Supporting information

Heavy metal ion discrimination based on distinct interaction between single-stranded DNA and methylene blue

Li Li,[a] Bing Liu,[a] and Zhengbo Chen*[b]

[a] College of Chemistry and Chemical Engineering, Xinxiang University, Xinxiang 453003, China

[b] Department of Chemistry, Capital Normal University, Beijing, 100048, China

E-mail: czb979216@sina.com

24A	24C	24T	Correct %
■			88.6
	■		97.1
		■	68.6
■	■		97.5
■		■	97.1
	■	■	97.1
■	■	■	100

Fig. S1 Jackknifed classification matrix obtained using LDA based on 24A-MB, 24C-MB, and 24T-MB for the 9 metal ion discrimination.

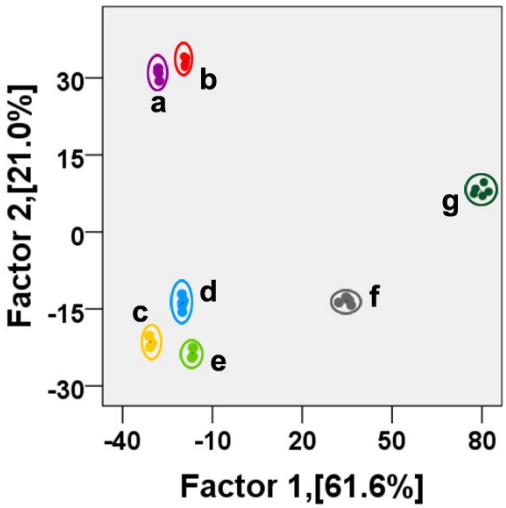

Fig. S2 Canonical score plot for discrimination mixtures of the 9 metal ions at different molar ratios (total metal ion concentration: 30 nM). a: Fe^{3+}: Cd^{2+}: Pb^{2+}: Hg^{2+}: Ag^{+}: Sn^{4+}: Ni^{2+}: Mn^{2+}: Cu^{2+}=2:1:1:1:1:1:1:1:1; b: Fe^{3+}: Cd^{2+}: Pb^{2+}: Hg^{2+}: Ag^{+}: Sn^{4+}: Ni^{2+}: Mn^{2+}: Cu^{2+}=1:2:1:1:1:1:1:1:1; c: Fe^{3+}: Cd^{2+}: Pb^{2+}: Hg^{2+}: Ag^{+}: Sn^{4+}: Ni^{2+}: Mn^{2+}: Cu^{2+}=1:1:1:1:1:2:1:1:1; d: Fe^{3+}: Cd^{2+}: Pb^{2+}: Hg^{2+}: Ag^{+}: Sn^{4+}: Ni^{2+}: Mn^{2+}: Cu^{2+}=1:1:1:1:2:1:1:1:1; e: Fe^{3+}: Cd^{2+}: Pb^{2+}: Hg^{2+}: Ag^{+}: Sn^{4+}: Ni^{2+}: Mn^{2+}: Cu^{2+}=1:1:1:1:1:1:1:1:2; f: Fe^{3+}: Cd^{2+}: Pb^{2+}: Hg^{2+}: Ag^{+}: Sn^{4+}: Ni^{2+}: Mn^{2+}: Cu^{2+}=1:1:2:1:1:1:1:1:1; and g: Fe^{3+}: Cd^{2+}: Pb^{2+}: Hg^{2+}: Ag^{+}: Sn^{4+}: Ni^{2+}: Mn^{2+}: Cu^{2+}=1:1:1:2:1:1:1:1:1.

Table S1. The training matrix of the colorimetric response patterns against 9 metal ions using this sensor assay. The concentrations of 24A, 24C, and 24T are all 4.16 μM. MB, 41.67 μM; TE (10 mM Tris, 1 mM EDTA, pH=8.0), metal ions: 30 nM. Each value is the average of 5 experimental values. The solutions containing the same metal ions were regarded as 5 samples.

