Supporting Information:

Postage stamp size array sensor for the sensitive screen test of heavy-metal ions

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Text S1. pH effect on Zn^{2+} detection at 2 mg/L by postage stamp-sized array sensor.

The pH effect was investigated using the representative heavy-metal ion Zn^{2+} at its wastewater discharge standard concentration. A universal flatbed scanner was used to collect array sensor images. After digitizing the red, green, and blue values of each heterocyclic azo indicator dyes, the colour changes could be easily obtained by subtracting images before and after exposure to heavy-metal ions. Control experiments were performed using distilled water without any addition of heavy-metal ions. It is noticeable that the control experiments also showed color changes simply due to the wetting of the indicators. Thus the difference map of each heavy-metal ion was achieved by subtracting individual red, green, and blue values of indicators after exposure to heavy-metal ion and distilled water. The array sensor showed clearer colour changes with the increasing of basicity (SI, Figure S2). Because many heavy-metal ions form insoluble hydroxides at high pH, we studied the color changes of indicators in the presence of heavy-metal ions at pH = 6.5.

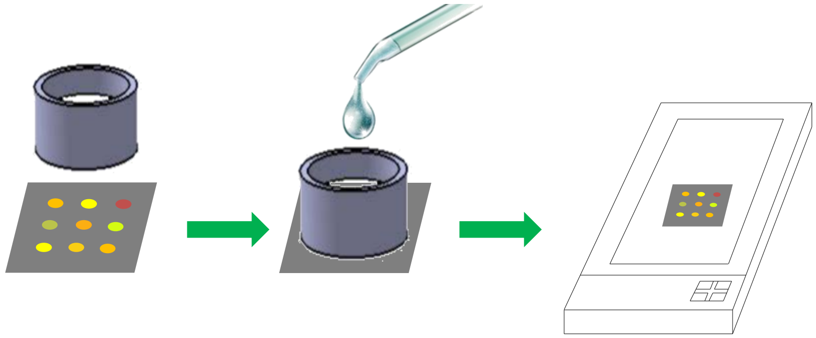

Figure S1. The experimental set-up.

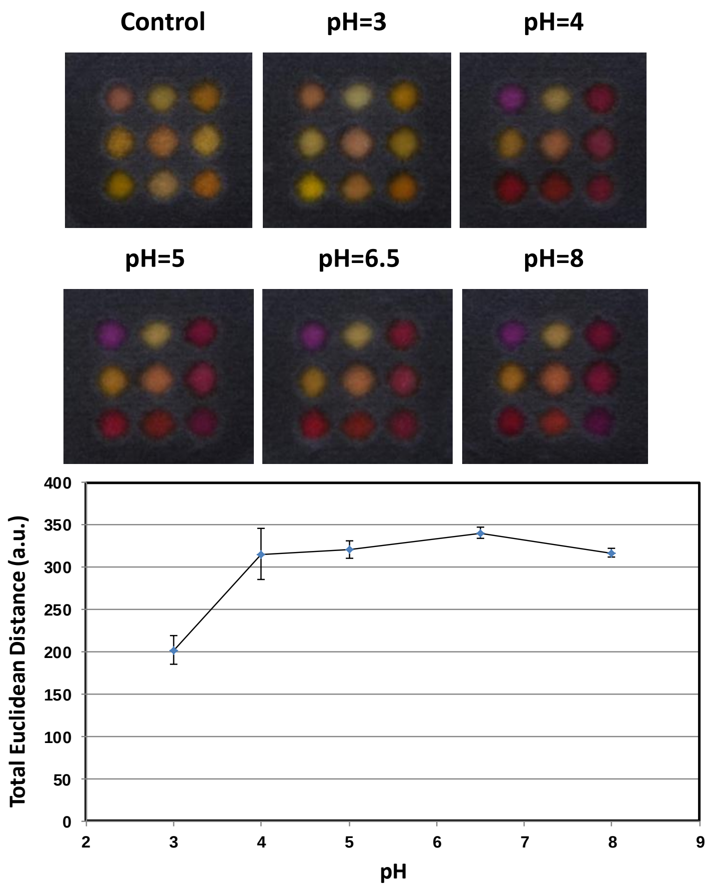

Figure S2. pH effect on Zn^{2+} detection at its wastewater discharge standard concentration (2 mg/L) by enrichment-based heterocyclic azo dyes array sensor.

