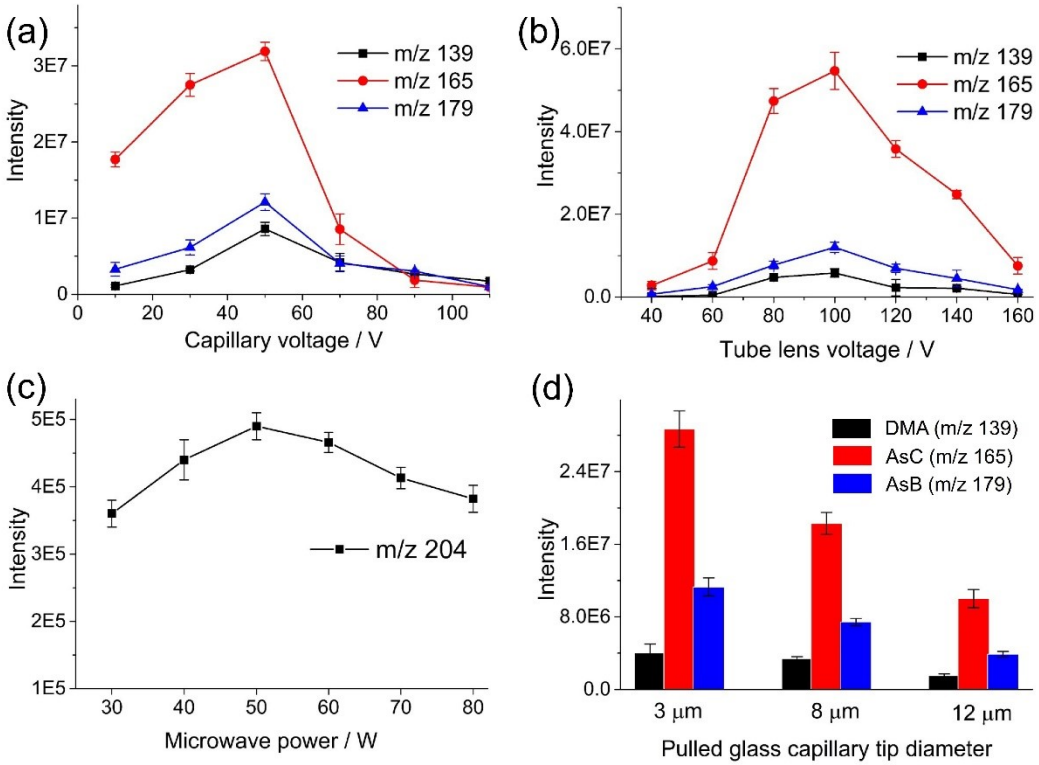

Figure S1 (a),(b) Influence of capillary voltage of MS and tube lens voltage on signal intensity of DMA (m/z 139), AsC (m/z 165) and AsB (m/z 179) in positive ion mode; (c) Influence of microwave power on signal intensity of iAs ($H_3AsO_4 + NO_3^-$, m/z 204) in negative ion mode; (d) Influence of the pulled glass capillary tip diameter on signal intensity of DMA (m/z 139), AsC (m/z 165) and AsC (m/z 179).

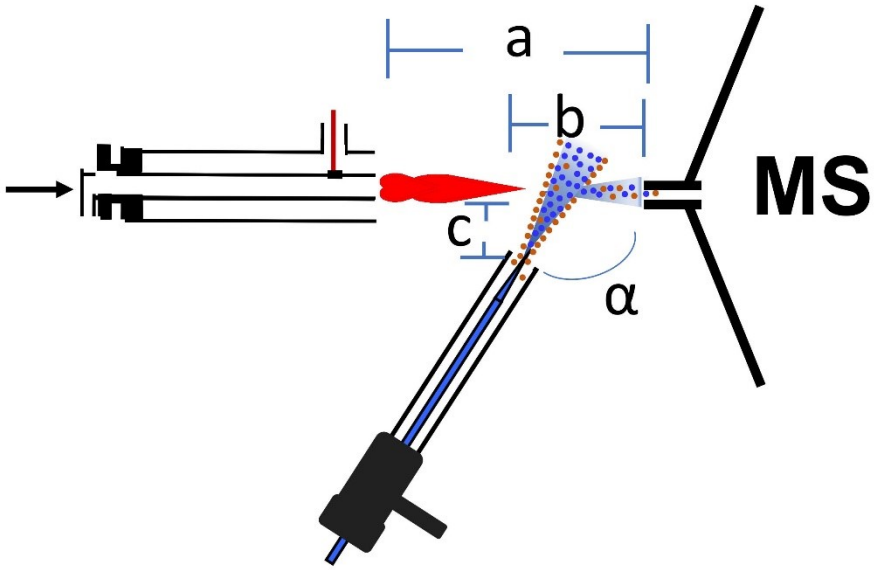

Figure S2 Schematic illustration of the setup of sample introduction system. The distance ***a*** between the MPT tip and the ion entrance of the LTQ instrument was 2.0 cm; the distance ***b*** between the tips of MPT plasma and MS inlet was 1.0 cm. The distance ***c*** between sample introduction device and MPT plasma was 0.5 cm. The angle ***α*** formed between sample introduction device and the axis of the sampling cone was 120°.