Metal ions	$OD_{660\ nm}/OD_{538\ nm}$ - 24A	$OD_{660\ nm}/OD_{538\ nm}$ - 24C	$OD_{660\ nm}/OD_{538\ nm}$ UV-24T
Cd^{2+}	6.89989	0.436959	2.24039
Cd^{2+}	6.795175	0.44035	2.143229
Cd^{2+}	6.736045	0.42281	2.215474
Cd^{2+}	7.058236	0.429389	2.185682
Cd^{2+}	6.683715	0.44669	2.194076
Hg^{2+}	0.180407	0.574044	2.099671
Hg^{2+}	0.181651	0.578362	2.185484
Hg^{2+}	0.17958	0.536162	2.246259
Hg^{2+}	0.177995	0.558569	2.071244
Hg^{2+}	0.184869	0.573948	2.049621
Pb^{2+}	5.078908	0.424927	4.662048
Pb^{2+}	4.905491	0.437931	4.349206
Pb^{2+}	5.234437	0.403813	4.092794
Pb^{2+}	4.676821	0.411648	4.251412
Pb^{2+}	5.312602	0.43041	4.330655
Ag^{+}	3.734088	0.651296	8.879277
Ag^{+}	3.529801	0.660766	7.787879
Ag^{+}	4.317881	0.633585	8.915176
Ag^{+}	3.419925	0.631506	8.027735
Ag^{+}	3.579051	0.642841	8.049715
Cu^{2+}	1.312931	1.495085	6.817053
Cu^{2+}	1.288999	1.477026	5.313725
Cu^{2+}	1.342985	1.422968	6.781707
Cu^{2+}	1.360172	1.43167	6.857888
Cu^{2+}	1.303951	1.493555	5.974246
Sn^{4+}	3.847242	0.784198	2.808635
Sn^{4+}	3.666115	0.783562	3.261111
Sn^{4+}	4.1243	0.740629	2.830918
Sn^{4+}	3.796173	0.759578	3.06725
Sn^{4+}	3.636661	0.763427	2.766368
Ni^{2+}	3.749175	1.617463	3.942068
Ni^{2+}	3.938742	1.575541	4.65
Ni^{2+}	3.934658	1.631325	3.893531
Ni^{2+}	3.920466	1.575773	4.201977
Ni^{2+}	4.20505	1.647533	4.267319
Fe^{3+}	10.51881	0.509785	3.964694
Fe^{3+}	10.46026	0.507589	4.083333

Fe^{3+}	10.17219	0.507402	4.68742
Fe^{3+}	10.32529	0.4923	4.043584
Fe^{3+}	10.51391	0.50657	3.861747
Mn^{2+}	2.951537	1.567911	6.244578
Mn^{2+}	2.700646	1.530575	7.055556
Mn^{2+}	2.94458	1.532628	6.461163
Mn^{2+}	2.625397	1.512149	5.969868
Mn^{2+}	2.780332	1.534678	6.139714

Table S2. Training matrix of the response patterns against Ag^{+} and Sn^{4+} at different concentrations, respectively, as well as the mixtures of these two metal inons with various molar ratios (total concentration 30 nM) using this sensor array. Each value is the average of 5 experimental values.

Metal ions	$OD_{660\ nm}/OD_{538\ nm}$ -24A	$OD_{660\ nm}/OD_{538\ nm}$ -24C	$OD_{660\ nm}/OD_{538\ nm}$ -24T
100% Sn^{4+}	0.680964	1.66815	1.040487
100% Sn^{4+}	0.704868	1.689187	1.02582
100% Sn^{4+}	0.692976	1.676293	1.035266
100% Sn^{4+}	0.694128	1.675224	1.047384
100% Sn^{4+}	0.687949	1.686882	1.036907
100% Ag^{+}	0.603494	1.284727	1.33066
100% Ag^{+}	0.626723	1.298879	1.316665
100% Ag^{+}	0.61992	1.297277	1.336706
100% Ag^{+}	0.620545	1.306563	1.336867
100% Ag^{+}	0.605296	1.28695	1.320938
10% Ag^{+} +90% Sn^{4+}	1.583563	1.14387	1.038741
10% Ag^{+} +90% Sn^{4+}	1.656984	1.161285	1.0274
10% Ag^{+} +90% Sn^{4+}	1.631939	1.150428	1.033728
10% Ag^{+} +90% Sn^{4+}	1.620457	1.149502	1.055509
10% Ag^{+} +90% Sn^{4+}	1.58164	1.152318	1.049264
30% Ag^{+} +70% Sn^{4+}	0.766362	1.636497	1.013374
30% Ag^{+} +70% Sn^{4+}	0.79568	1.653561	1.013114
30% Ag^{+} +70% Sn^{4+}	0.779808	1.652771	1.016968
30% Ag^{+} +70% Sn^{4+}	0.790272	1.666748	1.029518
30% Ag^{+} +70% Sn^{4+}	0.775627	1.655255	1.026291
50% Ag^{+} +50% Sn^{4+}	0.716699	1.845555	0.953408
50% Ag^{+} +50% Sn^{4+}	0.724888	1.883157	0.945227
50% Ag^{+} +50% Sn^{4+}	0.707496	1.862498	0.962179
50% Ag^{+} +50% Sn^{4+}	0.731265	1.872278	0.967871
50% Ag^{+} +50% Sn^{4+}	0.716505	1.867421	0.951605
70% Ag^{+} +30% Sn^{4+}	0.694374	1.592701	1.020982
70% Ag^{+} +30% Sn^{4+}	0.719685	1.613048	1.018047
70% Ag^{+} +30% Sn^{4+}	0.705364	1.618918	1.033196
70% Ag^{+} +30% Sn^{4+}	0.71219	1.617401	1.045859
70% Ag^{+} +30% Sn^{4+}	0.707113	1.62479	1.03328
90% Ag^{+} +10% Sn^{4+}	0.642375	1.494504	1.091238
90% Ag^{+} +10% Sn^{4+}	0.667916	1.516516	1.079115
90% Ag^{+} +10% Sn^{4+}	0.641187	1.48306	1.090098
90% Ag^{+} +10% Sn^{4+}	0.64956	1.492642	1.109763
90% Ag^{+} +10% Sn^{4+}	0.634445	1.501629	1.091686