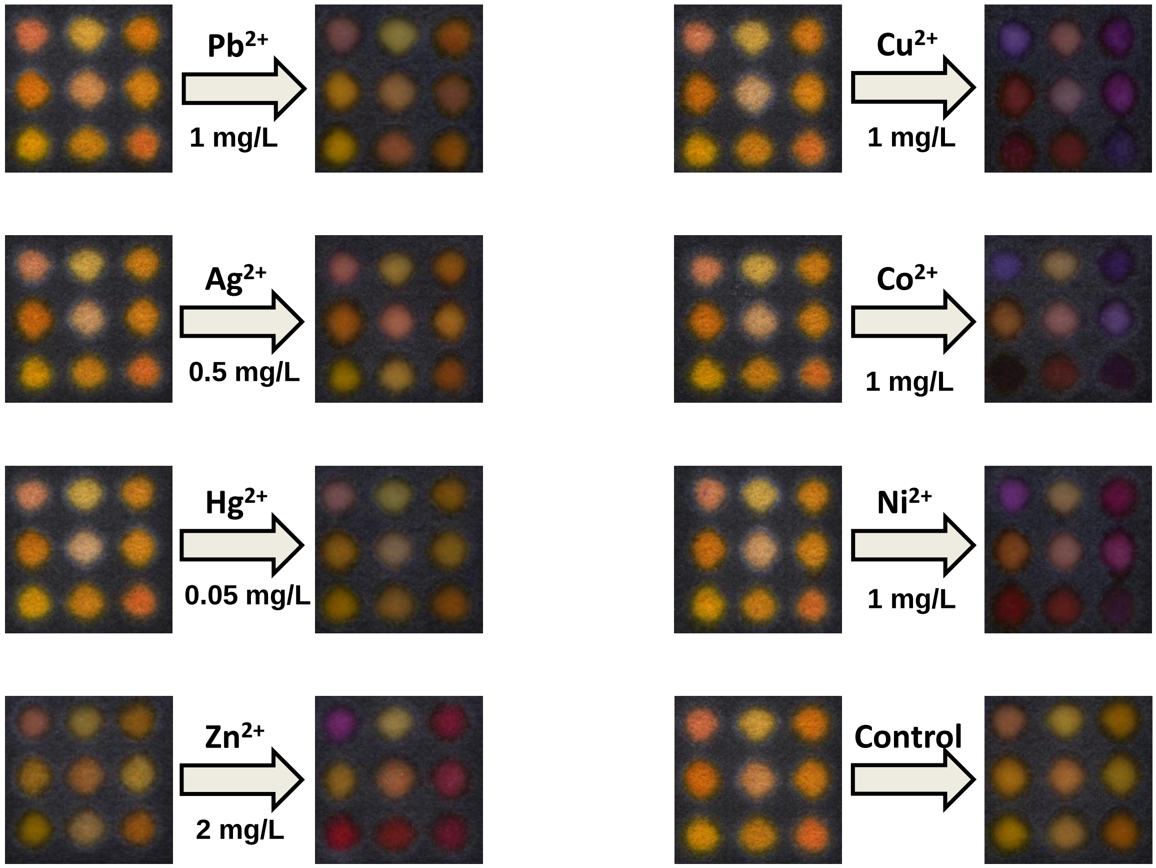

Figure S3. The colour responses of heterocyclic azo dyes array for seven heavy-metal ions at their wastewater discharge standard concentrations.