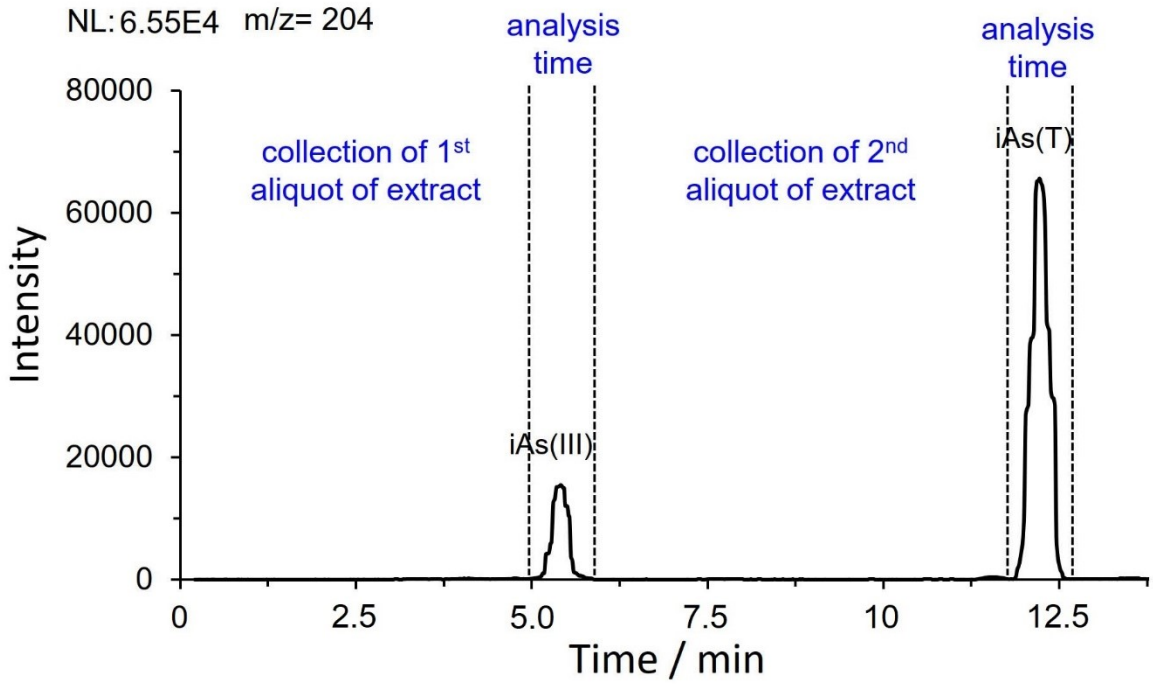

Figure S3 Extracted ion chromatogram of m/z 204 from online analysis of crayfish tissue sample (muscle) by EESI-HG-MPT-MS for quantification of inorganic As species. Each peak means one analysis of the online accumulated extracts (*e.g.* 200 μL). Both iAs(III) and total inorganic As (iAs(T)) were detected under pH of 6.6, with citrate acid-sodium citrate as buffer solution. The concentration of As(V) was calculated by subtraction of iAs(T) and As(III).

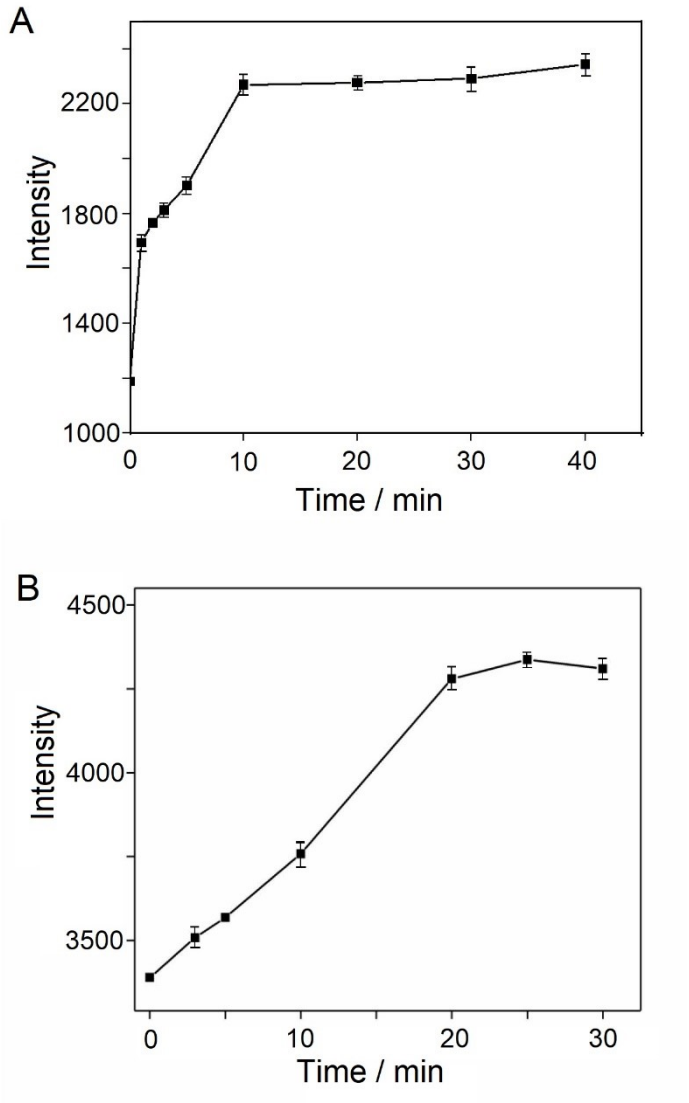

Figure S4 Pre-reduction of iAs(V) by KI-ascorbic acid (10%-5%) (A) and L-cysteine (5%) (B) at pH around 6.6. Compared with thioglycolic acid (TGA, 2%) as reductant, higher concentrations of reagents and longer reaction time (at least 10 min) were required when using reductants of KI or L-cysteine.