Table S3. The training matrix of the colorimetric response patterns against Cd^{2+} with different concentrations (30-200 nM) using this sensor assay. Each value is the average of 5 experimental values.

Metal ions	$OD_{660\ nm}/OD_{538\ nm}$ -24A	$OD_{660\ nm}/OD_{538\ nm}$ -24C	$OD_{660\ nm}/OD_{538\ nm}$ -24T
30 nM	6.630085	0.428108	0.313651
30 nM	6.765218	0.431262	0.317853
30 nM	6.521465	0.412386	0.321482
30 nM	6.715621	0.424448	0.309565
30 nM	6.413628	0.419562	0.320548
60 nM	5.037929	0.470758	0.225586
60 nM	5.142335	0.486623	0.237158
60 nM	5.215352	0.474017	0.214656
60 nM	5.065123	0.469598	0.221487
60 nM	4.986482	0.491232	0.232112
90 nM	3.516556	0.51655	0.141613
90 nM	3.475831	0.504568	0.161231
90 nM	3.611231	0.523235	0.156735
90 nM	3.395122	0.524118	0.149513
90 nM	3.595131	0.519776	0.144528
120 nM	2.829139	0.556606	0.06592
120 nM	2.796323	0.561952	0.064985
120 nM	2.712335	0.568623	0.063875
120 nM	2.864988	0.581265	0.065212
120 nM	2.672321	0.546952	0.065653
200 nM	1.207506	0.673977	0.025184
200 nM	1.262335	0.695301	0.028323
200 nM	1.315321	0.684532	0.026245
200 nM	1.229883	0.675632	0.025436
200 nM	1.398876	0.686941	0.024821

Table S4. Identification of unknown metal ion samples at 30 nM using 24T. The metal ions in red font indicate that these metal ions were not correctly identified.

