Supplementary Data

Amino-functionalized graphene oxide/neutral alumina nanocomposite based solid-phase extraction coupled with ion chromatography-mass spectrometry for the determination of trace haloacetic acids in drinking water

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Supporting Information

Table S1. The pK_a values of HAAs

Compound	pK_a	Ref.
Monochloroacetic acid (MCAA)	2.86	1
Monobromoacetic acid (MBAA)	2.90	1
Monoiodoacetic acid (MIAA)	3.18	1
Dichloroacetic acid (DCAA)	1.26	1
Dibromoacetic acid (DBAA)	1.39	1
Bromochloroacetic acid (BCAA)	1.39	2
Diiodoacetic acid (DIAA)	2.24	2
Chlorodibromoacetic acid (CDBAA)	1.09	2
Dichlorobromoacetic acid (DCBAA)	1.09	2
Trichloroacetic acid (TCAA)	0.64	1
Acetate acid(AC)	4.74	1

Table S2. Adsorption capacity of GO-RNH_2/Al_2O_3 for HAAs

Analyte	MCAA	MBAA	MIAA	DCAA	DBAA	BCAA	DIAA	DCBAA	CDBAA	TCAA
Mean±SD [a] (mg g^{-1})	12.1±0.2	12.6±0.4	11.7±0.4	10.6±0.3	11.3±0.4	10.9±0.3	11.2±0.4	11.5±0.5	11.3±0.4	10.3±0.3

[a] Mean values and standard deviations of three independent samples.

Table S3. The Box-Behnken design built for parameter selection

Run	Independent factor					Extraction recovery (%)									
	A [a]	*B*	*C*	*D*	*E*	MCAA	MBAA	MIAA	DCAA	DBAA	BCAA	DIAA	CDBAA	DCBAA	TCAA
1	0.25	2.5	2.5	10	6	89.1	89.5	90.1	88.1	89.8	88.5	90.2	87.1	87.9	91.1
2	0.5	2.5	1	10	6	95.2	95.1	96.2	93.2	96.2	94.1	95.2	92.2	93.9	94.4
3	0.1	5	2.5	10	6	85.3	84.2	86.2	83.2	86.1	85.2	87.2	84.2	84.9	86.8
4	0.1	2.5	2.5	10	2	90.4	91.2	91.4	91.4	92.5	91.2	90.4	90.4	92.1	91.4
5	0.1	2.5	5	10	6	85.3	85.2	86.2	85.2	86.1	85.4	84.2	86.7	86.1	83.2
6	0.25	2.5	5	10	10	75.4	75.1	74.1	75.1	73.2	74.3	70.2	73.1	75.3	72.1
7	0.25	2.5	2.5	15	2	90.4	91.2	92.1	93.1	94.6	93.2	92.1	93.1	92.6	93.1
8	0.25	1	2.5	5	6	84.2	84.2	83.5	83.5	84.3	84.5	84.5	85.5	85.1	85.2
9	0.25	1	2.5	10	2	91.3	92.5	92.1	93.1	91.8	93.5	93.1	92.3	92.4	93.5
10	0.25	5	1	10	6	88.3	88.1	88.1	89.1	88.6	88.7	88.6	89.4	87.9	89.1
11	0.25	2.5	1	10	10	75.5	72.5	74.2	73.2	72.4	73.5	72.2	73.3	71.7	72.2
12	0.25	5	2.5	5	6	88.1	88.2	88.6	89.6	88.6	88.5	88.4	90.6	89.1	88.4
13	0.5	2.5	2.5	5	6	90.3	90.2	90.5	91.5	90.6	90.2	90.3	92.5	91.4	91.2
14	0.5	5	2.5	10	6	94.4	94.4	93.1	94.1	94.3	94.4	94.3	93.4	95.1	94.6
15	0.5	1	2.5	10	6	89.3	89.4	88.1	89.1	89.1	87.8	89.3	89.4	88.1	88.6
16	0.1	2.5	2.5	5	6	85.2	85.8	84.2	83.7	86.3	83.8	84.5	85.3	85.1	84.9
17	0.25	2.5	2.5	5	10	74.2	74.7	73.2	74.2	74.5	74.7	73.5	72.2	72.7	73.2

