Supporting information

Trace metal determination in high-salinity water using ion imprinted helical tube demineralizer on-line combined with ICP-MS

Contents

SI-1. Preparation of the ion imprinted material

The ingredients for preparing the ion imprinted polymer include imprint ions, a silicon source, a silane coupling agent, a surfactant, and a templating agent. Ion imprinted polymers can be synthesized using step-by-step or one-step methods. In this study, a one-step synthesis method named the “evaporation induced by self-assembly” method was used. In this method, a silicon source in an organic solvent (e.g., ethanol, acetonitrile, or another protonated solvent) was hydrolyzed in an acidic system. The produced oligosilicates interacted with surfactant molecules in the solvent, and the silicon material formed crosslinks and polymerizes as the solvent evaporates. A mesoporous structure rapidly assembled with the surfactant acting as a template for the mesopores. The polymer was then calcined or the template agent was removed in another way.

A specified amount of calcium nitrate, magnesium nitrate, or sodium nitrate was added to 100 mL of distilled water. The mixture was stirred for 1 h until the salt was

fully dissolved. The silane coupling agent 3-aminopropyl triethoxysilane (6.2 g) was added to 250 mL absolute ethanol and the mixture was stirred at 120 rpm for 1 h at 45°C until the agent was completely dissolved. While the liquid was still being stirred, 2.3 g of 25% (by weight) tetramethyl ammonium hydroxide was added dropwise. The templating agent polyethylene glycol (4.4 g) was added to 250 mL absolute ethanol and the mixture was stirred at 120 rpm for 1 h at 45°C until the agent was completely dissolved, then the solution was allowed to stand for 1 h. Equal amounts of the three solutions described above were mixed, and 200 mL of the silicon source tetraethyl orthosilicate was added, then the mixture was allowed to stand for 24 h. The mixture was then ultrasonicated for 1 h to volatilize the solvent. The product was transferred to a stainless steel autoclave lined with Teflon, and then heated to 100°C for 48 h to crystallize the product. The mixture was cooled and the product was separated using a suction filter system and then washed with distilled water and dried at 60°C for 20 h. A 2 g aliquot of the dried product was extracted by Soxhlet extraction with 400 mL of acidified ethanol (250 mL ethanol and 16 mL 36% (by weight) concentrated hydrochloric acid) for 24 h. The mixture was then neutralized by adding $NaHCO_3$ solution, and the product was filtered, washed until the washings were neutral, and dried in vacuo at 80°C for 24 h. The dried product was ground and stored in a desiccator. Processing the calcium nitrate, magnesium nitrate, and sodium nitrate this way gave the products Ca(II)-IIP, Mg(II)-IIP, and Na(I)-IIP, respectively.

SI-2. ICP-MS operating conditions

Table S1 iCAP Q operating conditions

Instrument parameter name	value
RF power	1500KW
Plasma gas (Ar) flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.2 L min^{-1}
Nebulizer gas flow rate	0.9 L min^{-1}

Sample uptake rate	1 L min^{-1}
Collision cell	Helium 4.5 L min^{-1}
Cleaning time	45s
Sampler (nickel) orifice	1.1 mm
Skimmer (nickel) orifice	0.9 mm
Internal standard element	^{6}Li、^{45}Sc、^{89}Y、^{103}Rh、^{115}In、^{159}Tb、^{165}Ho、^{209}Bi

Table S2 EXPEC 7000 operating conditions

Instrument parameter name	**value**
RF power	1550KW
Plasma gas (Ar) flow rate	14 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Nebulizer gas flow rate	1.13 L min^{-1}
Collision cell	Helium 1.07 L min^{-1}
Cleaning time	45s
Extraction	-177V
Internal standard element	^{6}Li、^{45}Sc、^{89}Y、^{103}Rh、^{115}In、^{159}Tb、^{165}Ho、^{209}Bi