Samples	OD_{660nm}/OD_{538nm} -24T	Identification	Verification
1	2.24039	Cd^{2+}	Cd^{2+}
2	2.143229	Cd^{2+}	**Hg^{2+}**
3	2.215474	Cd^{2+}	Cd^{2+}
4	2.185682	Cd^{2+}	Cd^{2+}
5	2.194076	Cd^{2+}	Cd^{2+}
6	2.099671	Hg^{2+}	Hg^{2+}
7	2.185484	Hg^{2+}	**Cd^{2+}**
8	2.246259	Hg^{2+}	**Cd^{2+}**
9	2.071244	Hg^{2+}	Hg^{2+}
10	2.049621	Hg^{2+}	Hg^{2+}
11	4.662048	Pb^{2+}	Pb^{2+}
12	4.349206	Pb^{2+}	Pb^{2+}
13	4.092794	Pb^{2+}	**Fe^{3+}**
14	4.251412	Pb^{2+}	**Ni^{2+}**
15	4.330655	Pb^{2+}	Pb^{2+}
16	8.879277	Ag^{+}	Ag^{+}
17	7.787879	Ag^{+}	Ag^{+}
18	8.915176	Ag^{+}	Ag^{+}
19	8.027735	Ag^{+}	Ag^{+}
20	8.049715	Ag^{+}	Ag^{+}
21	6.817053	Cu^{2+}	**Mn^{2+}**
22	5.313725	Cu^{2+}	**Pb^{2+}**
23	6.781707	Cu^{2+}	**Mn^{2+}**
24	6.857888	Cu^{2+}	**Mn^{2+}**
25	5.974246	Cu^{2+}	Cu^{2+}
26	2.808635	Sn^{4+}	Sn^{4+}
27	3.261111	Sn^{4+}	Sn^{4+}
28	2.830918	Sn^{4+}	Sn^{4+}
29	3.06725	Sn^{4+}	Sn^{4+}
30	2.766368	Sn^{4+}	Sn^{4+}
31	3.942068	Ni^{2+}	**Fe^{3+}**
32	4.65	Ni^{2+}	**Pb^{2+}**
33	3.893531	Ni^{2+}	**Fe^{3+}**
34	4.201977	Ni^{2+}	Ni^{2+}
35	4.267319	Ni^{2+}	**Pb^{2+}**
36	3.964694	Fe^{3+}	Fe^{3+}
37	4.083333	Fe^{3+}	Fe^{3+}
38	4.68742	Fe^{3+}	**Pb^{2+}**
39	4.043584	Fe^{3+}	Fe^{3+}

40	3.861747	Fe^{3+}	Fe^{3+}
41	6.244578	Mn^{2+}	**Cu^{2+}**
42	7.055556	Mn^{2+}	Mn^{2+}
43	6.461163	Mn^{2+}	Mn^{2+}
44	5.969868	Mn^{2+}	**Cu^{2+}**
45	6.139714	Mn^{2+}	**Cu^{2+}**

Table S5. Identification of unknown metal ion samples at 30 nM using 24C+ 24T.

Samples	OD_{660nm}/OD_{538nm} -24C	OD_{660nm}/OD_{538nm} -24T	Identification	Verification
1	0.436959	2.24039	Cd^{2+}	Cd^{2+}
2	0.44035	2.143229	Cd^{2+}	Cd^{2+}
3	0.42281	2.215474	Cd^{2+}	Cd^{2+}
4	0.429389	2.185682	Cd^{2+}	Cd^{2+}
5	0.44669	2.194076	Cd^{2+}	Cd^{2+}
6	0.574044	2.099671	Hg^{2+}	Hg^{2+}
7	0.578362	2.185484	Hg^{2+}	Hg^{2+}
8	0.536162	2.246259	Hg^{2+}	Hg^{2+}
9	0.558569	2.071244	Hg^{2+}	Hg^{2+}
10	0.573948	2.049621	Hg^{2+}	Hg^{2+}
11	0.424927	4.662048	Pb^{2+}	Pb^{2+}
12	0.437931	4.349206	Pb^{2+}	Pb^{2+}
13	0.403813	4.092794	Pb^{2+}	Pb^{2+}
14	0.411648	4.251412	Pb^{2+}	Pb^{2+}
15	0.43041	4.330655	Pb^{2+}	Pb^{2+}
16	0.651296	8.879277	Ag^{+}	Ag^{+}
17	0.660766	7.787879	Ag^{+}	Ag^{+}
18	0.633585	8.915176	Ag^{+}	Ag^{+}
19	0.631506	8.027735	Ag^{+}	Ag^{+}
20	0.642841	8.049715	Ag^{+}	Ag^{+}
21	1.495085	6.817053	Cu^{2+}	**Mn^{2+}**
22	1.477026	5.313725	Cu^{2+}	Cu^{2+}
23	1.422968	6.781707	Cu^{2+}	Cu^{2+}
24	1.43167	6.857888	Cu^{2+}	Cu^{2+}
25	1.493555	5.974246	Cu^{2+}	Cu^{2+}
26	0.784198	2.808635	Sn^{4+}	Sn^{4+}
27	0.783562	3.261111	Sn^{4+}	Sn^{4+}
28	0.740629	2.830918	Sn^{4+}	Sn^{4+}
29	0.759578	3.06725	Sn^{4+}	Sn^{4+}
30	0.763427	2.766368	Sn^{4+}	Sn^{4+}
31	1.617463	3.942068	Ni^{2+}	Ni^{2+}
32	1.575541	4.65	Ni^{2+}	Ni^{2+}
33	1.631325	3.893531	Ni^{2+}	Ni^{2+}
34	1.575773	4.201977	Ni^{2+}	Ni^{2+}
35	1.647533	4.267319	Ni^{2+}	Ni^{2+}
36	0.509785	3.964694	Fe^{3+}	Fe^{3+}
37	0.507589	4.083333	Fe^{3+}	Fe^{3+}
38	0.507402	4.68742	Fe^{3+}	Fe^{3+}
39	0.4923	4.043584	Fe^{3+}	Fe^{3+}
40	0.50657	3.861747	Fe^{3+}	Fe^{3+}

