Supporting Information

Title:

A Novel Spectroscopy-Deep Learning Approach for Aqueous Multi-Heavy Metal Detection

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Supporting Information contains:

Number of Supporting Texts: 2

Number of Supporting Figures: 5

Number of Supporting Tables: 4

Supporting Texts

Text S1. The selection method of the mixed chromogenic agents

The process of screening chromogenic agents was conducted using a well cavity plate. Different water quality parameters (As, Cr, Cu, Ni, Pb) were employed to stimulate chromogenic reactions. Subsequent photographs of these reactions underwent computational analysis, and the corresponding RGB values were quantified using the given color difference distance formula as follows.

$$\Delta E_i = \sqrt{(R_i - R_{ck})^2 + (G_i - G_{ck})^2 + (B_i - B_{ck})^2}$$

Where ΔE_i represents the chromatic aberration distance between the chromogenic reaction point of the i-th well cavity plate and the blank control reaction point,R_i represents the R value of the i-th image, G_i represents the G value of the i-th image, B_i represents the B value of the i-th image, and R_{ck}, G_{ck}, and B_{ck} represent the R, G, and B values of the blank control image, respectively.

Greater discrepancies in values indicate more pronounced color changes, rendering them preferable as leading candidates for experimental chromogenic agents.

Text S2. Calculation of instant concentration labels

The concentration of the substance to be measured in the experiment was dynamically changing, and the spectral pictures captured by the image detector carried the real-time concentration information of these substances. We calculated the exact concentration information of various substances according to the amount of substances added and the total volume of solution in the reaction cell. These data will serve as "concentration labels" for the spectral images in subsequent deep learning processes. The specific calculation formula is as follows:

$$C_i = \frac{m_i}{V_i}$$

Where C_i is the concentration value of the substance at a certain time in the reaction process, m_i is the mass of the substance at a certain time, and V_i is the total volume of the solution in the reaction pool at a certain time.