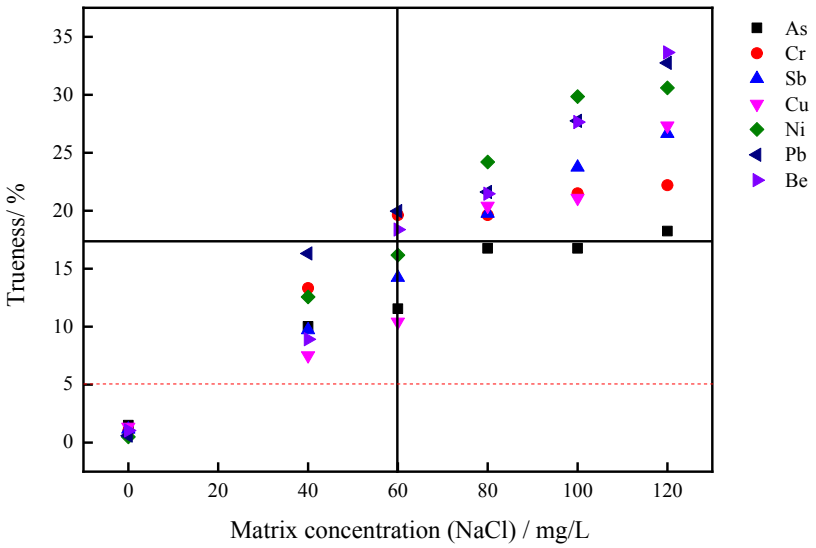
SI-3 The LOD of iCAP Q before the use of the desalination device

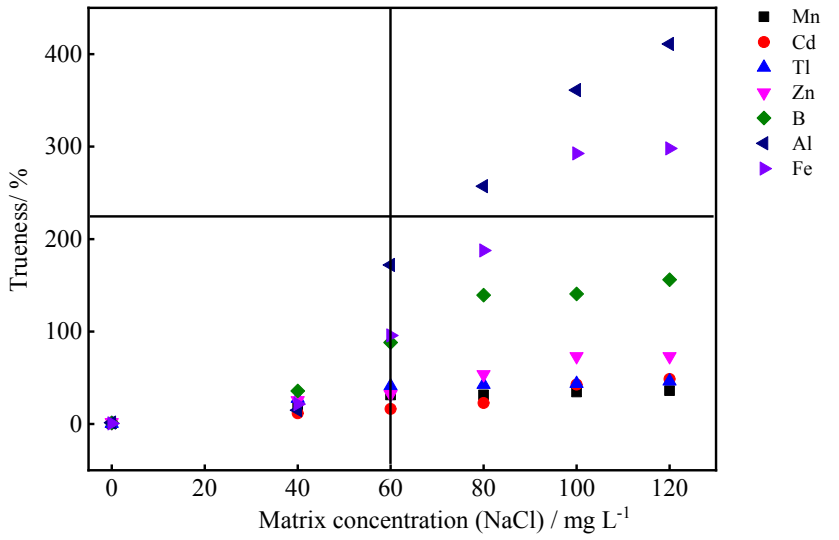
Table S3 The LOD of each element before the desalination device was used

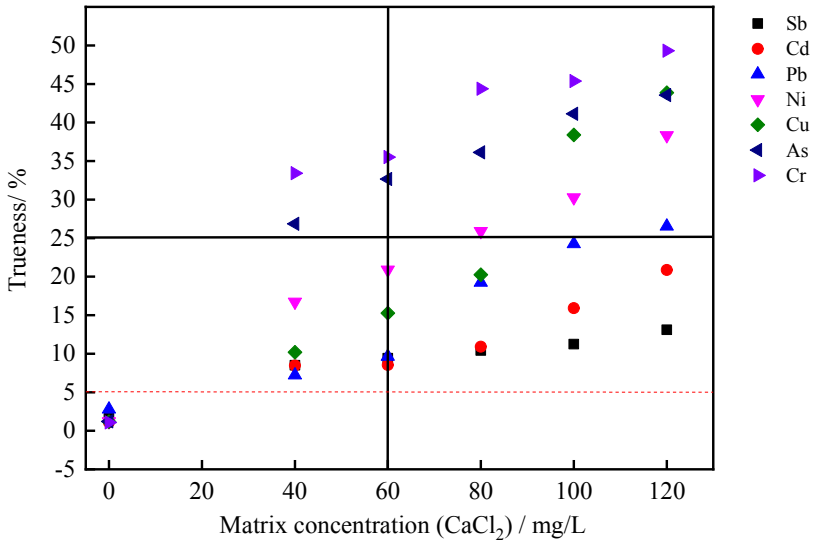
Element	Be	B	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sb	Tl	Pb
LOD μg/L	0.016	0.356	0.041	0.011	0.023	0.122	0.061	0.031	0.066	0.023	0.005	0.006	0.002	0.005