41	1.567911	6.244578	Mn^{2+}	Mn^{2+}
42	1.530575	7.055556	Mn^{2+}	Mn^{2+}
43	1.532628	6.461163	Mn^{2+}	Mn^{2+}
44	1.512149	5.969868	Mn^{2+}	Mn^{2+}
45	1.534678	6.139714	Mn^{2+}	Mn^{2+}

Table S6. Identification of unknown metal ion samples at 30 nM using 24A + 24C + 24T.

Samples	OD_{660nm}/OD_{538nm} -24A	OD_{660nm}/OD_{538nm} -24C	OD_{660nm}/OD_{538nm} -24T	Identification	Verification
1	6.89989	0.436959	2.24039	Cd^{2+}	Cd^{2+}
2	6.795175	0.44035	2.143229	Cd^{2+}	Cd^{2+}
3	6.736045	0.42281	2.215474	Cd^{2+}	Cd^{2+}
4	7.058236	0.429389	2.185682	Cd^{2+}	Cd^{2+}
5	6.683715	0.44669	2.194076	Cd^{2+}	Cd^{2+}
6	0.180407	0.574044	2.099671	Hg^{2+}	Hg^{2+}
7	0.181651	0.578362	2.185484	Hg^{2+}	Hg^{2+}
8	0.17958	0.536162	2.246259	Hg^{2+}	Hg^{2+}
9	0.177995	0.558569	2.071244	Hg^{2+}	Hg^{2+}
10	0.184869	0.573948	2.049621	Hg^{2+}	Hg^{2+}
11	5.078908	0.424927	4.662048	Pb^{2+}	Pb^{2+}
12	4.905491	0.437931	4.349206	Pb^{2+}	Pb^{2+}
13	5.234437	0.403813	4.092794	Pb^{2+}	Pb^{2+}
14	4.676821	0.411648	4.251412	Pb^{2+}	Pb^{2+}
15	5.312602	0.43041	4.330655	Pb^{2+}	Pb^{2+}
16	3.734088	0.651296	8.879277	Ag^{+}	Ag^{+}
17	3.529801	0.660766	7.787879	Ag^{+}	Ag^{+}
18	4.317881	0.633585	8.915176	Ag^{+}	Ag^{+}
19	3.419925	0.631506	8.027735	Ag^{+}	Ag^{+}
20	3.579051	0.642841	8.049715	Ag^{+}	Ag^{+}
21	1.312931	1.495085	6.817053	Cu^{2+}	Cu^{2+}
22	1.288999	1.477026	5.313725	Cu^{2+}	Cu^{2+}
23	1.342985	1.422968	6.781707	Cu^{2+}	Cu^{2+}
24	1.360172	1.43167	6.857888	Cu^{2+}	Cu^{2+}
25	1.303951	1.493555	5.974246	Cu^{2+}	Cu^{2+}
26	3.847242	0.784198	2.808635	Sn^{4+}	Sn^{4+}
27	3.666115	0.783562	3.261111	Sn^{4+}	Sn^{4+}
28	4.1243	0.740629	2.830918	Sn^{4+}	Sn^{4+}
29	3.796173	0.759578	3.06725	Sn^{4+}	Sn^{4+}
30	3.636661	0.763427	2.766368	Sn^{4+}	Sn^{4+}
31	3.749175	1.617463	3.942068	Ni^{2+}	Ni^{2+}
32	3.938742	1.575541	4.65	Ni^{2+}	Ni^{2+}
33	3.934658	1.631325	3.893531	Ni^{2+}	Ni^{2+}
34	3.920466	1.575773	4.201977	Ni^{2+}	Ni^{2+}
35	4.20505	1.647533	4.267319	Ni^{2+}	Ni^{2+}
36	10.51881	0.509785	3.964694	Fe^{3+}	Fe^{3+}
37	10.46026	0.507589	4.083333	Fe^{3+}	Fe^{3+}
38	10.17219	0.507402	4.68742	Fe^{3+}	Fe^{3+}