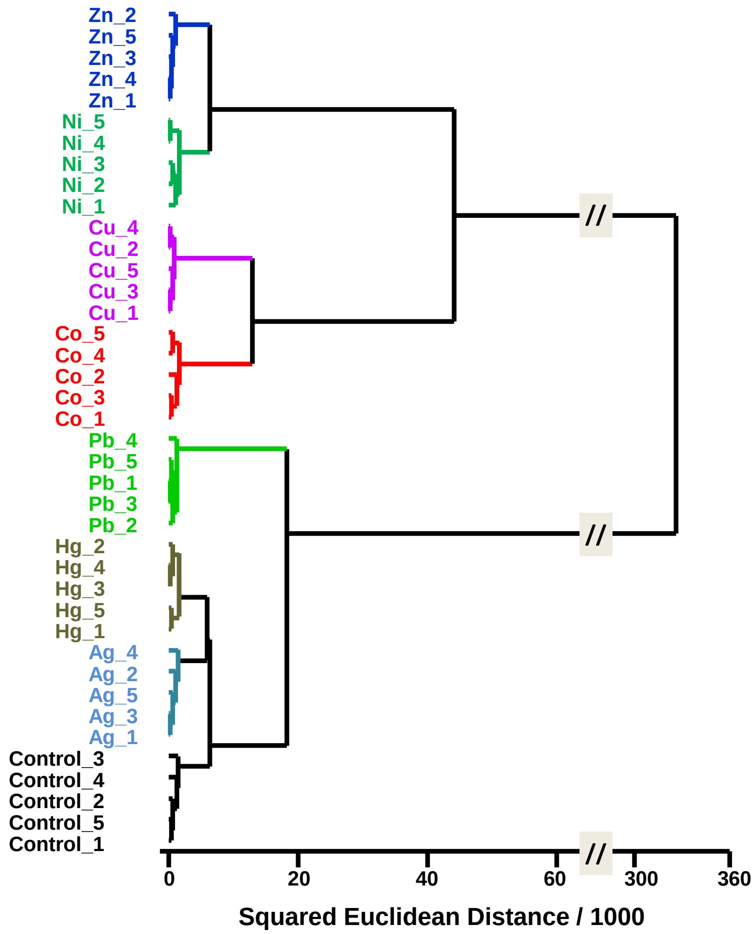

Figure S4. Hierarchical cluster analysis for seven heavy-metal ions at their wastewater discharge standard concentration and a control. All experiments were run in quintuplicate trials. No confusions or errors in classifications or errors in classification were observed in 40 trials.