Supporting Figures

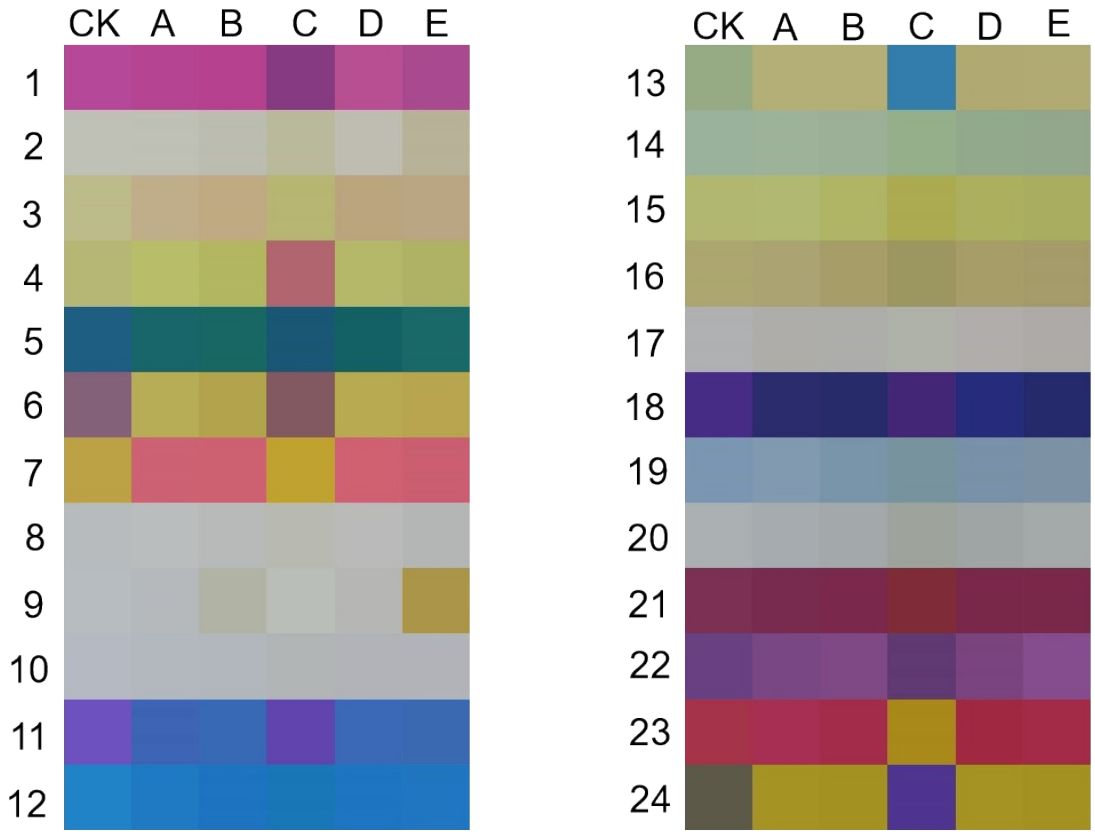

Fig. S1. Plot of titration experiments with well cavity plate. CK denotes the incorporation of ultrapure water as the sole substrate, while A to E denote the incorporation of 50 mg/L solutions of arsenic (As), nickel (Ni), chromium (Cr), lead (Pb), and copper (Cu) as substrates, respectively. Numbers 1 to 20 correspond to the introduction of various chromogenic agents.

