Selective hydride generation- cryotrapping- ICP-MS for arsenic speciation analysis at picogram levels: analysis of river and sea water reference materials and human bladder epithelial cells

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Supplementary information:

Table S1:
ISIS program for HG-CT-ICP-MS System 1

Step	Duration, s	Scan	Pump 1, rps	Pump 2, rps	Valve 1	Aux1 (heating power)	Aux 2 (heating indicator)
1	<P1>	-	0	<P17>	LOAD	OFF	OFF
2	<P2>	-	<P12>	<P15>	LOAD	OFF	OFF
3	<P3>	-	<P13>	0	INJECT	OFF	OFF
4	<P4>	-	<P13>	<P16>	INJECT	OFF	OFF
5	<P5>	-	0	0	INJECT	OFF	OFF
6	12	-	0	0	INJECT	OFF	ON
7	<P6>	-	0	0	INJECT	ON	ON
8	<P7>	Start	0	0	INJECT	ON	ON
9	<P8>	-	0	0	INJECT	OFF	OFF
10	<P9>	-	0	0	INJECT	ON	ON
11	<P10>	-	0	<P17>	INJECT	ON	ON
12	<P11>	-	<P14>	<P17>	INJECT	OFF	OFF
13	1	-	0	0	LOAD	OFF	OFF

Parameters	Description	Unit	Default value
<P1>	Time Pre-cool	s	30
<P2>	Time Prefill	s	5
<P3>	Time HG, P2 OFF	s	90*
<P4>	Time HG, P2 ON	s	0*
<P5>	Time Delay	s	80
<P6>	Time Acq. delay	s	5
<P7>	Time Acquisition 1	s	37**
<P8>	Time Acq. 2 (Heat off)	s	7
<P9>	Time Acquisition 3	s	*22***
<P10>	Time U-Tube cleaning	s	35
<P11>	Time HG cleaning	s	50
<P12>	P1 Rate Prefill	rps	0.25
<P13>	P1 Rate HG	rps	0.25
<P14>	P1 Rate Post-run	rps	0
<P15>	P2 Rate Prefill	rps	0.5
<P16>	P2 Rate HG	rps	0
<P17>	P2 Rate Post-run	rps	0.65

** for 500 µl loop*
*** Set to the approximate MAs peak maximum retention time.*
*** (64s – (<P6>+ <P7>)), to keep total heating time constant.*

Table S2: FIAS program for HG-CT-ICP-MS Systems 2 and 3

Step	Time, s	Pump 1	Pump 2	Inj. Vent	Remote 5 (heating)	
P	30	0	100	Fill	-	Precooling of U tube
1	25*	40	100	Fill	-	Prefill of injection loop
2	60*	40	0	Inject	-	HG step
3	90	0	0	Inject	-	Liquid nitrogen Dewar is removed 7 sec before the end of Step 3
4	42**	0	0	Fill	ON	READ step; hydrides released from U-tube
5	7	0	0	Inject	-	Heating break to improve DMAs- $TMAs^{V}O$ resolution
6	22***	0	0	Fill	ON	
7	35	0	120	Inject	ON	U-tube drying
8	3	0	0	Fill	-	

** for 500 µl loop*
*** set to the approximate MAs peak retention time.*
**** (64sec- Step4), to keep total heating time (steps 4 to 7) constant.*

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Table S3. Results of comparative BEC sample analyses.

Sample code	Cells per 300 ul	System 2 (UNC) pg As per 300 ul aliquot ± 95% confidence inteval									System 1 (IAC) pg As per 300ul aliquot ± 95% confidence inteval								
		iAs			MAs			DMAs			iAs			MAs			DMAs		
904	710500	676	±	21	180	±	17	21	±	8	811	±	26	203	±	3	24	±	1
994	198000	345	±	23	46	±	11	11	±	8	362	±	22	45	±	1	10	±	1
995	198000	60	±	14	25	±	17	192	±	8	72	±	9	24	±	2	188	±	9
1105	283200	60	±	31	9	±	28	17	±	29	89	±	9	10	±	1	20	±	1
1107	201600	1220	±	80	29	±	28	15	±	29	1242	±	76	26	±	2	11	±	1
1167	88200	139	±	13	40	±	12	32	±	11	138	±	6	45	±	2	44	±	3
1168	514500	253	±	19	127	±	25	21	±	8	249	±	6	103	±	3	24	±	1
1171	737450	645	±	24	167	±	25	40	±	8	670	±	9	149	±	3	38	±	2
1183	168300	216	±	13	91	±	11	176	±	11	231	±	9	94	±	2	172	±	7
1196	563500	92	±	16	12	±	20	5	±	10	99	±	9	95	±	22	7	±	1
1199	264600	56	±	16	10	±	20	9	±	10	39	±	6	10	±	1	11	±	1

Fig. S1. Stability of the HG-CT-ICP-MS signals of a mixed standard 200 pg mL^{-1} iAs^{V} and 100 pg mL^{-1} MAs^{V} and $DMAs^{V}$, after cys treatment; B- blank. * Injection error.