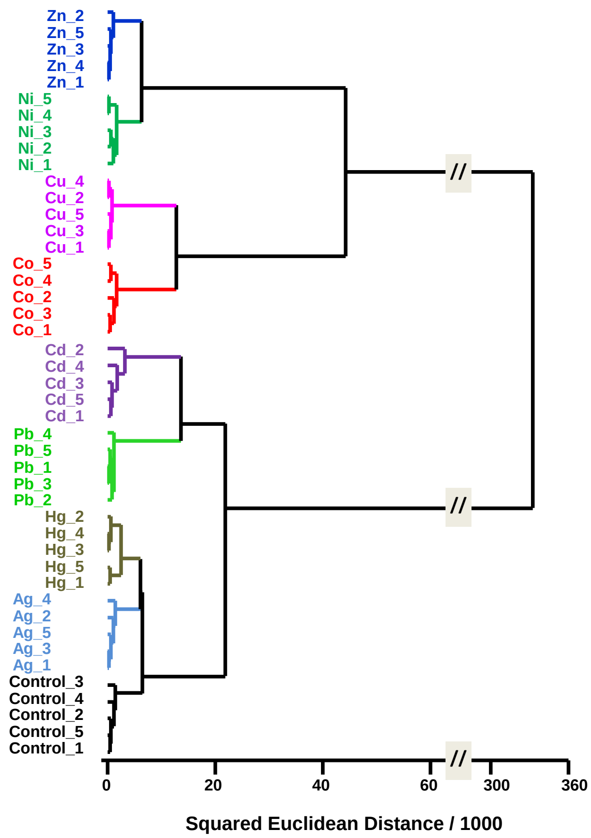

Figure S5. Hierarchical cluster analysis for Cd^{2+} at its five-fold wastewater discharge standard concentration and seven heavy-metal ions and a control. All experiments were run in quintuplicate trials. No confusions or errors in classifications or errors in classification were observed in 45 trials.

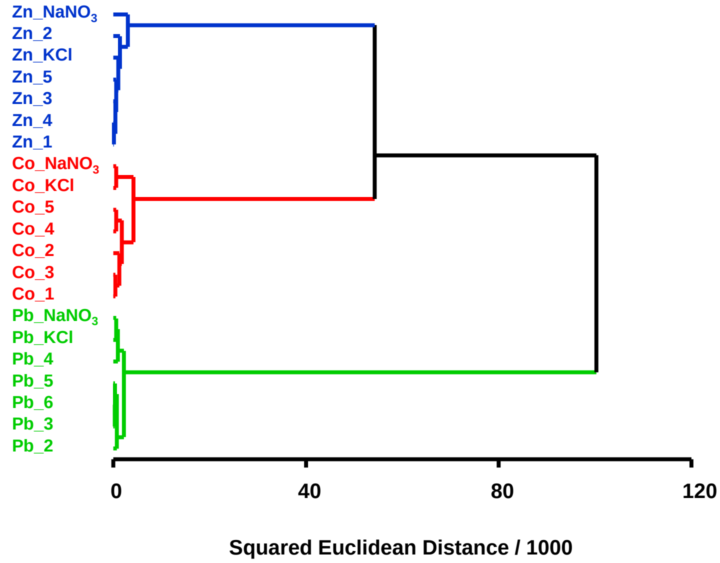

Figure S6. Hierarchical cluster analysis for three representative heavy-metal ions (Zn^{2+}, Pb^{2+}, and Co^{2+}) at their wastewater discharge standard concentration and the mixture of heavy-metal ions and interference ions, e.g., Na^{+}, K^{+}, Cl^{-}, and NO_3^{-}.