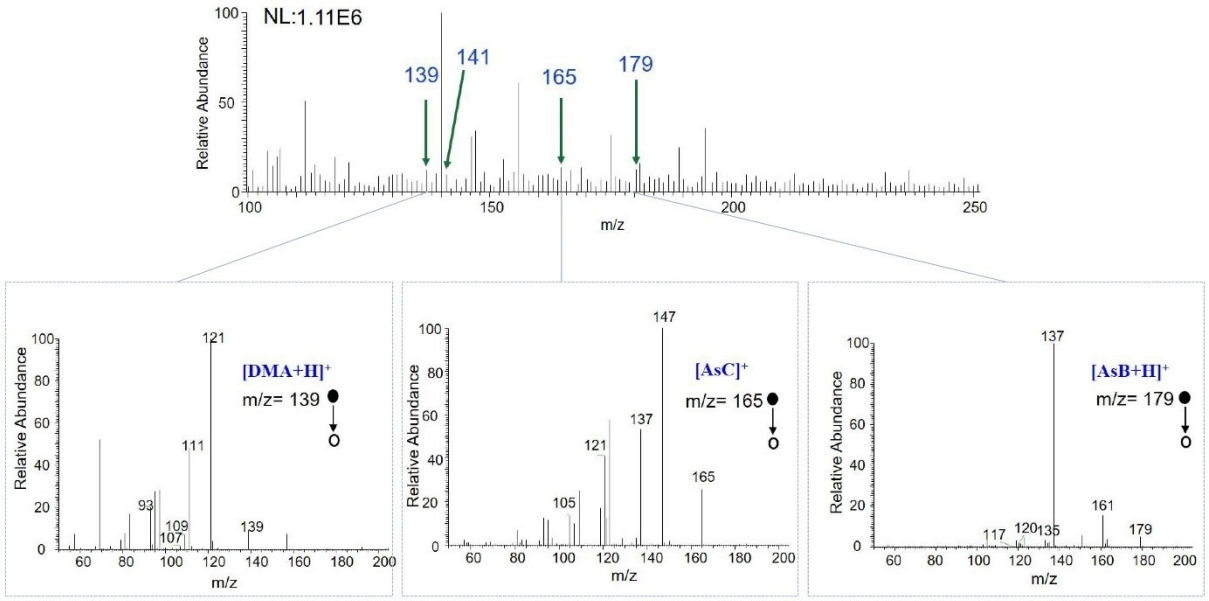

Figure S5 Online direct speciation analysis of As in raw crayfish sample (muscle) by EESI-HG-MPT-MS. Various As species were detected in positive ion mode. DMA (m/z 139), AsC (m/z 165), AsB (m/z 179). CID analysis showed that m/z 139 generated characteristic fragmented ions at m/z 93, 107, 109, 111 and 121, with m/z 121 as the main fragment. m/z 165 generated the characteristic fragmented ions at m/z 105, 121, 137 and 147, with m/z 147 and 121 as main ions. m/z 179 yielded fragmented ions at m/z 117, 120, 135, 137 and 161, with m/z 120, 137 and 161 as main peaks.

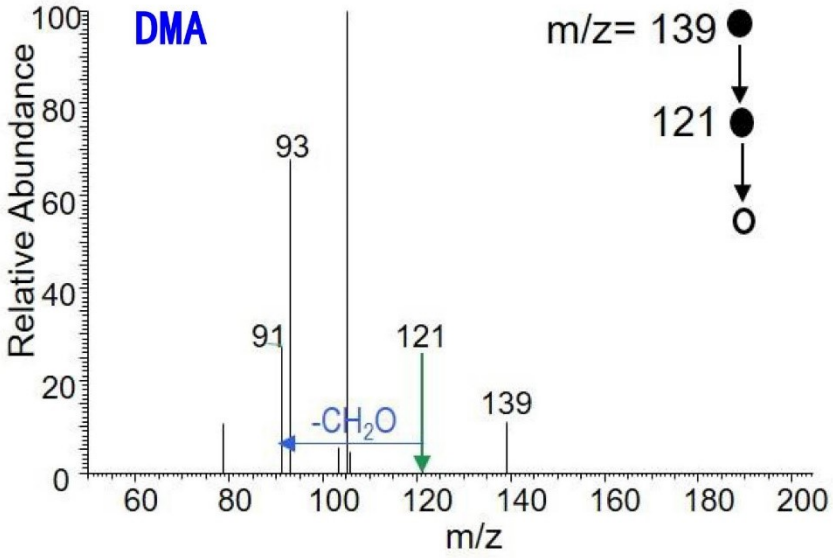

Figure S6 CID analysis of DMA from online direct analysis of raw crayfish sample (muscle) by EESI-HG-MPT-MS. Further CID analysis of m/z 139→121showed that m/z 121 mainly generated m/z 91 by losing -CH_2O.