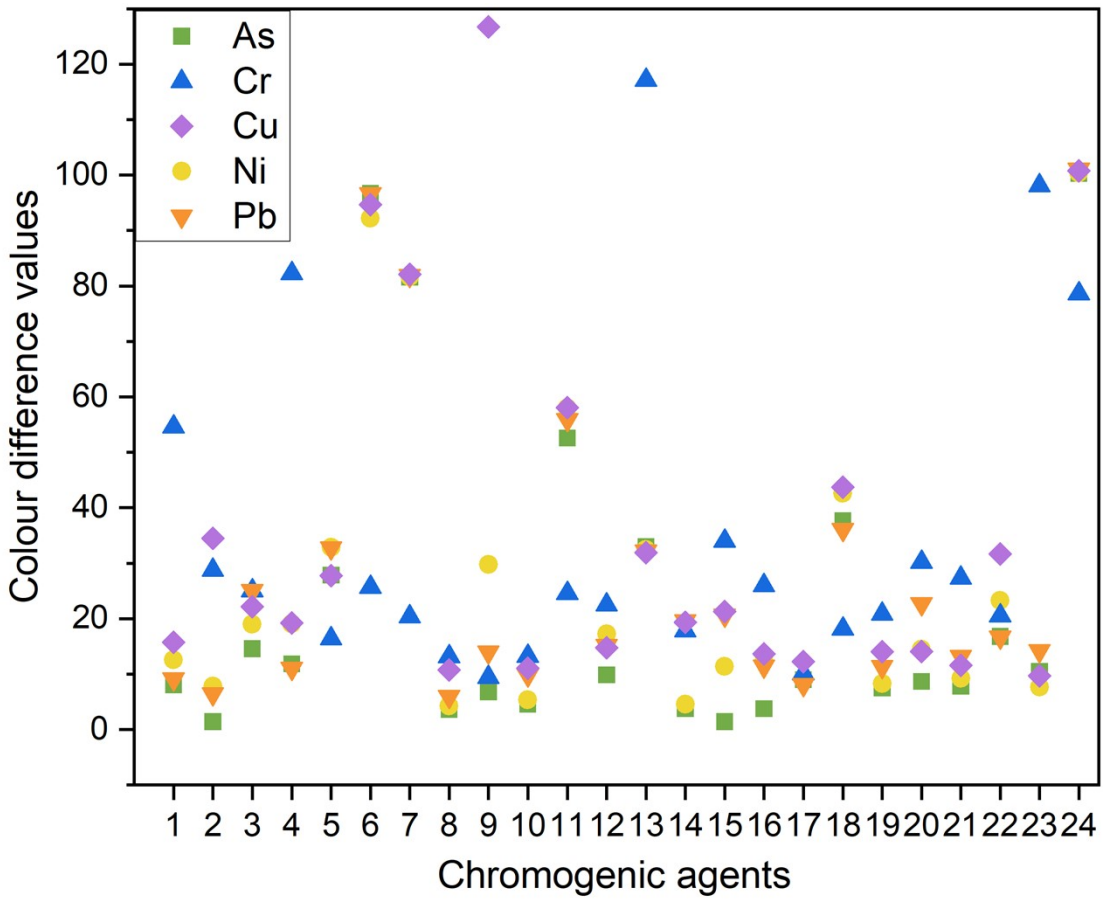

Fig. S2. Plot of color difference values for the well cavity plate titration experiment.

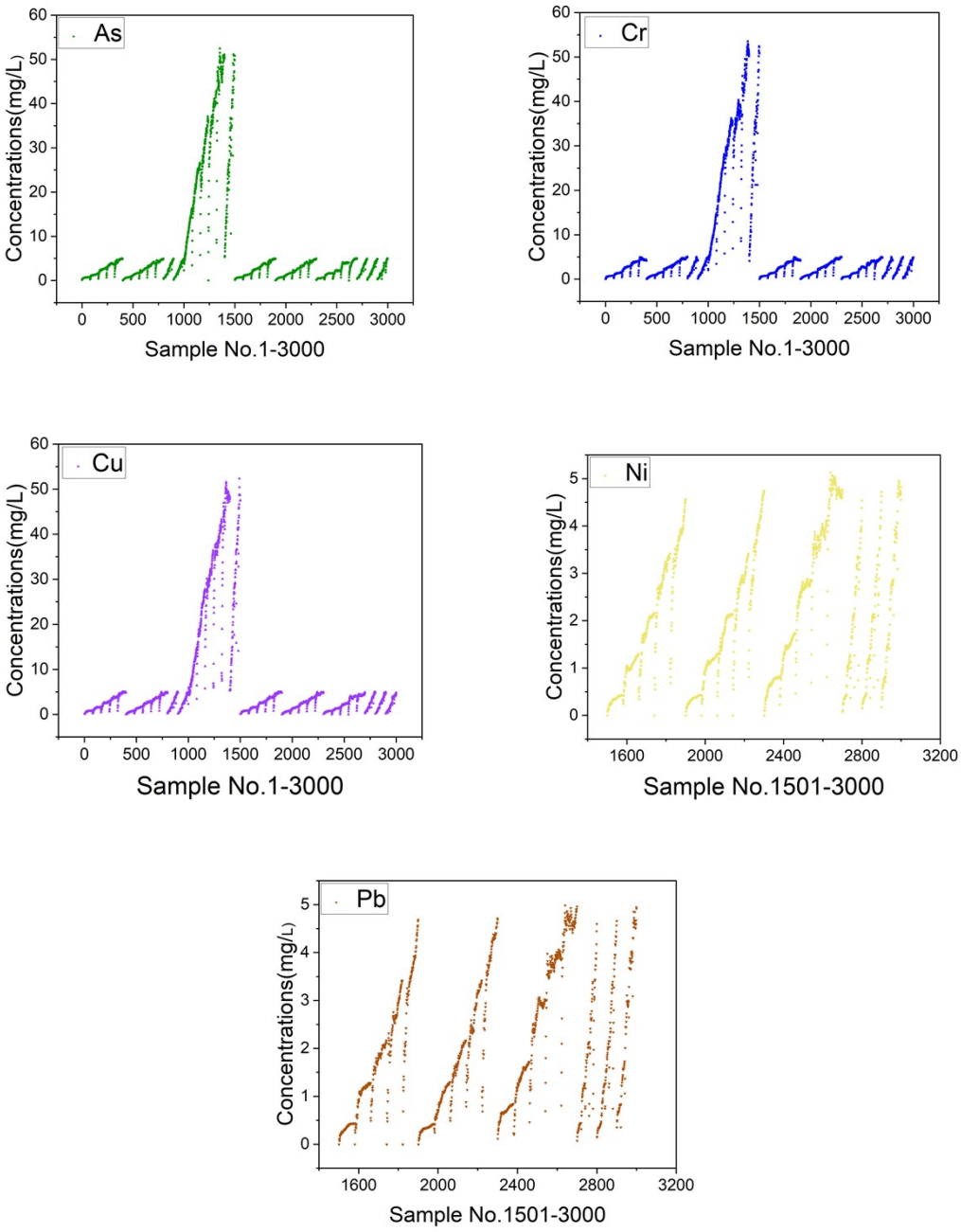

Fig. S3. Plot of sample concentration distribution.