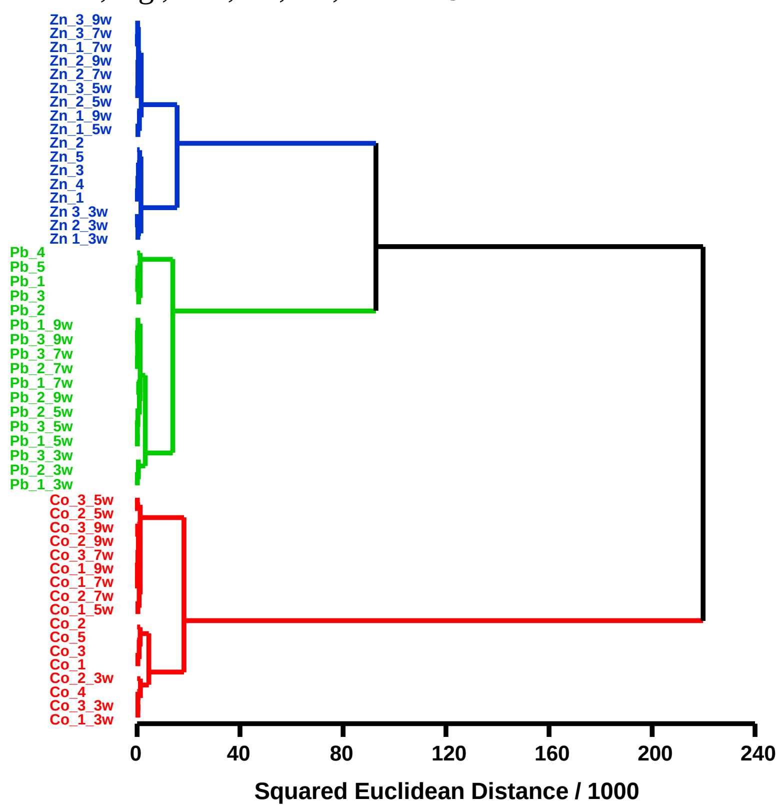

Figure S7. Hierarchical cluster analysis for three representative heavy-metal ions (Zn^{2+}, Pb^{2+}, and Co^{2+}) at their wastewater discharge standard concentration using enrichment-based heterocylic azo dyes array sensor stored in polyethylene bags under N_2 for 1, 3, 5, 7, and 9 weeks.

Table S1. Full digital database (R=red, G=green, B=blue values) of sensor array for seven heavy-metal ions.