18	0.1	2.5	1	10	6	82.3	82.1	83.1	80.1	84.2	80.5	82.1	84.2	83.2	83.1
19	0.25	5	2.5	10	10	79.4	78.2	78.2	78.8	79.2	76.2	75.2	76.8	73.2	74.2
20	0.25	1	2.5	10	10	72.3	71.1	73.1	73.4	73.1	71.2	71.1	72.5	73.4	71.3
21	0.25	2.5	2.5	10	6	82.3	82.1	83.5	84.6	84.3	84.1	85.5	84.6	85.5	82.7
22	0.5	2.5	2.5	15	6	88.4	89.2	89.5	89.5	88.9	89.8	90.5	88.4	89.8	91.6
23	0.1	2.5	2.5	10	10	70.4	70.1	71.2	70.6	70.3	70.5	71.5	70.3	71.6	70.5
24	0.5	2.5	2.5	10	2	98.5	99.1	98.1	98.9	98.8	100.3	98.4	99.8	101.1	98.1
25	0.25	5	2.5	15	6	88.6	88.9	89.1	90.4	88.5	92.9	90.1	90.7	93.7	91.1
26	0.25	1	5	10	6	86.7	86.5	85.4	87.4	86.2	86.4	86.4	87.9	86.6	86.7
27	0.5	2.5	2.5	10	10	83.6	81.2	83.1	82.1	83.5	80.2	82.4	82.5	83.1	81.9
28	0.25	2.5	1	10	2	90.2	92.5	91.3	92.3	91.9	93.1	93.2	93.1	94.2	94.1
29	0.25	5	2.5	10	2	93.1	94.5	92.8	93.8	94.2	94.5	96.8	93.3	95.1	97.9
30	0.25	2.5	2.5	15	10	70.2	70.1	71.2	70.2	74.1	70.1	75.2	73.2	73.5	72.2
31	0.25	2.5	2.5	10	6	82.6	82.5	84.1	85.1	86.4	84.5	86.1	85.9	84.8	87.1
32	0.25	2.5	2.5	10	6	83.1	83.1	84.2	85.2	85.9	84.1	87.2	85.5	80.5	88.1
33	0.5	2.5	5	10	6	90.3	92.5	91.2	90.2	90.3	92.5	90.2	90.4	93.1	91.4
34	0.1	2.5	2.5	15	6	85.2	84.6	83.2	84.2	84.2	84.6	84.2	85.6	84.2	85.2
35	0.25	2.5	5	5	6	83.5	86.1	84.1	86.2	86.4	87.1	84.6	86.7	88.1	86.7
36	0.25	2.5	5	15	6	86.1	86.1	85.1	86.1	86.4	88.1	86.2	87.3	88.2	88.2
37	0.25	5	5	10	6	88.3	88.2	89.2	88.2	89.4	90.2	89.6	88.6	91.3	89.2

38	0.1	1	2.5	10	6	82.3	82.2	81.5	80.5	81.2	82.2	81.3	80.2	83.2	83.2
39	0.25	2.5	5	10	2	92.5	92.3	93.1	93.1	92.4	95.3	92.5	92.6	96.1	93.1
40	0.25	1	1	10	6	85.3	85.2	86.1	86.5	85.3	86.2	81.4	84.5	87.1	82.4
41	0.25	2.5	2.5	5	2	91.3	93.2	92.1	92.1	94.1	94.2	91.1	93.7	95.1	91.7
42	0.25	2.5	1	5	6	86.7	86.1	86.2	86.2	86.5	87.1	84.2	87.2	86.2	85.2
43	0.25	2.5	2.5	10	6	83.8	84.5	86.9	87.9	86.2	85.5	85.3	88.9	86.2	86.1
44	0.25	1	2.5	15	6	82.9	82.1	84.5	84.5	84.4	83.1	84.6	84.6	84.3	85.7
45	0.25	2.5	1	15	6	85.1	85.3	86.5	87.5	85.2	86.3	84.5	87.5	85.5	85.2
46	0.25	2.5	2.5	10	6	83.8	84.5	84.3	87.3	85.9	87.5	85.3	88.7	88.5	86.6

[a] *A~E* mean GO-RNH_2/Al_2O_3 mass (g), acetone -to-methanol ratio, volume of eluent (mL), sample volume (mL) and sample pH, respectively.