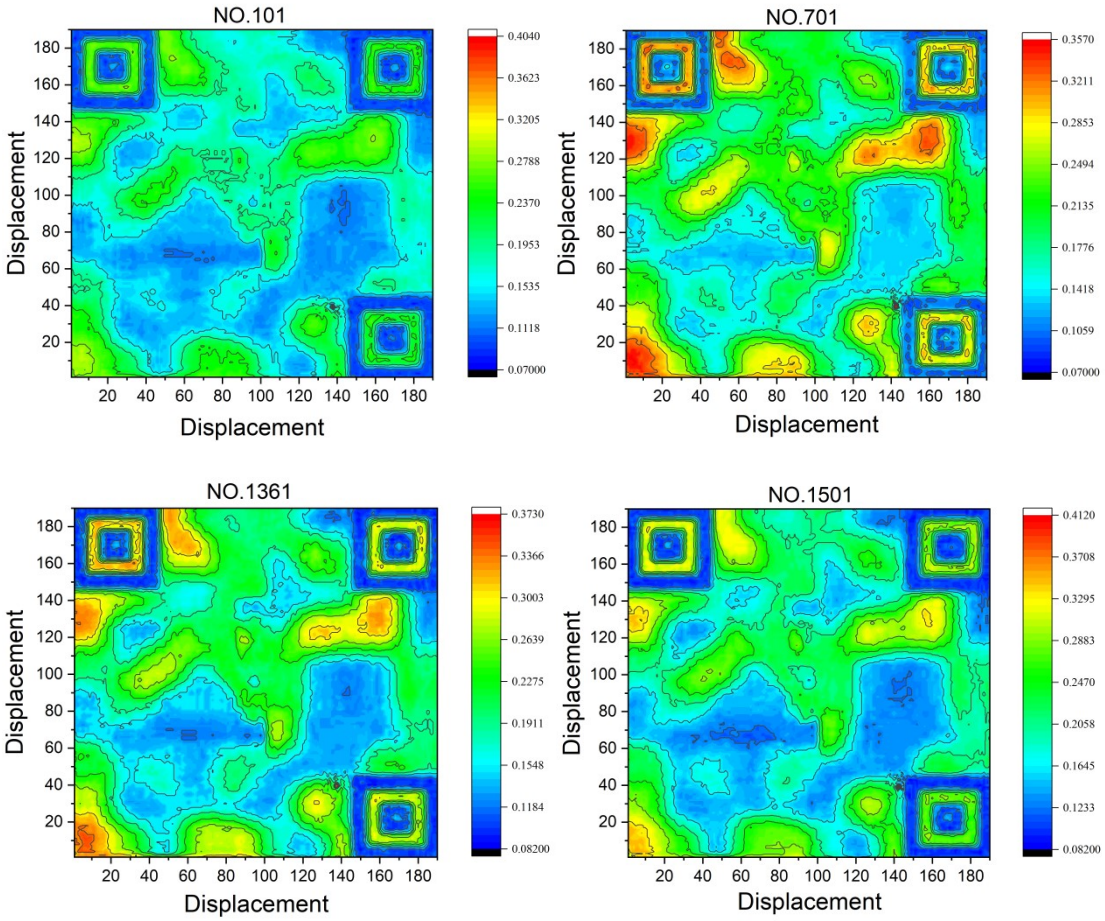

Fig. S4. Grey-scale contour maps of different feature images (sheet 101, 701, 1361 and 1501). Indicating that the spectroscopic apparatus can acutely capture information about the different concentrations of the sample, forming a unique characteristic spectral image.