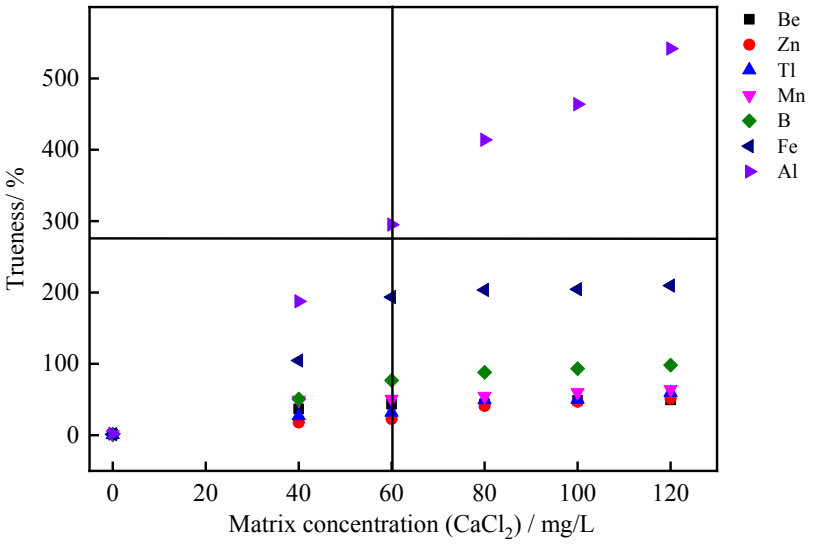
SI-4 Trueness of the metal ion concentrations determined in the presence of different salt matrix concentrations before the desalination device was used

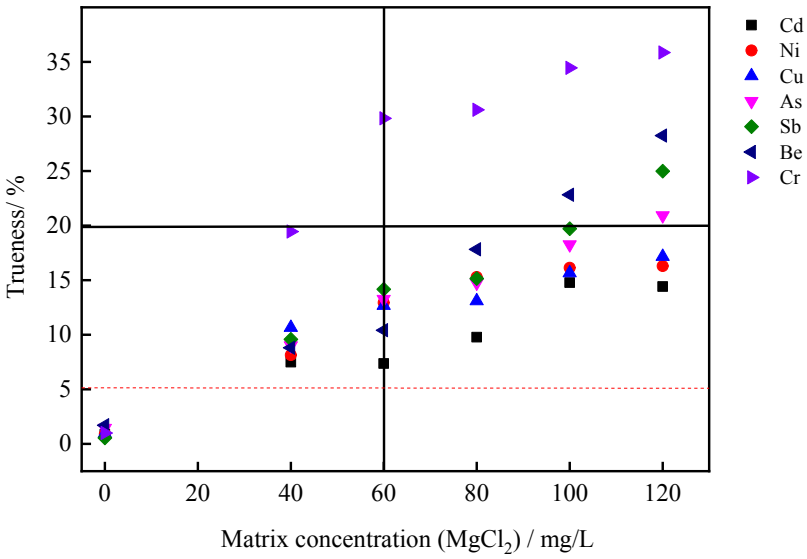
It can be seen from Fig. S1 that the trueness of the metal ion concentrations determined in the absence of a salt matrix before the desalination device was used were <5% but that the trueness ~~were~~ was 5%–1000% when the salt matrix concentrations were 40–120 mg/L. The trueness increased as the salt matrix concentration increased when the desalination device was not used.