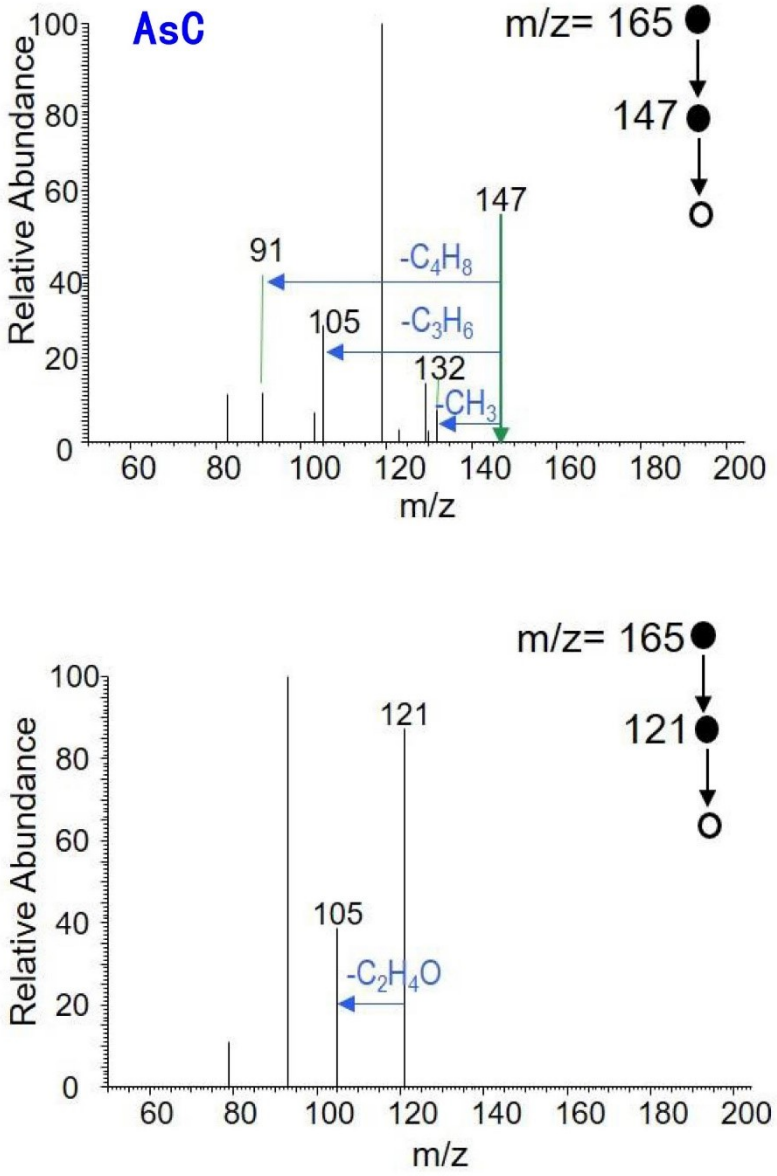

Figure S7 CID analysis of AsC from online direct analysis of raw crayfish sample (muscle) by EESI-HG-MPT-MS. Further CID analysis of m/z 165→147 and 165→121 showed that m/z 147 mainly produced ions of m/z 91, 105 and 132 by losing -C_4H_8, -C_3H_6 and -CH_3, respectively. m/z 121 mainly generated m/z 105 by losing -C_2H_4O.

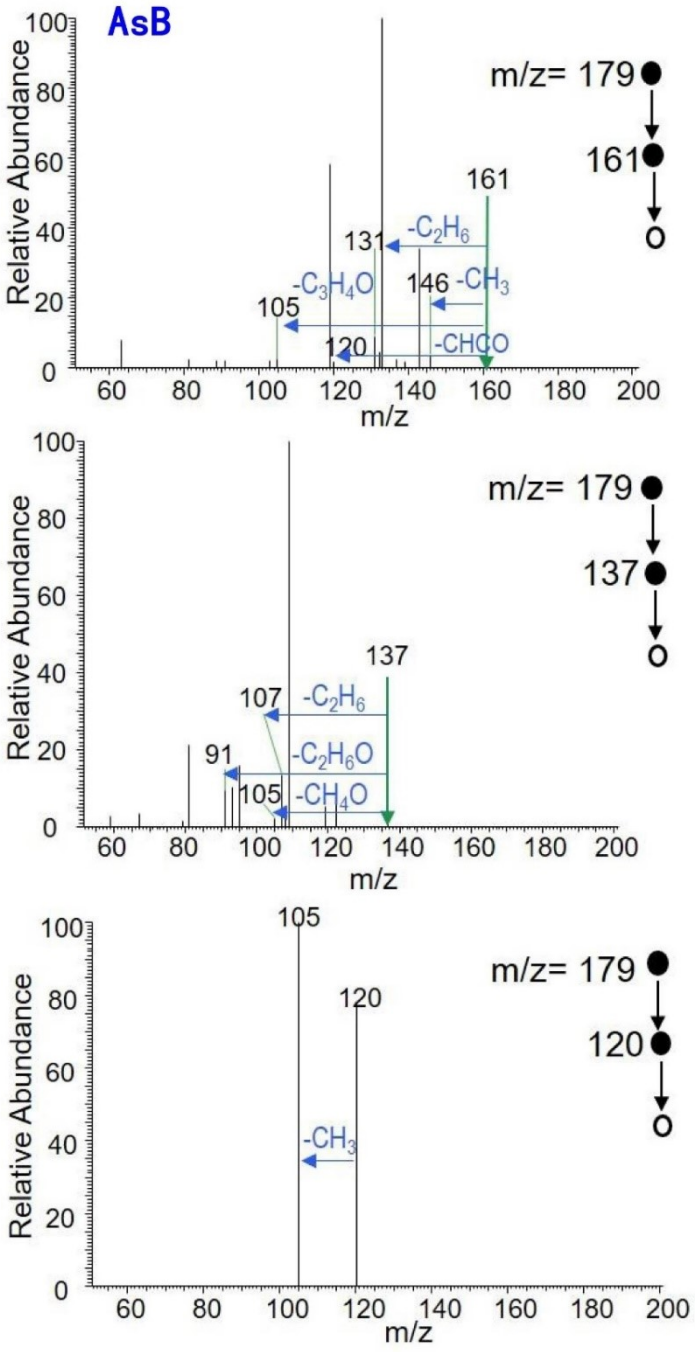

Figure S8 CID analysis of AsB from online direct analysis of raw crayfish sample (muscle) by EESI-HG-MPT-MS. Further CID analysis of m/z 179→161, 179→137 and 179→120 showed that m/z 161 mainly produced fragmented ions of m/z 105, 120,131 and 146 by losing $-C_3H_4O$, -CHCO, $-C_2H_6$ and $-CH_3$, respectively; m/z 137 mainly generated ions of m/z 91, 105 and 107 by losing $-C_2H_6O$, $-CH_4O$, and $-C_2H_6$, respectively; m/z mainly generated characteristic ion of m/z 105 by losing $-CH_3$.