Table S4. The equations of responses for ten HAAs in terms of natural factors

Analyte	Equation [a]
MCAA	R=84.12+3.97A+1.95B-0.025C-0.41D-8.54E+0.53AB-1.95AC-0.47AD+1.27AE-0.35BC+0.45BD+1.33BE+1.05CD-0.60CE-0.78DE+2.93A^2+1.55B^2+1.29C^2-0.065D^2-1.87E^2
MBAA	R=84.37+4.11A+1.97B+0.32C-0.69D-9.59E+0.75AB-1.43AC+0.050AD+0.80AE-0.30BC+0.70BD+1.28BE+0.20CD+0.70CE-0.65DE+2.75A^2+1.20B^2+1.28C^2+0.20D^2-2.00E^2
MIAA	R=85.52+3.92A+1.94B-0.21C-0.075D-9.04E+0.075AB-2.03AC+0.00001AD+1.30AE+0.45BC-0.13BD+1.10BE+0.18CD-0.48CE-0.50DE+2.17A^2+0.74B^2+0.78 C^2-0.60D^2-2.46E^2
DCAA	R=86.37+4.36A+1.82B+0.21C-0.094D-9.39E+0.58AB-2.03AC-0.63AD+1.00AE-0.45BC-0.050BD+1.17BE-0.35CD+0.27CE-1.25DE+0.88A^2+0.69B^2+0.22C^2-0.37D^2-2.63E^2
DBAA	R=86.42+3.80A+2.09B+6.25×10^{-3}C-0.31D-9.38E+0.075AB-1.95AC+0.10AD+1.73AE-0.025BC-0.050BD+0.93BE+0.32CD+0.075CE-0.23DE+1.84A^2+0.32B^2+0.019C^2-0.24D^2-2.49E^2
BCAA	R=85.70+4.12A+2.23B+0.61C-0.13D-10.29E+0.90AB-1.63AC-0.30AD+0.15AE+0.32BC+1.45BD+1.00BE+0.45CD-0.35CE-0.90DE+1.43A^2+0.83B^2+1.10C^2+0.22D^2-2.47E^2
DIAA	R=86.60+4.07A+2.41B+0.16C+0.39D-9.77E-0.22AB-1.78AC+0.12AD+0.73AE-1.00BC+0.40BD+0.10BE+0.33CD-0.32CE+0.18DE+1.67A^2+0.50B^2-0.89C^2-0.62 D^2-3.09E^2
CDBAA	R=86.78+3.86A+1.88B+0.12C-0.21D-9.65E+0.00001AB-1.07AC-1.10AD+0.70AE-1.05BC+0.25BD+0.82BE+0.075CD+0.075CE+0.40DE+1.13A^2+0.16B^2+0.22 C^2+0.17D^2-3.32E^2
DCBAA	R=85.57+4.07A+1.88B+0.94C-0.062D-10.26E+1.33AB-0.93AC-0.18AD+0.62AE+0.97BC+1.35BD-

	$0.72BE+0.20CD+0.43CE+0.82DE+2.21A^2+0.92B^2+1.25C^2+0.42D^2+2.19E^2$
TCAA	$R=86.95+3.97A+2.17B+0.31C+0.36D-10.33E+0.60AB-0.78AC+0.025AD+1.18AE-1.05BC+0.55BD-0.38BE+0.38CD+0.22CE-0.60DE+1.50A^2+0.48B^2-0.49C^2-0.28D^2-3.47E^2$

[a] Meanings of *A~E* are the same as those of Table S2; *R* expresses the measured recovery of HAAs.