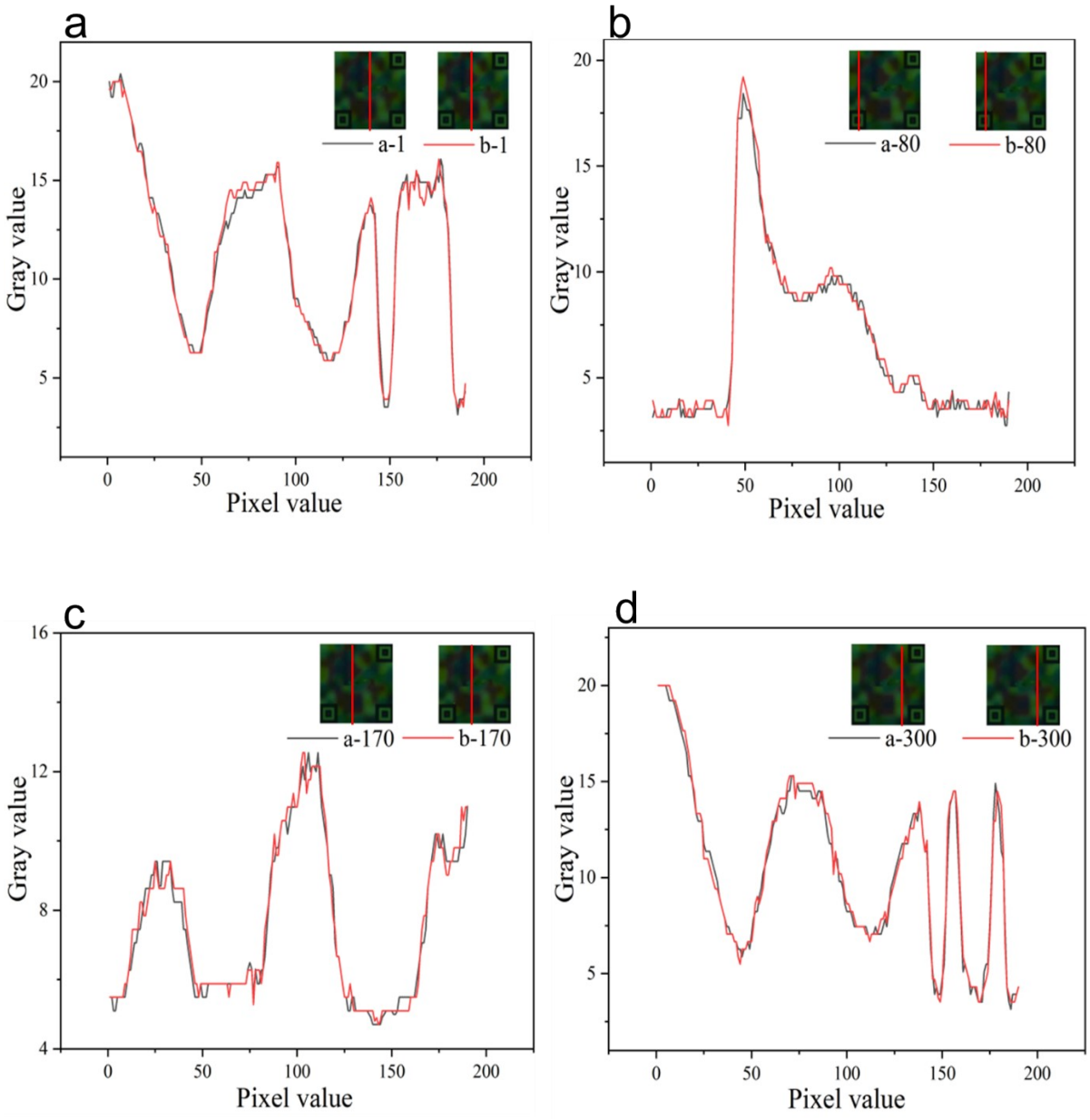

Fig. S5. Repeatability of feature images. (a) gray value information at x=95px for the feature image of sample #1 and its replica. (b) gray value information at x=11px for the feature image of sample #80 and its replica. (c) gray value information at x=89px for the feature image of sample #170 and its replica. (d) gray value information at x=150px for the feature image of sample #300 and its replica.