Mn
Cd
Tl
Zn
B
Al
Fe
Trueness/ %
400
300
200
100
0
0
20
40
60
80
100
120
Matrix concentration (NaCl) / mg L-1


Sb
Cd
Pb
Ni
Cu
As
Cr
Trueness/ %
50
45
40
35
30
25
20
15
10
5
0
-5
0
20
40
60
80
100
120
Matrix concentration (CaCl2) / mg/L


Be
Zn
Tl
Mn
B
Fe
Al
Trueness/ %
0
100
200
300
400
500
0
20
40
60
80
100
120
Matrix concentration ($CaCl_2$) / mg/L


Cd
Ni
Cu
As
Sb
Be
Cr
Trueness/ %
0
5
10
15
20
25
30
35
0
20
40
60
80
100
120
Matrix concentration ($MgCl_2$) / mg/L

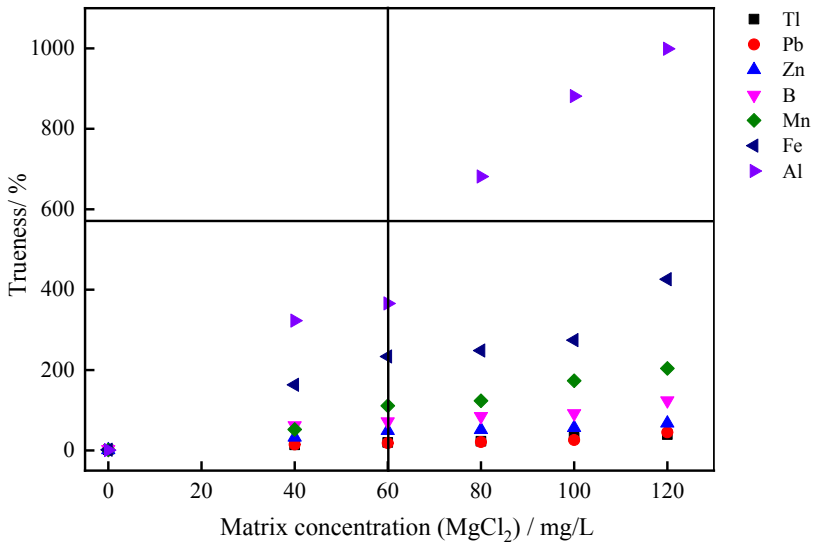


Fig. S1 Trueness of the metal ion concentrations determined in the presence of different salt matrix concentrations before the desalination device was used

SI-5 Recoveries of the analytes in the presence of different salt matrices before and after the desalination device was used

Tests were performed at salt matrix concentrations of 40–120 mg/L before the desalination device was used. The highest recovery was 76~~.10~~% at a NaCl concentration of 40 mg/L. The lowest recovery was ~~21.83~~22% at a $MgCl_2$ concentration of 120 mg/L.

Table S4 Recoveries in the presence of NaCl before the desalination device was used

matrix concentration	Recovery %													
mg/L	Be	B	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sb	Tl	Pb
40	75	71	74	72	67	73	75	65	74	74	70	73	74	72
60	66	66	71	61	60	64	69	60	69	63	66	68	64	65
80	61	51	65	59	54	54	66	52	55	58	54	59	58	58
100	58	41	61	51	48	49	59	34	50	51	48	51	51	53
120	40	22	50	44	24	40	52	20	42	46	41	45	48	51

Table S5 Recoveries in the presence of $CaCl_2$ before the desalination device was used

matrix concentration	Recovery %													
mg/L	Be	B	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sb	Tl	Pb
40	73	72	66	69	72	69	71	73	62	74	75	68	74	72
60	64	60	53	63	60	60	64	67	56	69	60	63	69	65
80	57	53	41	55	57	51	55	60	49	54	59	54	60	58
100	51	46	31	50	49	36	48	55	34	48	50	48	57	53
120	44	40	28	49	41	20	41	50	20	41	45	41	50	51

Table S6 Recoveries in the presence of $MgCl_2$ before the desalination device was used

matrix concentration	Recovery %													
mg/L	Be	B	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sb	Tl	Pb
40	72	72	66	70	72	66	70	74	63	72	75	66	71	71
60	62	60	52	63	58	61	66	66	55	69	61	61	69	64
80	57	53	40	53	51	45	54	59	48	52	56	57	60	57
100	50	46	34	50	47	31	45	52	36	47	49	48	58	52
120	45	40	22	46	40	22	40	48	20	40	40	42	51	50