Table S5. ANOVA for the influences of five parameters on the recoveries of ten HAAs in synthetic water samples.

Analyte	MCAA		MBAA		MIAA		DCAA		DBAA		BCAA		DIAA		CDBAA		DCBAA		TCAA	
	p-Value	*r* [a]	*p*-Value	*r*	*p*-Value	*r*	*p*-Value	*r*	*p*-Value	*r*	*p*-Value	*r*	*p*-Value	*r*	*p*-Value	*r*	*p*-Value	*r*	*p*-Value	*r*
Model	< 0.0001	/	< 0.0001	/	< 0.0001	/	< 0.0001	/	< 0.0001	/	< 0.0001	/	< 0.0001	/	< 0.0001	/	< 0.0001	/	< 0.0001	/
Intercept	/	84.1	/	84.4	/	85.5	/	86.4	/	86.4	/	85.7	/	86.6	/	86.8	/	85.6	/	87.0
A [b]	< 0.0001	4.0	< 0.0001	4.1	< 0.0001	3.9	< 0.0001	4.4	< 0.0001	3.8	< 0.0001	4.1	< 0.0001	4.1	< 0.0001	3.9	< 0.0001	4.1	< 0.0001	4.0
B	0.0002	2.0	0.0001	2.0	0.0001	1.9	< 0.0001	1.8	< 0.0001	2.1	< 0.0001	2.2	< 0.0001	2.4	0.0001	1.9	0.0009	1.9	< 0.0001	2.2
C	0.955	-0.02	0.465	0.3	0.627	-0.2	0.584	0.2	0.988	0.006	0.121	0.6	0.710	0.2	0.780	0.1	0.070	0.9	0.488	0.3
D	0.357	-0.4	0.122	-0.7	0.860	-0.08	0.8089	-0.09	0.454	-0.3	0.746	-0.1	0.353	0.4	0.628	-0.2	0.901	-0.06	0.413	0.4
E	< 0.0001	-8.5	< 0.0001	-9.6	< 0.0001	-9.0	< 0.0001	-9.4	< 0.0001	-9.4	< 0.0001	-10.3	< 0.0001	-9.8	< 0.0001	-9.6	< 0.0001	-10.3	< 0.0001	-10.3
AB	0.556	0.5	0.391	0.8	0.930	0.08	0.460	0.6	0.928	0.08	0.250	0.9	0.789	-0.2	1.00	0	0.196	1.3	0.497	0.6
AC	0.036	-2.0	0.110	-1.4	0.023	-2.0	0.014	-2.0	0.026	-2.0	0.043	-1.6	0.043	-1.8	0.213	-1.1	0.362	-0.9	0.382	-0.8
AD	0.594	-0.5	0.954	0.05	1.000	0	0.427	-0.6	0.904	0.1	0.698	-0.3	0.882	0.1	0.203	-1.1	0.862	-0.2	0.977	0.02
AE	0.160	1.3	0.361	0.8	0.134	1.3	0.204	1.0	0.046	1.7	0.846	0.2	0.392	0.7	0.413	0.7	0.536	0.6	0.189	1.2
BC	0.694	-0.4	0.730	-0.3	0.600	0.4	0.562	-0.5	0.976	-0.03	0.674	0.3	0.241	-1.0	0.224	-1.0	0.338	1.0	0.239	-1.1
BD	0.614	0.4	0.423	0.7	0.883	-0.1	0.949	-0.05	0.952	-0.05	0.069	1.5	0.635	0.4	0.769	0.2	0.188	1.4	0.533	0.6
BE	0.145	1.3	0.151	1.3	0.202	1.1	0.138	1.2	0.271	0.9	0.202	1.0	0.905	0.1	0.336	0.8	0.474	-0.7	0.670	-0.4