Supporting Tables

Table S1. The list of chromogenic agents for screening.

Number	Chromogenic agent	Number	Chromogenic agent
1	Chromium blue SE	13	Bromocresol green
2	Nitroso R salt	14	Naphthol green B
3	Chrome azurol S	15	Pyrogallol red
4	Alizarin red monohydrate	16	Pyrocatechol violet
5	Malachite green	17	Aluminon
6	Xylenol orange	18	Ethyl Violet
7	Methyl orange	19	Eriochrome black T
8	Tiron	20	Sulfosalicylic acid
9	Sodium diethyldithiocarbamate trihydrate	21	Neutral red
10	L-Ascorbic acid	22	Calcium reagent sodium carboxylate
11	Crystal violet	23	Methyl red-Thymol blue
12	Methylene blue tvihydrate	24	Bromophenol blue

Table S2. Background values of sample water quality indicators.

Number	Coordinates	PH	Cr(μg/L)	As(μg/L)	Cu(μg/L)	Ni(μg/L)	Pb(μg/L)
A1	(33°54′3″N, 109°54′56″E)	8.81	ND	0.6	0.32	ND	ND
A2	(35°1′10″N, 108°53′4″E)	8.52	ND	0.65	0.53	ND	ND
A3	(34°31′54″N, 107°1′18″E)	8.82	ND	0.6	0.6	ND	ND

Table S3. Partial random addition table in experiments.

Number	Ultrapure water	Cr	As	Cu	Number	Ultrapure water	Cr	As	Cu
1	1	0	1	1	1	0	1	1	1
2	2	0	1	0	2	0	1	1	1
3	0	1	1	1	3	2	0	0	1
4	1	0	1	1	4	1	1	1	0
5	2	1	0	0	5	0	1	1	1
6	1	1	1	0	6	2	1	0	0
7	2	1	0	0	7	0	1	1	1
8	0	1	1	1	8	2	0	0	1
9	2	0	0	1	9	0	1	1	1
10	0	1	1	1	10	1	1	1	0
11	2	0	0	1	11	1	0	1	1
12	1	1	0	1	12	1	0	1	1
13	1	1	0	1	13	1	1	1	0
14	0	1	1	1	14	2	0	0	1
15	1	1	1	0	15	2	0	0	1
16	2	1	0	0	16	2	1	0	0
17	2	0	1	0	17	1	1	1	0
18	1	0	1	1	18	1	1	0	1
19	2	0	0	1	19	1	0	1	1
20	1	0	1	1	20	1	0	1	1
21	3	0	0	0	21	2	0	0	1
22	1	1	1	0	22	1	1	0	1
23	1	1	0	1	23	2	0	1	0
24	2	0	1	0	24	2	1	0	0
25	1	1	0	1	25	2	1	0	0
26	1	1	1	0	26	2	0	1	0
27	2	0	1	0	27	1	1	0	1
28	1	1	0	1	28	1	1	1	0
29	0	1	1	1	29	1	1	0	1
30	2	0	0	1	30	2	0	1	0
31	2	0	0	1	31	2	0	0	1
32	0	1	1	1	32	2	0	1	0
33	1	1	1	0	33	2	0	0	1
34	1	1	1	0	34	1	1	0	1
35	2	0	0	1	35	1	1	0	1
36	0	1	1	1	36	1	1	0	1
37	1	1	0	1	37	1	0	1	1
38	2	0	0	1	38	1	0	1	1
39	1	1	1	0	39	1	1	0	1