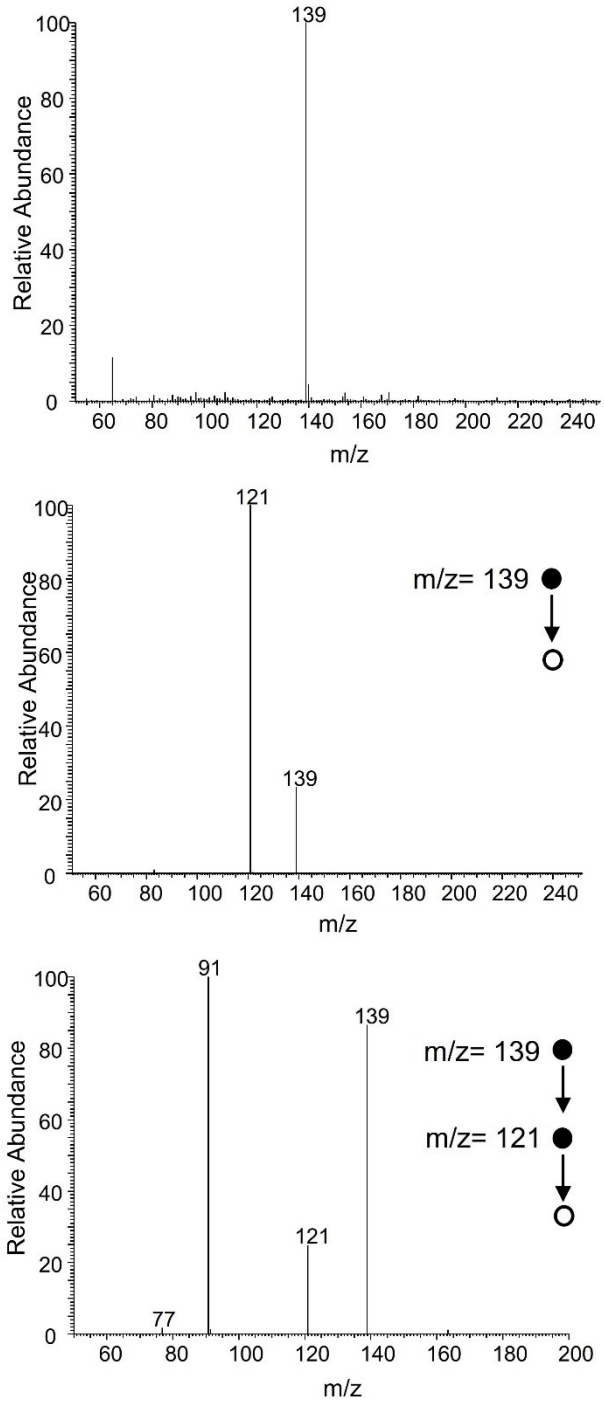

Figure S9 Direct analysis of DMA standard (1.0 mg/L)by EESI-HG-MPT-MS in positive ion mode. CID analysis showed that m/z 139 produced the characteristic fragmented ion of m/z 121, and m/z 121 further generated fragmented ion of m/z 91.

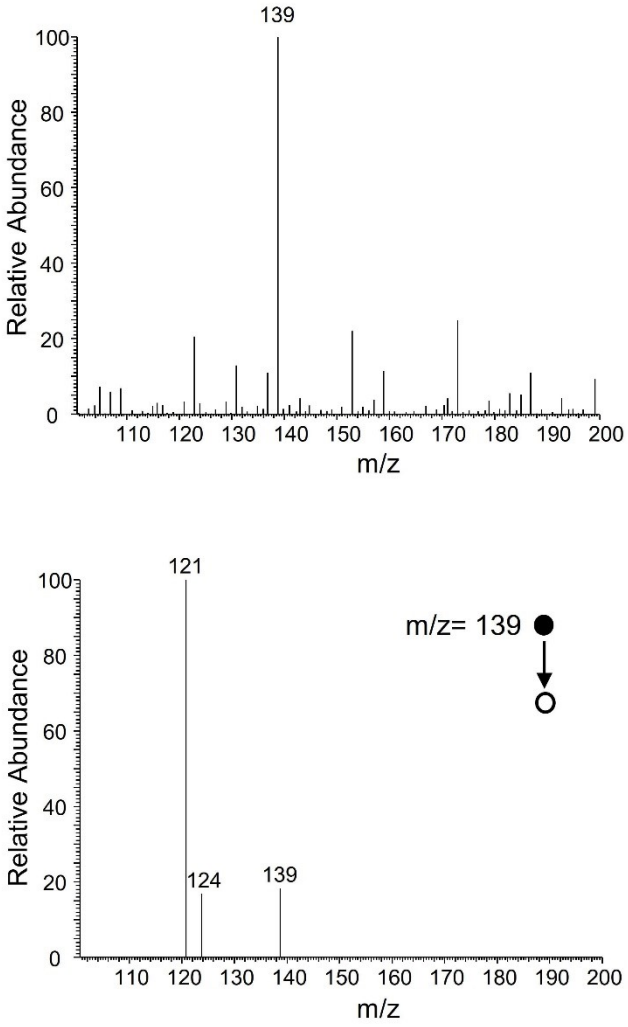

Figure S10 Direct analysis of MMA standard (1.0 mg/L)by EESI-HG-MPT-MS in negative ion mode. CID analysis showed that m/z 139 ($[MMA-H]^-$) produced the characteristic fragmented ion of m/z 121.