	R1	G1	B1	R2	G2	B2	R3	G3	B3	R4	G4	B4	R5	G5	B5	R6	G6	B6	R7	G7	B7	R8	G8	B8	R9	G9	B9
Control_1	-58.227	-21.457	-11.838	-60.461	-32.727	-5.5403	-62.852	-22.635	-10.247	-59.445	-13.707	-4.9934	-59.332	-34.382	-20.367	-65.651	-22.748	4.81506	-65.629	-37.387	-7.0845	-62.408	-26.225	18.2351	-66.325	-24.955	-26.478
Control_2	-67.717	-20.876	-10.189	-71.871	-41.038	-7.3263	-69.675	-21.711	-10.524	-70.173	-13.865	1.4214	-64.925	-35.709	-17.801	-74.536	-25.025	-1.1889	-71.491	-41.947	-5.7028	-71.717	-28.28	18.9643	-74.74	-27.413	-27.269
Control_3	-74.021	-27.324	-14.514	-59.226	-35.815	-10.684	-75.391	-26.762	-11.801	-45.538	-4.1361	2.04491	-43.347	-29.268	-21.153	-65.852	-17.148	1.22325	-57.285	-28.971	-4.7332	-46.807	-16.771	20.1704	-76.04	-28.32	-27.551
Control_5	-70.563	-28.096	-19.363	-70.624	-39.453	-12.063	-68.733	-23.351	-13.37	-67.363	-17.554	-5.6196	-61.981	-35.737	-21.244	-62.674	-20.242	-2.0964	-60.68	-33.822	-6.8336	-57.911	-20.705	20.5601	-56.931	-25.24	-23.892
Control_4	-71.296	-31.452	-19.812	-74.46	-50.077	-17.774	-68.498	-30.461	-16.575	-49.765	-15.493	-1.0991	-61.262	-45.036	-29.91	-50.647	-19.226	-1.9498	-58.112	-30.526	-10.734	-61.098	-31.151	2.80185	-61.029	-25.654	-27.708
Pb_2	-101.78	-42.266	-1.181	-70.137	-37.568	-4.4016	-90.513	-49.123	-3.0013	-73.946	-14.509	4.25892	-49.255	-34.801	-22.935	-90.444	-56.443	20.1017	-74.49	-46.141	-4.0779	-57.461	-44.355	21.967	-74.461	-29.959	-22.161
Pb_3	-92.277	-40.771	-2.4558	-74.299	-39.079	-1.8454	-93.576	-48.935	-6.1334	-72.734	-11.806	3.14531	-70.258	-37.794	-18.04	-94.638	-55.223	15.2827	-60.804	-40.956	-6.6645	-61.617	-49.41	19.6156	-67.67	-29.506	-22.871
Pb_4	-89.841	-36.777	3.21532	-68.634	-35.033	1.9683	-73.807	-45.811	2.24174	-56.044	-10.367	1.74373	-68.707	-39.466	-18.469	-95.47	-57.753	14.6222	-62.919	-36.349	-2.9432	-71.448	-51.53	21.1863	-86.732	-34.295	-23.408
Pb_5	-105.25	-44.152	-5.0145	-75.729	-41.63	-4.1281	-101.61	-57.848	-1.1149	-73.888	-11.671	5.26024	-75.207	-40.905	-23.139	-107.21	-62.662	15.4465	-64.001	-43.458	-6.3857	-60.367	-49.65	20.8019	-72.514	-30.824	-19.262
Pb_1	-97.009	-42.198	-2.716	-68.304	-35.481	-2.5878	-87.6	-58.605	1.65126	-71.604	-18.985	1.34346	-68.569	-43.046	-22.679	-97.724	-60.964	21.5733	-62.256	-47.775	-4.2761	-65.793	-50.89	22.7992	-69.196	-28.543	-16.495
Ag_1	-64.02	-44.004	-10.193	-55.614	-40.025	-10.346	-53.948	-43.123	-8.0304	-62.794	-26.705	-1.7318	-58.162	-59.287	-28.086	-64.388	-32.129	2.06077	-49.089	-34.172	-5.6143	-55.116	-26.75	12.3501	-81.279	-43.044	-21.395
Ag_2	-56.775	-38.987	-11.926	-56.814	-46.304	-15.687	-60.844	-41.108	-5.8085	-46.066	-23.137	0.25231	-47.728	-53	-22.4	-46.264	-23.898	4.78864	-52.165	-29.453	-5.5165	-50.477	-18.835	19.7873	-77.259	-38.594	-15.511
Ag_3	-61.893	-44.214	-12.267	-53.4	-43.061	-14.692	-54.049	-42.725	-7.7477	-51.531	-26.551	-1.0898	-56.425	-55.911	-25.02	-55.486	-30.089	2.05813	-62.754	-39.107	-4.4914	-55.564	-28.845	10.609	-76.894	-44.892	-17.214