CD	0.244	1.0	0.818	0.2	0.837	0.2	0.652	-0.4	*0.696*	0.3	0.561	0.5	0.699	0.3	0.930	0.08	0.843	0.2	0.670	0.4
CE	0.502	-0.6	0.423	0.7	0.577	-0.5	0.723	0.3	*0.928*	0.08	0.651	-0.4	0.699	-0.3	0.930	0.08	0.674	0.4	0.798	0.2
DE	0.387	-0.8	0.457	-0.7	0.557	-0.5	0.116	-1.3	*0.786*	-0.2	0.250	-0.9	0.835	0.2	0.639	0.4	0.416	0.8	0.497	-0.6
A^2	< *0.0001*	2.9	< *0.0001*	2.8	0.0008	2.2	0.104	0.9	*0.003*	1.8	0.011	1.4	0.007	1.7	0.059	1.1	*0.003*	2.2	0.018	1.5
B^2	0.015	1.6	0.051	1.2	0.207	0.7	0.199	0.7	0.572	0.3	0.123	0.8	0.385	0.5	0.783	0.2	*0.187*	0.9	0.424	0.5
C^2	0.041	1.3	0.037	1.3	0.184	0.8	0.677	0.2	*0.973*	0.02	0.043	1.1	0.128	-0.9	*0.696*	0.2	*0.076*	1.2	0.416	-0.5
D^2	0.914	-0.06	0.729	0.2	0.303	-0.6	0.479	-0.4	*0.670*	-0.2	0.679	0.2	0.282	-0.6	0.761	0.2	0.535	0.4	0.640	-0.3
E^2	0.004	-1.9	0.002	-2.0	0.0002	-2.5	< *0.0001*	-2.6	0.0001	-2.5	< *0.0001*	-2.5	< *0.0001*	-3.1	< *0.0001*	-3.3	*0.003*	-2.2	< *0.0001*	-3.5
Lack of fit	0.953	/	0.988	/	0.977	/	0.589	/	0.695	/	0.829	/	0.741	/	0.617	/	*0.954*	/	0.988	/
R^2	0.9563	/	0.9643	/	0.9622	/	0.9700	/	0.9650	/	0.9742	/	0.9676	/	0.9650	/	*0.9565*	/	0.9671	/
Adj- R^2	0.9213	/	0.9358	/	0.9320	/	0.9460	/	0.9369	/	0.9535	/	0.9416	/	0.9369	/	0.9217	/	0.9407	/
Adeq-precision	21.1	/	23.6	/	22.9	/	26.6	/	23.7	/	27.9	/	24.6	/	23.8	/	21.3	/	24.3	/

[a] Coefficient.
[b] Meanings of *A~E* are the same as those of Table S2

Table S6. Comparisons of results of the GO-RNH_2 and LC-NH_2 based SPE for the determination of ten HAAs in synthetic water samples

SPE	Statistical parameter	MCAA	MBAA	MIAA	DCAA	DBAA	BCAA	DIAA	DCBAA	CDBAA	TCAA
GO-RNH_2	Mean±*SD* [a]	20.8±0.8	21.9±0.9	21.6±0.8	21.4±1.4	23.1±0.4	20.9±0.5	20.2±0.8	21.7±0.7	20.3±0.5	22.3±1.2
	Error (%)	16.8	12.9	13.6	14.6	7.6	16.4	19.4	13.2	18.8	10.8
LC-NH_2	Mean±*SD*	20.6±0.4	20.8±1.1	21.8±0.4	18.6±0.7	22.7±0.4	21.0±0.5	19.6±0.6	21.3±0.8	20.7±0.7	22.7±1.7
	Error (%)	17.8	16.8	12.8	18.5	9.2	16.0	21.6	14.7	17.2	9.2
	t-value [b]	0.515	1.767	0.608	1.505	1.935	0.368	1.254	0.767	0.954	0.450

[a] Mean values and standard deviations of six independent samples spiked at 25.0 μg L^{-1} for each analyte.

[b] The critical value $t_{0.05,10}$=2.228.