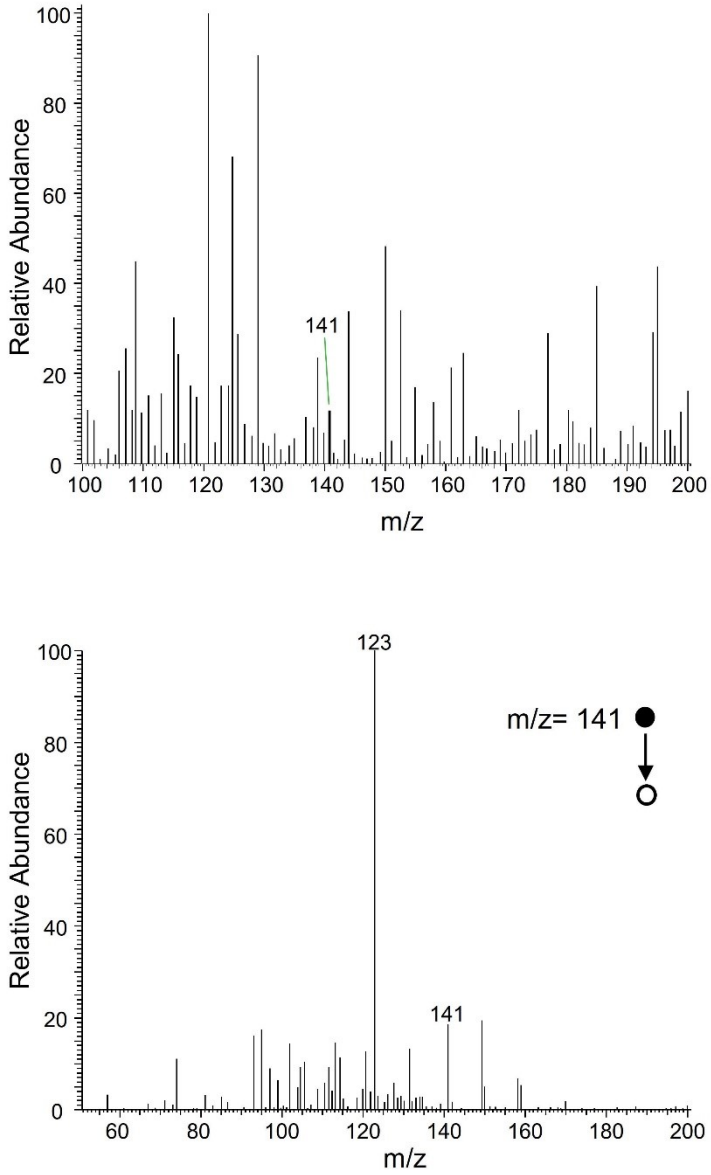

Figure S11 Direct analysis of MMA standard (1.0 mg/L)by EESI-HG-MPT-MS in positive ion mode. CID analysis showed that m/z 141 ($[MMA+H]^+$) produced the characteristic fragmented ion of m/z 123.

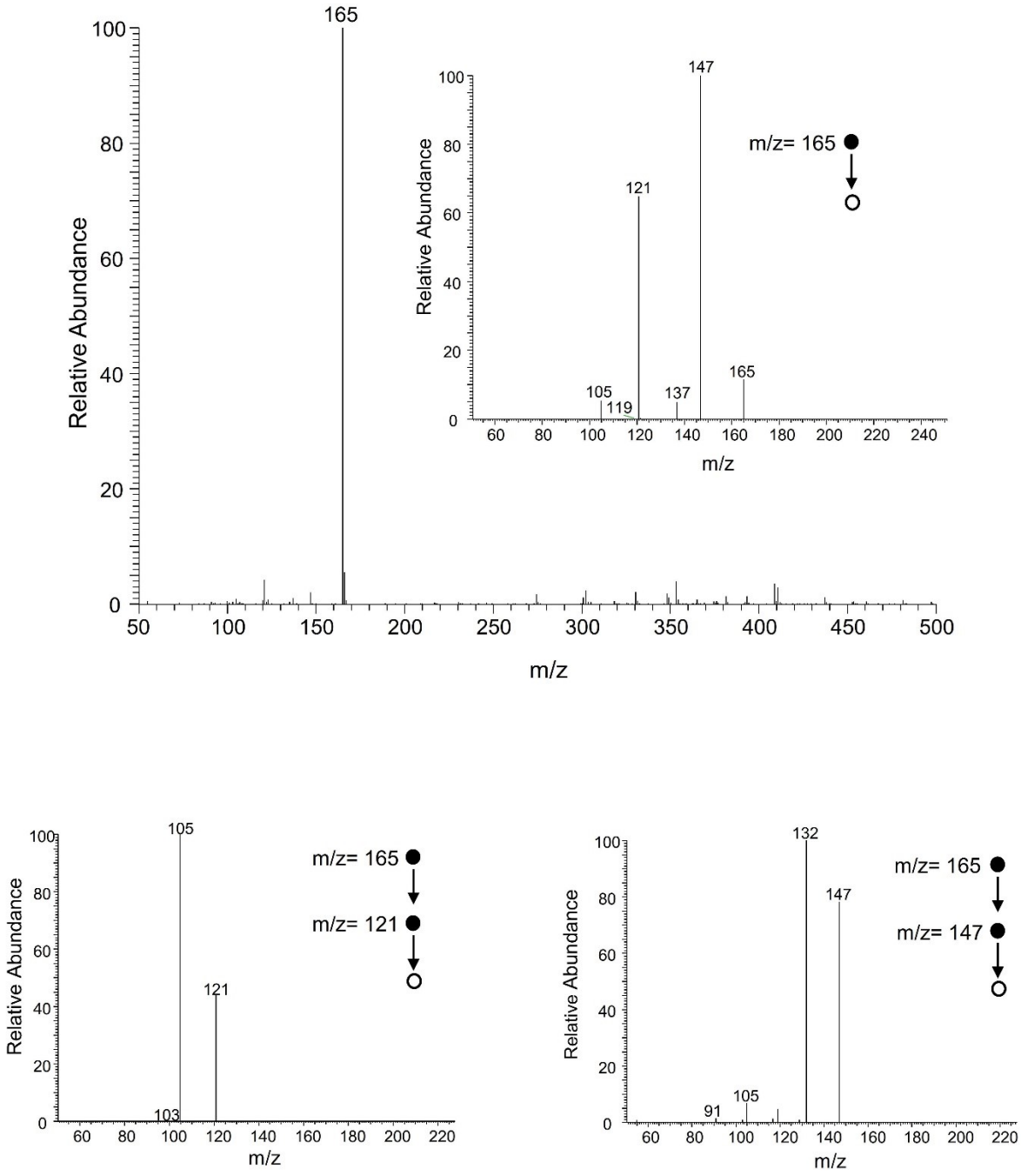

Figure S12 Direct analysis of AsC standard (1.0 mg/L)by EESI-HG-MPT-MS in positive ion mode. CID analysis showed that m/z 165 ($[AsC]^+$) produced the characteristic fragmented ion of m/z 147, 137, 121, 119 and 105, with m/z 121 and 147 as the main fragments. Further CID analysis showed that m/z 121 generated m/z 105, and m/z 147 generated m/z 91, 105 and 132.