40	0	1	1	1	40	1	1	1	0
41	1	1	0	1	41	3	0	0	0
42	1	0	1	1	42	0	1	1	1
43	1	1	0	1	43	1	1	0	1
44	3	0	0	0	44	1	0	1	1
45	2	0	1	0	45	2	1	0	0
46	2	1	0	0	46	1	0	1	1
47	1	1	0	1	47	2	0	1	0
48	1	0	1	1	48	1	0	1	1
49	2	0	1	0	49	0	1	1	1
50	1	1	1	0	50	1	1	0	1
51	0	1	1	1	51	2	1	0	0
52	2	0	1	0	52	1	1	1	0
53	2	0	0	1	53	2	0	1	0
54	2	0	0	1	54	2	0	0	1
55	1	1	1	0	55	2	1	0	0
56	0	1	1	1	56	2	0	1	0
57	1	1	1	0	57	2	0	0	1
58	2	0	1	0	58	2	0	0	1
59	2	0	0	1	59	1	1	1	0
60	1	1	1	0	60	1	0	1	1
61	3	0	0	0	61	1	1	0	1
62	2	1	0	0	62	2	1	0	0
63	0	1	1	1	63	3	0	0	0
64	2	0	0	1	64	2	0	0	1
65	0	1	1	1	65	0	1	1	1
66	2	1	0	0	66	1	0	1	1
67	0	1	1	1	67	2	0	0	1
68	2	0	0	1	68	1	1	1	0
69	1	1	1	0	69	1	1	1	0
70	1	0	1	1	70	2	0	1	0
71	1	1	0	1	71	3	0	0	0
72	1	1	1	0	72	1	1	1	0
73	1	1	0	1	73	1	1	0	1
74	1	0	1	1	74	1	1	1	0
75	3	0	0	0	75	1	1	1	0
76	0	1	1	1	76	1	1	1	0
77	0	1	1	1	77	2	0	1	0
78	2	0	1	0	78	0	1	1	1
79	2	0	1	0	79	0	1	1	1
80	1	1	1	0	80	3	0	0	0
81	0	1	1	1	81	0	1	1	1
82	0	1	1	1	82	0	1	1	1
83	1	1	0	1	83	1	0	1	1

84	2	0	0	1	84	0	1	1	1
85	1	0	1	1	85	1	1	0	1
86	2	0	1	0	86	0	1	1	1
87	1	1	0	1	87	0	1	1	1
88	1	0	1	1	88	0	1	1	1
89	0	1	1	1	89	2	0	1	0
90	0	1	1	1	90	1	1	0	1
91	1	0	1	1	91	0	1	1	1
92	0	1	1	1	92	1	1	0	1
93	1	1	1	0	93	1	1	1	0
94	2	0	1	0	94	1	0	1	1
95	1	1	0	1	95	1	1	1	0
96	0	1	1	1	96	0	1	1	1
97	0	1	1	1	97	0	1	1	1
98	2	0	0	1	98	0	1	1	1
99	2	0	1	0	99	1	1	0	1
100	1	0	1	1	100	0	1	1	1

Note: 0 means no addition and 1 means addition of the solution, a total of six mother liquor concentrations (5, 10, 20, 30, 35, 50 mg/L) were used in the experiments.

Table S4. Detailed architecture of CNNs.

ResNet-50		
Layer	Layer (type)	Output Shape
0	Input Layer	(None, 224, 224, 3)
1	Convolution Layer	(None, 112, 112, 64)
2	Batch Normalization Layer	(None, 112, 112, 64)
3	Ramp	(None, 112, 112, 64)
4	Padding Layer	(None, 113, 113, 64)
5	Pooling Layer	(None, 56, 56, 64)
6	NetGraph (12 nodes)	(None, 56, 56, 256)
7	NetGraph (10 nodes)	(None, 56, 56, 256)
8	NetGraph (10 nodes)	(None, 56, 56, 256)
9	NetGraph (12 nodes)	(None, 28, 28, 512)
10	NetGraph (10 nodes)	(None, 28, 28, 512)
11	NetGraph (10 nodes)	(None, 28, 28, 512)
12	NetGraph (10 nodes)	(None, 28, 28, 512)
13	NetGraph (12 nodes)	(None, 14, 14, 1024)
14	NetGraph (10 nodes)	(None, 14, 14, 1024)
15	NetGraph (10 nodes)	(None, 14, 14, 1024)
16	NetGraph (10 nodes)	(None, 14, 14, 1024)
17	NetGraph (10 nodes)	(None, 14, 14, 1024)
18	NetGraph (10 nodes)	(None, 14, 14, 1024)
19	NetGraph (12 nodes)	(None, 7, 7, 2048)
20	NetGraph (10 nodes)	(None, 7, 7, 2048)
21	NetGraph (10 nodes)	(None, 7, 7, 2048)
22	Pooling Layer	(None, 1, 1, 2048)
23	Flatten Layer	Vector (None, 2048)
24	Linear Layer	Vector (None, 1000)
25	Ramp	Vector (None, 1000)
26	Linear Layer	Vector (None, X)
27	Output	Vector (None, X)