Table S7 Recoveries in the mix presence of NaCl, $MgCl_2$ and $CaCl_2$ after the desalination device was used

matrix concentration	Recovery %													
120 mg/L	Be	B	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sb	Tl	Pb
NaCl,	107	105	105	106	105	105	105	103	104	103	106	106	106	107
$MgCl_2$	99	98	98	94	94	93	96	96	96	99	100	100	93	94
$CaCl_2$	94	94	93	88	89	87	92	91	92	97	97	98	87	89

SI-6 Determination results, RSDs and spike recoveries of real samples measured by iCAP Q with the desalination device

Table S8 Determination results and RSDs of real samples NO.1 with the desalination device

Element	1 μg/L	2 μg/L	3 μg/L	4 μg/L	5 μg/L	AVE μg/L	RSD
9Be	0.013	0.013	0.013	0.014	0.013	0.014	3.61
11B	226.498	228.156	228.986	225.533	229.008	227.636	0.68
27Al	0.756	0.752	0.748	0.784	0.758	0.760	1.85
52Cr	0.331	0.329	0.328	0.348	0.327	0.333	2.67
55Mn	0.035	0.035	0.035	0.036	0.035	0.035	1.44
57Fe	881.561	887.124	882.688	887.307	891.276	885.991	0.44

60Ni	1.272	1.266	1.259	1.308	1.287	1.278	1.52
63Cu	235.801	237.617	235.449	237.697	238.367	236.986	0.54
66Zn	9.972	9.922	9.873	10.433	9.911	10.022	2.32
75As	4.326	4.304	4.343	4.365	4.400	4.348	0.85
111Cd	0.026	0.026	0.026	0.028	0.025	0.027	3.97
121Sb	0.205	0.204	0.206	0.213	0.203	0.207	1.87
205Tl	0.009	0.009	0.009	0.010	0.009	0.010	1.62
208Pb	1.420	1.413	1.425	1.480	1.397	1.427	2.20

Table S9 Determination results and RSDs of real samples NO.2 with the desalination device

Element	1 μg/L	2 μg/L	3 μg/L	4 μg/L	5 μg/L	AVE μg/L	RSD
9Be	0.010	0.009	0.010	0.010	0.009	0.010	1.87
11B	232.797	232.663	234.757	236.136	233.482	233.967	0.63
27Al	0.778	0.771	0.778	0.807	0.774	0.782	1.82
52Cr	0.629	0.647	0.653	0.652	0.578	0.632	5.00
55Mn	873.320	871.953	879.801	880.795	882.673	877.708	0.54
57Fe	845.616	846.335	853.952	852.061	851.363	849.866	0.43
60Ni	4.280	4.373	4.412	4.439	4.002	4.301	4.13
63Cu	706.574	704.454	710.794	712.818	715.981	710.124	0.66
66Zn	19.161	21.653	19.847	20.911	19.741	20.263	4.94
75As	4.706	4.714	4.756	4.881	4.589	4.729	2.22
111Cd	0.026	0.025	0.026	0.027	0.025	0.026	1.87
121Sb	0.791	0.797	0.804	0.820	0.762	0.795	2.69
205Tl	0.007	0.007	0.007	0.007	0.006	0.007	3.77
208Pb	0.414	0.402	0.406	0.429	0.430	0.416	3.12

Table S10 Determination results and RSDs of real samples NO.3 with the desalination device

Element	1 μg/L	2 μg/L	3 μg/L	4 μg/L	5 μg/L	AVE μg/L	RSD
9Be	0.052	0.052	0.053	0.054	0.052	0.053	1.87
11B	197.825	196.836	198.608	200.182	200.646	198.819	0.80
27Al	2.832	2.818	2.843	2.963	2.775	2.846	2.46
52Cr	0.079	0.079	0.079	0.083	0.077	0.079	3.07
55Mn	343.856	342.137	345.216	350.247	346.464	345.584	0.89
57Fe	881.047	880.682	888.608	890.810	886.226	885.475	0.51
60Ni	2.400	2.388	2.409	2.458	2.405	2.412	1.11
63Cu	14.319	14.248	14.376	14.794	14.219	14.391	1.62
66Zn	4.247	4.226	4.264	4.426	4.179	4.268	2.20
75As	2.251	2.240	2.260	2.387	2.174	2.262	3.42
111Cd	0.057	0.057	0.058	0.060	0.056	0.058	2.80
121Sb	0.081	0.081	0.082	0.086	0.077	0.082	4.07