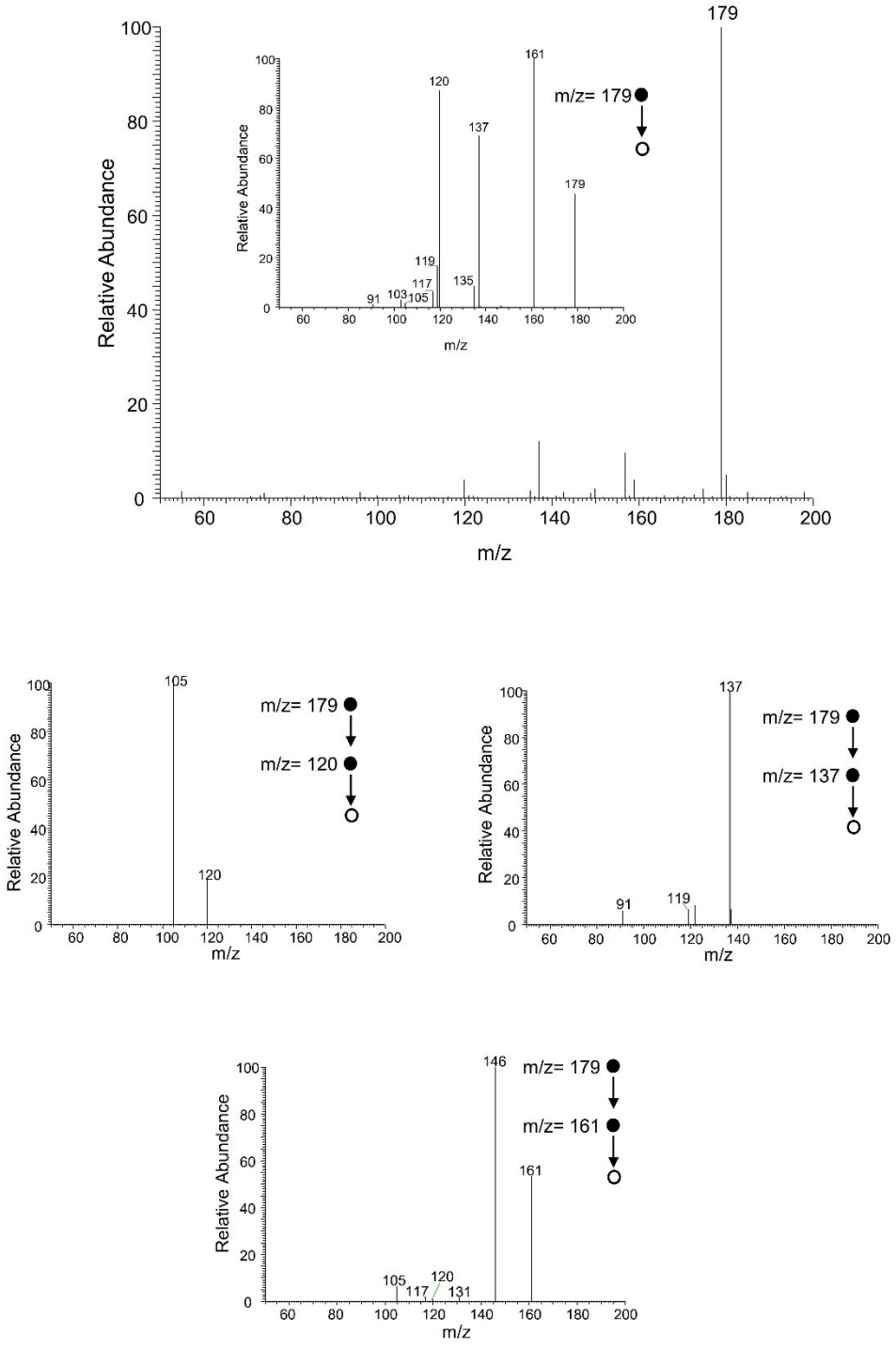

Figure S13 Direct analysis of AsB standard (1.0 mg/L)by EESI-HG-MPT-MS in positive ion mode. CID analysis showed that m/z 179 ([AsB+H]$^+$) produced the characteristic fragmented ion of m/z 161, 137 and 120. Further CID analysis showed that m/z 121 generated m/z 105; m/z 137 generated m/z 91 and 119; m/z 161 produced fragmented ions of m/z 105, 117, 120 and 131.