Ag_5	-71.719	-42.112	-12.238	-64.807	-47.843	-14.386	-62.343	-48.775	-5.5456	-64.306	-30.963	-3.9934	-69.881	-62.445	-28.799	-66.908	-35.749	3.44122	-52.66	-36.295	-8.1149	-68.526	-29.4	11.6962	-83.997	-47.247	-17.473
Ag_4	-62.847	-45.465	-13.143	-45.486	-36.731	-10.094	-65.704	-49.643	-8.1995	-48.273	-27.386	-0.1215	-41.444	-48.465	-26.604	-55.861	-41.731	-4.1664	-52.262	-34.201	-5.4742	-38.338	-27.589	-7.4967	-74.309	-47.07	-18.737
Co_1	-125.54	-63.708	23.9128	-78.083	-57.273	0.16116	-147.47	-88.749	46.679	-88.569	-39.162	14.4782	-82.445	-65.859	-17.696	-131.41	-70.028	65.7728	-166.92	-114.16	8.52708	-117.09	-83.857	4.09115	-161.13	-84.495	-2.7477
Co_2	-121.31	-64.092	23.8811	-83.079	-61.462	-2.8441	-129.96	-87.189	43.7847	-92.655	-56.213	0.26684	-69.621	-62.283	-25.552	-107.12	-54.855	76.8454	-163.08	-110.38	10.469	-117.39	-83.867	5.91678	-153.82	-80.749	1.50198
Co_3	-120.38	-64.889	28.4848	-70.542	-54.639	1.95244	-137.5	-86.465	37.148	-85.855	-34.139	13.9326	-81.151	-61.906	-13.317	-119.97	-64.235	63.5958	-158.25	-110.99	8.64729	-112.4	-81.164	3.59974	-148.58	-80.769	-0.2246
Co_4	-112.46	-58.984	28.0449	-69.746	-54.832	2.82695	-131.56	-83.955	46.4333	-71.875	-30.152	17.148	-67.359	-55.017	-8.0357	-110.22	-57.337	72.0436	-143.85	-98.411	10.2655	-102.01	-74.366	9.78996	-140.19	-75.555	4.11889
Co_5	-123.14	-64.621	23.5548	-80.297	-58.127	2.8811	-132.44	-81.166	53.9987	-80.353	-33.21	17.6671	-79.978	-61.057	-9.1295	-113.38	-57.391	73.7556	-158.5	-110.8	7.19419	-107.73	-80.831	7.83355	-139.73	-77.697	3.63408
Cu_1	-102.5	-54.88	35.8943	-74.151	-71.947	10.6975	-110.39	-82.353	55.2048	-92.694	-58.864	16.2655	-82.553	-63.258	-3.6552	-98.744	-75.945	64.1479	-124.96	-104.38	20.9524	-99.473	-79.785	9.1823	-135.32	-60.355	27.2959
Cu_2	-112.57	-61.745	29.6592	-83.454	-77.935	5.20872	-114.49	-85.185	49.8626	-90.826	-62.968	12.8045	-97.04	-74.077	-11.322	-114.96	-88.34	55.2721	-128.96	-107.92	17.8666	-104.42	-83.369	8.00925	-142.03	-65.267	21.0779
Cu_3	-105.25	-58.518	35.6552	-67.199	-73.45	7.78467	-106.65	-79.474	52.9102	-99.242	-66.373	13.5931	-83.092	-68.217	-7.5878	-107.37	-85.513	55.5443	-128.01	-106.34	23.3144	-98.017	-80.176	9.26288	-141.75	-64.604	24.2761
Cu_4	-106.88	-54.462	33.9657	-77.193	-72.564	5.36592	-123.23	-85.387	49.4993	-95.59	-65.834	13.6671	-88.065	-69.018	-12.14	-116.13	-90.449	54.9894	-125.04	-107.63	19.6143	-104.26	-84.79	4.44782	-143.93	-66.657	25.7675
Cu_5	-94.218	-51.404	46.2682	-76.992	-74.966	5.1638	-102.06	-81.588	50.5126	-97.581	-63.962	15.3263	-94.359	-68.682	-7.3157	-111.04	-84.243	56.9657	-132.14	-107.05	17.2682	-108.67	-84.658	6.70145	-143.62	-67.597	23.675
Ni_1	-93.761	-70.296	20.8864	-69.823	-57.679	-3.7437	-102.36	-94.826	15.465	-72.015	-34.757	13.8362	-84.773	-64.112	-12.919	-107.65	-87.573	35.0462	-120.26	-109.6	10.7252	-112.92	-90.308	0.35799	-133.56	-71.111	3.98547