205Tl	0.008	0.008	0.008	0.008	0.008	0.008	1.87
208Pb	0.501	0.498	0.508	0.520	0.491	0.504	2.16

Table S11 Determination results and RSDs of real samples NO.4 with the desalination device

Element	1 µg/L	2 µg/L	3 µg/L	4 µg/L	5 µg/L	AVE µg/L	RSD
9Be	0.009	0.009	0.009	0.010	0.009	0.009	1.83
11B	207.586	207.139	209.003	209.684	209.735	208.630	0.58
27Al	0.545	0.543	0.548	0.565	0.538	0.548	1.91
52Cr	0.129	0.129	0.129	0.134	0.129	0.130	1.80
55Mn	29.723	29.574	29.840	31.157	29.067	29.872	2.60
57Fe	381.260	379.353	382.768	383.942	388.555	383.176	0.90
60Ni	3.099	3.096	3.098	3.310	2.922	3.105	4.43
63Cu	474.256	474.881	476.306	478.564	479.189	476.639	0.46
66Zn	27.520	27.220	27.465	28.737	27.350	27.658	2.22
75As	4.373	4.351	4.307	4.536	4.408	4.395	1.98
111Cd	0.031	0.031	0.031	0.033	0.030	0.031	2.99
121Sb	0.107	0.106	0.109	0.111	0.105	0.108	2.40
205Tl	0.007	0.007	0.007	0.008	0.007	0.008	1.87
208Pb	0.291	0.287	0.299	0.312	0.284	0.295	3.86

Table S12 Determination results and RSDs of real samples NO.5 with the desalination device

Element	1 µg/L	2 µg/L	3 µg/L	4 µg/L	5 µg/L	AVE µg/L	RSD
9Be	0.010	0.010	0.010	0.010	0.010	0.010	2.39
11B	231.774	230.615	232.691	235.501	234.113	232.939	0.82
27Al	0.521	0.532	0.537	0.544	0.486	0.524	4.37
52Cr	0.272	0.269	0.271	0.282	0.271	0.273	1.83
55Mn	211.987	210.927	212.825	214.757	214.765	213.052	0.80
57Fe	818.859	819.221	826.594	826.265	823.929	822.974	0.45
60Ni	3.924	3.905	3.940	4.070	3.881	3.944	1.87
63Cu	854.769	856.478	848.232	858.152	847.538	853.034	0.57
66Zn	4.710	4.796	4.839	4.885	4.438	4.734	3.75
75As	5.708	5.751	5.803	5.721	5.701	5.737	0.73
111Cd	0.033	0.033	0.033	0.034	0.032	0.033	2.08
121Sb	0.350	0.348	0.352	0.351	0.358	0.352	1.06
205Tl	0.006	0.006	0.006	0.006	0.006	0.006	0.98
208Pb	3.357	3.386	3.417	3.482	3.228	3.374	2.78

Table S13 Determination results of spiked recoveries with the desalination device

Element	No.1 µg/L	No.2 µg/L	No.3 µg/L	No.4 µg/L	No.5 µg/L

9Be	9.264	10.027	9.715	9.927	19.265
11B	707.620	711.974	684.106	711.968	727.348
27Al	9.818	10.134	11.698	9.788	9.703
52Cr	10.085	10.257	9.370	8.880	9.756
55Mn	483.715	1368.108	840.224	525.072	698.772
57Fe	1369.204	1353.520	1407.867	889.896	1335.285
60Ni	11.064	14.272	12.362	12.878	13.738
63Cu	723.506	1191.764	502.391	962.839	1323.634
66Zn	18.537	29.192	13.524	37.022	13.546
75As	14.339	14.109	12.055	14.173	15.614
111Cd	9.926	10.006	9.927	9.862	10.079
121Sb	9.883	10.614	9.736	9.876	10.425
205Tl	9.274	8.993	8.905	9.406	9.430
208Pb	10.862	10.169	9.821	10.276	13.337