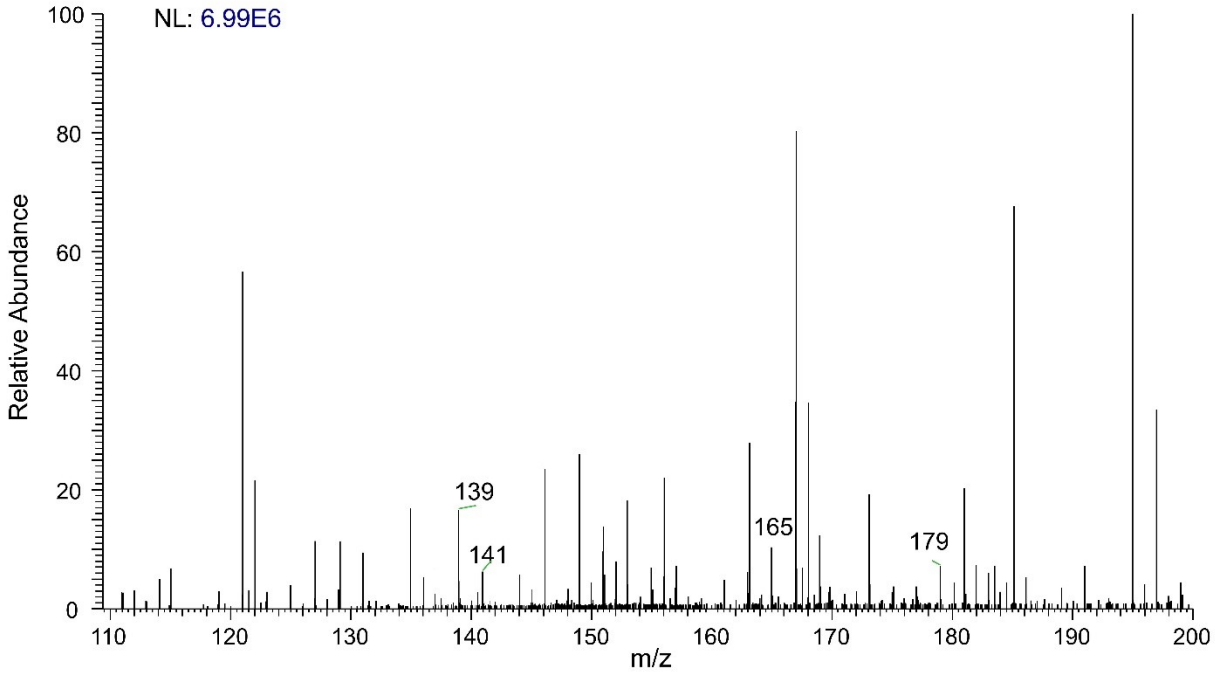

Figure S14 Online direct speciation analysis of As in raw laver (Porphyra) by EESI-HG-MPT-MS. Various As species were detected in positive ion mode. DMA (m/z 139), AsC (m/z 165), AsB (m/z 179).

Table S1 Direct speciation analysis of raw cray fish tissue samples by EESI-HG-MPT-MS. Spike experiments were conducted by online infusing mixed standards into raw samples. It can be seen from table S1 that, detected As species were in good agreement with the calculated values, with the spike recovery between 94-111%. (µg/kg)

	DMA	**MMA**	**AsC**	**AsB**	**As(III)**	**As(V)**
Sample	16.0±0.9	86.9±2.1	6.7±2.0	27.8±1.1	52.5±3.6	27.4±2.0
spike	10	50	10	50	50	50
detected	27.1±0.7	135.0±2.8	17.5±0.8	81.9±2.5	100.3±2	74.5±2.1
Spike recovery %	111.0±7.0	96.2±5.6	108.0±8.0	108.2±5.0	95.6±4.0	94.2±4.2

Table S2 Direct analysis of artificial sample by EESI-HG-MPT-MS (n = 3).

	DMA
Initial aqueous concentration (mg/L)	1.0
Residual aqueous concentration (mg/L)	0.21±0.03
Adsorbed (mg/L)	0.79±0.03
Adsorbed mass onto muscle (μg) ($C_{adsorbed} \times V_{bulk\ solution}$)	0.79±0.03
Calculated concentration (μg/g) ($m_{adsorbed} / m_{weighed}$)	7.74±0.3
Detected concentration (μg/g)	7.01±0.63

$V_{bulk\ solution}$ = 1.0 mL, $m_{weighed}$ = 0.102 g

Table S3 The analytical results of inorganic As species in different crayfish tissues by EESI-HG-MPT-MS with comparison of HG-AFS. Certified reference material of SRM 1643e was determined for mass control. (μg/kg)

Samples	**Species**	**EESI-HG-MPT-MS μg/L**	**HG-AFS μg/L**	**RE%**
muscle	As(III)	35.7 ± 2.1	34.9 ± 1.8	2.24
	As(T)	57.7 ± 1.9	58.2 ± 1.5	-0.87
	As(V)	22.0 ± 2.1	23.3 ± 1.8	-5.91
exoskeleton	As(III)	6.0 ± 1.1	6.8 ± 1.0	-13.33
	As(T)	21.5 ± 1.9	20.7 ± 0.9	3.72
	As(V)	15.5 ± 1.9	13.9 ± 1.0	10.32
SRM 1643e	As(III)	0.75 ± 0.1	0.68 ± 0.1	9.33
	As(T)	59.0 ± 1.1	58.4 ± 0.9	1.02
	As(V)	58.8 ± 1.1	57.7 ± 0.9	1.87
	Certified value	60.4 ± 0.7	60.4 ± 0.7	-

RE% = (values found by EESI-HG-MPT-MS −values found by HG-AFS) ÷ values found by EESI-HG-MPT-MS × 100%

For HG-AFS analysis, 1% $NaBH_4$ and 0.5% NaOH mixture was used as hydride generation reductant, a citrate acid-sodium citrate buffer with pH of 6.6 was used as the carrier solution.

Table S4 Direct speciation analysis of laver (porphyra) and kelp (seaweed) samples by EESI-HG-MPT-MS. (μg/g)

	DMA	**MMA**	**AsC**	**AsB**	**As(III)**	**As(V)**
laver (porphyra)	1.1 ± 0.1	0.2 ± 0.02	0.04	1.96 ± 0.05	n.d.	n.d.
kelp (seaweed)	0.1 ± 0.01	0.02 ± 0.01	n.d.	1.12 ± 0.05	n.d.	n.d.

n.d. = not detected

Table S5 Comparison between MPT-MS and ICP-MS on arsenic analysis.

	MPT-MS	**ICP-MS[1]**
Ar consumption (L/min)	~1	~16
Power (W)	30-200, adjustable	1100
Working condition	Ambient	Vacuum, ~10^{-4} Pa
Isotopic interference	-	$^{40}Ar^{35}Cl$
Detected form	$H_3AsO_4 \bullet NO_3^-$ (-)	As^+
Ionization	soft	hard
Detection limits (μg/L)	~0.02（with HG）	~0.01

(1) Hsieh, Y. J.; Jiang, S. J. Application of HPLC-ICP-MS and HPLC-ESI-MS Procedures for Arsenic Speciation in Seaweeds. *J. Agric. Food Chem.* **2012**, *60* (9), 2083–2089. https://doi.org/10.1021/jf204595d.