Ni_2	-91.651	-62.268	12.7028	-78.978	-63.777	-5.7635	-113.69	-96.849	16.5376	-79.787	-50.737	3.06605	-73.295	-64.199	-23.155	-103.48	-87.333	35.4333	-108.99	-107.25	2.59049	-90.954	-79.509	0.08719	-125.93	-73.086	-0.6156
Ni_3	-88.443	-67.502	23.8666	-71.83	-58.4	-1.5588	-102.43	-94.699	27.8811	-64.617	-39.458	8.58256	-71.827	-63.896	-19.468	-93.225	-82.892	48.4174	-101.99	-105.06	6.56011	-89.485	-81.875	3.67107	-129.93	-71.029	0.19815
Ni_4	-85.342	-66.487	20.4703	-55.9	-49.849	-1.3487	-94.811	-93.292	20.9987	-58.724	-42.911	4.57992	-62.336	-61.269	-20.391	-89.798	-86.72	29.6182	-98.092	-102.72	9.09643	-97.51	-84.232	1.96565	-129.08	-70.285	-4.2431
Ni_5	-89.885	-69.602	21.3686	-60.601	-52.769	0.04359	-101.98	-95.189	17.074	-55.524	-45.717	0.74769	-59.857	-62.375	-21.82	-87.338	-88.02	31.7992	-100.27	-104.82	8.75429	-99.671	-83.509	3.50198	-137.81	-72.882	-5.6499
Zn_1	-94.575	-77.457	14.2404	-66.976	-46.137	-5.3289	-89.469	-90.12	17.7081	-64.102	-18.106	8.68296	-61.734	-51.869	-25.092	-82.145	-77.534	34.535	-96.106	-112.68	17.5812	-94.996	-88.84	1.30911	-109.29	-76.419	2.02642
Zn_2	-91.083	-67.402	13.1268	-65.765	-47.35	-6.0845	-72.089	-80.246	21.609	-71.193	-19.254	8.28005	-77.221	-55.328	-26.908	-71.787	-73.737	35.358	-95.184	-109.01	11.9353	-93.402	-83.254	-0.8507	-109.7	-74.753	0.42008
Zn_3	-81.412	-75.996	15.5522	-61.962	-41.548	-0.8441	-86.203	-91.753	16.4042	-51.436	-10.49	12.9921	-53.03	-46.62	-18.989	-82.581	-85.917	30.0991	-95.571	-115.43	13.0449	-84.296	-88.193	-1.8758	-109.24	-77.341	1.92338
Zn_4	-92.716	-74.843	14.0251	-66.75	-44.026	-5.1955	-92.059	-92.843	14.2682	-64.659	-17.816	10.1506	-57.454	-47.564	-19.383	-77.976	-81.63	31.6169	-95.015	-110.44	15.5456	-85.502	-84.668	0.29458	-113.88	-74.075	-0.823
Zn_5	-77.773	-69.818	27.7952	-62.277	-38.76	4.28798	-92.074	-92.108	18.8507	-69.672	-17.312	17.1202	-67.429	-51.715	-20.771	-79.152	-79.847	38.0172	-95.896	-112.54	15.3844	-93.847	-89.407	-2.2576	-111.07	-77.168	0.82298
Hg_1	-87.339	-46.984	-8.6631	-78.723	-48.863	-12.186	-72.267	-51.026	-2.0568	-73.317	-23.509	1.78071	-67.785	-42.742	-19.205	-72.987	-38.956	6.45178	-68.297	-53.103	-2.2404	-69.639	-34.917	35.9181	-81.688	-35.841	-21.293
Hg_2	-65.808	-42.6	-5.8904	-50.674	-34.917	-9.4029	-59.05	-42.818	-0.7807	-56.697	-15.999	-0.4188	-54.304	-36.538	-17.161	-65.923	-37.198	4.40819	-65.202	-49.124	-4.0806	-59.343	-27.775	35.2761	-72.38	-35.308	-23.032
Hg_3	-71.638	-42.872	-3.9723	-53.096	-37.151	-9.2484	-59.548	-47.485	-3.852	-59.303	-18.478	0.81506	-43.668	-29.773	-11.984	-60.287	-34.024	11.3118	-64.951	-52.243	-5.2391	-48.309	-23.585	35.502	-58.638	-29.676	-12.58
Hg_4	-88.083	-51.272	-5.8758	-61.875	-40.757	-8.1876	-76.863	-53.551	-3.8494	-60.25	-19.457	0.03038	-58.827	-41.497	-19.333	-78.098	-41.26	4.60634	-66.956	-56.692	-1.1929	-66.678	-34.761	34.0304	-82.46	-40.638	-20.674
Hg_5	-70.217	-40.785	-3.5469	-57.337	-36.823	-8.6658	-63.448	-45.966	-2.8838	-49.491	-10.53	2.45707	-45.573	-31.402	-13.811	-63.605	-34.686	9.40555	-65.41	-49.723	-2.3052	-68.604	-31.847	32.9815	-74.366	-36.951	-20.188