SI-7 Determination results of real sample No.1 measured by EXPEC 7000 with the desalination device

Table S14 Determination results and RSDs of real sample No.1 measured inter-devices by EXPEC 7000 with the desalination device

Element	1 μg/L	2 μg/L	3 μg/L	4 μg/L	5 μg/L	AVE μg/L	RSD
9Be	0.013	0.012	0.013	0.013	0.014	0.013	3.26
11B	228.712	233.614	224.361	235.167	227.451	229.861	1.94
27Al	0.768	0.776	0.772	0.797	0.747	0.772	2.30
52Cr	0.339	0.349	0.347	0.337	0.332	0.341	2.05
55Mn	0.037	0.038	0.038	0.038	0.036	0.037	2.47
57Fe	887.721	897.314	892.827	881.642	901.405	892.182	0.87
60Ni	1.319	1.310	1.323	1.346	1.332	1.326	1.03
63Cu	237.954	247.617	235.449	239.867	234.862	239.150	2.15
66Zn	10.381	10.329	10.277	10.961	10.697	10.529	2.77
75As	4.580	4.557	4.498	4.641	4.739	4.603	1.99
111Cd	0.025	0.024	0.024	0.026	0.026	0.025	4.12
121Sb	0.212	0.211	0.213	0.218	0.211	0.213	1.35
205Tl	0.010	0.011	0.010	0.010	0.010	0.010	4.21
208Pb	1.452	1.424	1.437	1.513	1.469	1.459	2.37

Table S15 Determination results and RSDs of real sample No.1 measured intra-day by EXPEC 7000 with the desalination device

Element	1 μg/L	2 μg/L	3 μg/L	4 μg/L	5 μg/L	AVE μg/L	RSD
9Be	0.015	0.015	0.015	0.014	0.015	0.015	2.98
11B	232.182	231.492	230.926	229.612	232.772	231.3969	0.53
27Al	0.815	0.823	0.793	0.795	0.799	0.805	1.65
52Cr	0.364	0.360	0.352	0.353	0.356	0.357	1.42
55Mn	0.038	0.038	0.036	0.036	0.037	0.037	2.70
57Fe	913.136	912.240	916.721	907.617	902.171	910.3769	0.62
60Ni	1.370	1.390	1.320	1.310	1.310	1.34	2.79
63Cu	239.974	242.413	245.219	245.780	246.001	243.8774	1.07
66Zn	10.973	11.080	10.244	10.437	10.791	10.705	3.31
75As	4.590	4.545	4.311	4.366	4.578	4.478	2.90
111Cd	0.029	0.029	0.029	0.028	0.030	0.029	2.44
121Sb	0.224	0.227	0.206	0.217	0.221	0.219	3.72
205Tl	0.010	0.010	0.011	0.010	0.010	0.01	4.47
208Pb	1.559	1.554	1.498	1.503	1.491	1.521	2.15

Table S16 Determination results and RSDs of real sample No.1 measured inter-day by EXPEC 7000 with the desalination device

Element	1 μg/L	2 μg/L	3 μg/L	4 μg/L	5 μg/L	AVE μg/L	RSD
9Be	0.013	0.013	0.013	0.013	0.014	0.013	3.44
11B	228.457	227.756	225.385	226.117	226.220	226.787	0.56
27Al	0.777	0.774	0.737	0.729	0.723	0.748	3.43
52Cr	0.333	0.331	0.322	0.322	0.327	0.327	1.54
55Mn	0.036	0.036	0.034	0.034	0.035	0.035	2.86
57Fe	883.846	882.664	878.574	879.756	884.165	881.801	0.28
60Ni	1.293	1.281	1.249	1.237	1.230	1.258	2.20
63Cu	236.096	234.458	237.648	237.286	235.467	236.191	0.55
66Zn	10.210	10.306	9.815	9.516	9.468	9.863	3.91
75As	4.385	4.428	4.214	4.171	4.192	4.278	2.78
111Cd	0.026	0.026	0.026	0.027	0.026	0.026	1.72
121Sb	0.208	0.210	0.200	0.198	0.199	0.203	2.78
205Tl	0.009	0.009	0.009	0.009	0.010	0.009	4.97
208Pb	1.459	1.463	1.373	1.379	1.346	1.404	3.81