39	10.32529	0.4923	4.043584	Fe^{3+}	Fe^{3+}
40	10.51391	0.50657	3.861747	Fe^{3+}	Fe^{3+}
41	2.951537	1.567911	6.244578	Mn^{2+}	Mn^{2+}
42	2.700646	1.530575	7.055556	Mn^{2+}	Mn^{2+}
43	2.94458	1.532628	6.461163	Mn^{2+}	Mn^{2+}
44	2.625397	1.512149	5.969868	Mn^{2+}	Mn^{2+}
45	2.780332	1.534678	6.139714	Mn^{2+}	Mn^{2+}

Table S7. Training matrix of the response patterns against metal ions (each at 30 nM) in the presence of tap water using the sensor array.

Metal ions	$OD_{660\ nm}/OD_{538\ nm}$ - 24A	$OD_{660\ nm}/OD_{538\ nm}$ - 24C	$OD_{660\ nm}/OD_{538\ nm}$ - 24T
Cd^{2+}	0.877944	0.989211	1.050379
Cd^{2+}	0.868676	0.98256	1.055599
Cd^{2+}	0.883566	0.972536	1.044739
Cd^{2+}	0.864108	0.988728	1.020234
Cd^{2+}	0.88769	0.9536	1.051525
Hg^{2+}	0.054328	0.992698	1.015826
Hg^{2+}	0.052877	0.997162	1.018282
Hg^{2+}	0.052577	0.980823	1.02578
Hg^{2+}	0.050929	1.00161	1.010041
Hg^{2+}	0.054873	1.007898	1.016399
Pb^{2+}	0.867933	1.011022	0.946451
Pb^{2+}	0.85948	1.024691	0.958944
Pb^{2+}	0.866893	1.003333	0.949152
Pb^{2+}	0.858671	1.017214	0.93572
Pb^{2+}	0.858702	1.06877	0.940832
Ag^{+}	0.927716	0.953841	0.903045
Ag^{+}	0.922127	0.947523	0.903108
Ag^{+}	0.933488	0.940716	0.912136
Ag^{+}	0.923637	0.940666	0.89233
Ag^{+}	0.927611	0.950475	0.908052
Cu^{2+}	0.804987	1.01898	0.845456
Cu^{2+}	0.797384	1.016796	0.858673
Cu^{2+}	0.819785	0.995483	0.856765
Cu^{2+}	0.80555	1.00156	0.846687
Cu^{2+}	0.780876	1.038787	0.83713
Sn^{4+}	0.816606	1.102324	1.058435
Sn^{4+}	0.806518	1.126189	1.087476
Sn^{4+}	0.828042	1.096592	1.068301
Sn^{4+}	0.835208	1.130435	1.067163
Sn^{4+}	0.817069	1.134168	1.080343
Ni^{2+}	0.812692	1.071645	1.01492
Ni^{2+}	0.80978	1.069325	1.023218
Ni^{2+}	0.830242	1.056651	1.026501
Ni^{2+}	0.814467	1.051282	1.019013
Ni^{2+}	0.792839	1.068982	1.02774
Fe^{3+}	1.781011	1.009642	0.911094
Fe^{3+}	1.747461	1.007405	0.921537
Fe^{3+}	1.790204	0.995651	0.92579

Fe^{3+}	1.764451	0.99542	0.915137
Fe^{3+}	1.785715	0.993708	0.917807
Mn^{2+}	0.835658	0.97557	1.046073
Mn^{2+}	0.835171	0.977112	1.046873
Mn^{2+}	0.841831	0.962547	1.038991
Mn^{2+}	0.845102	0.970588	1.034089
Mn^{2+}	0.829499	0.972268	1.043057
Tap water	0.906237	1.102263	1.015502
Tap water	0.893211	1.11174	1.020253
Tap water	0.904705	1.110005	1.021764
Tap water	0.925048	1.108025	1.015381
Tap water	0.897072	1.105168	1.017921