Inception v1		
Layer	Layer (type)	Output Shape
0	Input Layer	(None, 224, 224, 3)
1	Convolution Layer	(None, 112, 112, 64)
2	Relu function	(None, 112, 112, 64)
3	Padding Layer	(None, 113, 113, 64)

4	Max Pooling Layer	(None, 56, 56, 64)
5	Local Response Normalization Layer	(None, 56, 56, 64)
6	Convolution Layer	(None, 56, 56, 64)
7	Relu function	(None, 56, 56, 64)
8	Convolution Layer	(None, 56, 56, 192)
9	Relu function	(None, 56, 56, 192)
10	Local Response Normalization Layer	(None, 56, 56, 192)
11	Max Padding Layer	(None, 57, 57, 192)
12	Pooling Layer	(None, 28, 28, 192)
13	Inception Net Graph	(None, 28, 28, 256)
14	Inception Net Graph	(None, 28, 28, 480)
15	Padding Layer	(None, 29, 29, 480)
16	Max Pooling Layer	(None, 14, 14, 480)
17	Inception Net Graph	(None, 14, 14, 512)
18	Inception Net Graph	(None, 14, 14, 512)
19	Inception Net Graph	(None, 14, 14, 512)
20	Inception Net Graph	(None, 14, 14, 512)
21	Inception Net Graph	(None, 14, 14, 512)
22	Padding Layer	(None, 7, 7, 832)
23	Inception Net Graph	(None, 7, 7, 832)
24	Linear Layer	(None, 7, 7, 832)
25	Inception Net Graph	(None, 7, 7, 1024)
26	Max Pooling Layer	(None, 1, 1, 1024)
27	Dropout Layer	(None, 1, 1, 1024)
28	Flatten Layer	(None, 1024)
29	Linear Layer	(None, 1000)
30	Ramp	(None, 1000)
31	Linear Layer	(None, X)
32	Output	(None, X)

SqueezeNet V1.1		
Layer	Layer (type)	Output Shape
0	Input Layer	(None, 227, 227, 3)
1	Convolution Layer	(None, 113, 113, 64)
2	Ramp	(None, 113, 113, 64)
3	Pooling Layer	(None, 56, 56, 64)
4	NetGraph (7 nodes)	(None, 56, 56, 128)
5	NetGraph (7 nodes)	(None, 56, 56, 128)

6	Padding Layer	(None, 57, 57, 128)
7	Pooling Layer	(None, 28, 28, 128)
8	NetGraph (7 nodes)	(None, 28, 28, 256)
9	NetGraph (7 nodes)	(None, 28, 28, 256)
10	Padding Layer	(None, 29, 29, 256)
11	Pooling Layer	(None, 14, 14, 256)
12	NetGraph (7 nodes)	(None, 14, 14, 384)
13	NetGraph (7 nodes)	(None, 14, 14, 384)
14	NetGraph (7 nodes)	(None, 14, 14, 512)
15	NetGraph (7 nodes)	(None, 14, 14, 512)
16	Dropout Layer	(None, 14, 14, 512)
17	Convolution Layer	(None, 14, 14, 1000)
18	Convolution Layer	(None, 14, 14, 1000)
19	Aggregation Layer	(None, 1000)
20	Flatten Layer	(None, 1000)
21	Ramp	(None, 1000)
22	Linear Layer	(None, X)
23	Output	(None, X)