SI-8 Determination results of standard sample CASS-5 measured by EXPEC 7000 with the desalination device

Note: The 95% confidence interval formula is $(T - Z_{a/2}\sigma,\ T - Z_{a/2}\sigma)$, where T is trueness (%), When confidence level is 95%, the Z value is 1.96, σ is the standard deviation of CASS-5 results.

Table S17 Determination results and RSDs of stardand sample CASS-5 measured inter-devices by EXPEC 7000 with the desalination device

Element	1 μg/L	2 μg/L	3 μg/L	4 μg/L	5 μg/L	AVE μg/L	RSD	Confidence
^{52}Cr	0.107	0.108	0.107	0.108	0.108	0.108	0.61	±0.001
^{55}Mn	2.56	2.61	2.60	2.62	2.57	2.59	1.03	±0.05
^{57}Fe	1.48	1.48	1.45	1.48	1.42	1.46	1.87	±0.05
^{60}Ni	0.326	0.317	0.311	0.329	0.322	0.321	2.25	±0.014
^{63}Cu	0.376	0.372	0.369	0.369	0.365	0.370	1.05	±0.008
^{66}Zn	0.694	0.706	0.709	0.711	0.690	0.702	1.34	±0.018
^{75}As	1.24	1.25	1.26	1.27	1.26	1.26	0.77	±0.02
^{111}Cd	0.0229	0.0239	0.0231	0.0241	0.0241	0.0236	2.40	±0.0011

Table S18 Determination results and RSDs of stardand sample CASS-5 measured intra-day by EXPEC 7000 with the desalination device

Element	1 μg/L	2 μg/L	3 μg/L	4 μg/L	5 μg/L	AVE μg/L	RSD	Confidence
^{52}Cr	0.107	0.107	0.109	0.109	0.108	0.108	0.93	±0.002
^{55}Mn	2.59	2.64	2.58	2.65	2.61	2.61	1.24	±0.06
^{57}Fe	1.45	1.50	1.44	1.42	1.44	1.45	2.09	±0.06
^{60}Ni	0.336	0.336	0.320	0.321	0.327	0.328	2.37	±0.015
^{63}Cu	0.385	0.374	0.369	0.380	0.377	0.377	1.59	±0.012
^{66}Zn	0.722	0.731	0.700	0.701	0.726	0.716	2.03	±0.028
^{75}As	1.29	1.26	1.30	1.27	1.24	1.27	1.72	±0.04
^{111}Cd	0.0237	0.0238	0.0240	0.0242	0.0243	0.0240	1.03	±0.0005

Table S19 Determination results and RSDs of stardand sample CASS-5 measured inter-day by EXPEC 7000 with the desalination device

Element	1 µg/L	2 µg/L	3 µg/L	4 µg/L	5 µg/L	AVE µg/L	RSD	Confidence
^{52}Cr	0.105	0.104	0.106	0.106	0.104	0.105	0.95	0.002
^{55}Mn	2.51	2.52	2.58	2.59	2.66	2.57	2.29	0.12
^{57}Fe	1.39	1.38	1.44	1.46	1.54	1.44	4.32	0.12
^{60}Ni	0.309	0.319	0.335	0.326	0.327	0.323	2.94	0.019
^{63}Cu	0.359	0.363	0.380	0.372	0.381	0.371	2.63	0.019
^{66}Zn	0.693	0.689	0.733	0.715	0.666	0.699	3.67	0.050
^{75}As	1.29	1.23	1.26	1.26	1.22	1.25	2.28	0.06
^{111}Cd	0.0236	0.0237	0.0236	0.0241	0.0245	0.0239	1.65	0.0008