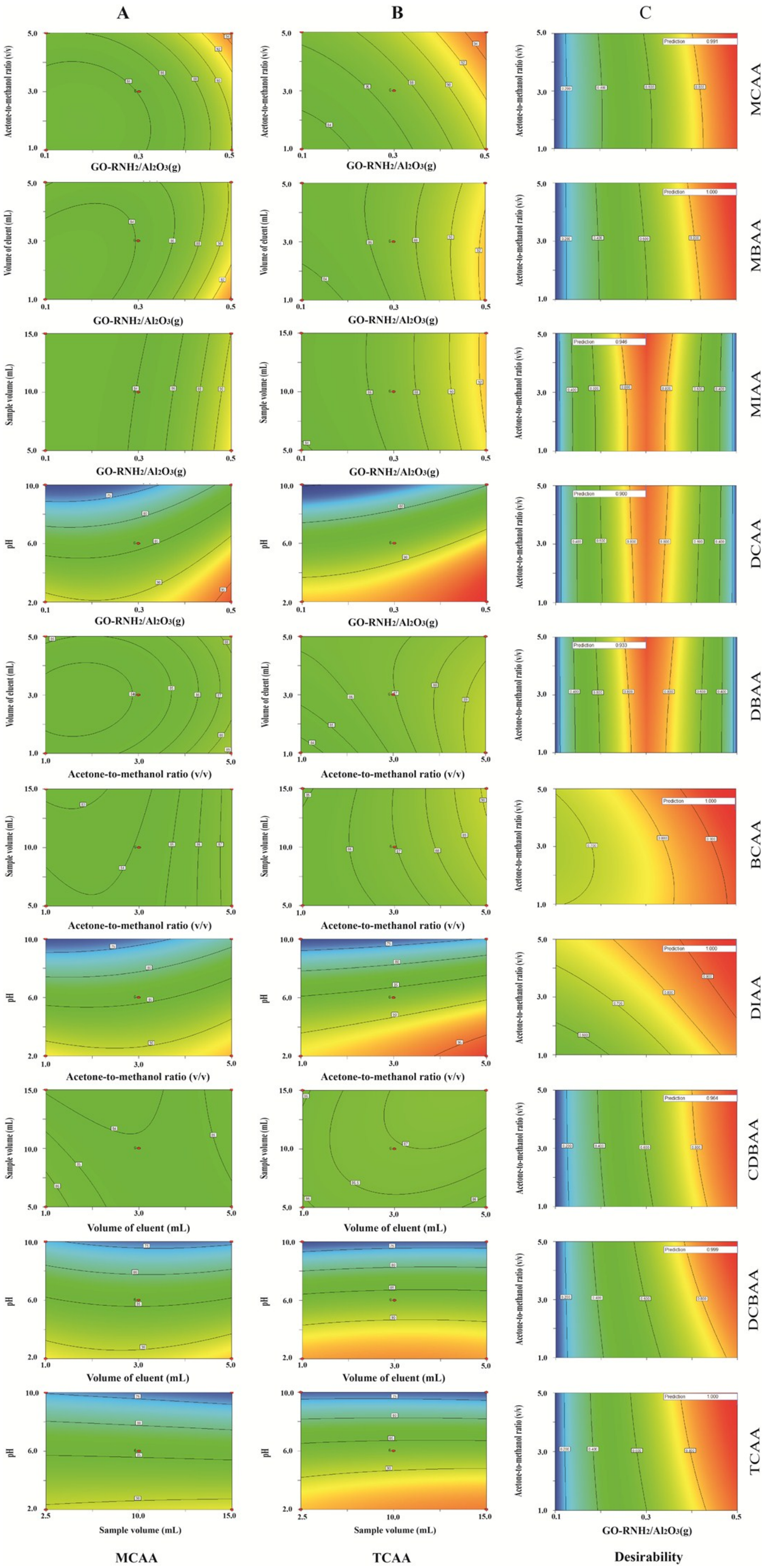
A
B
C
MCAA
MBAA
MIAA
DCAA
DBAA
BCAA
DIAA
CDBAA
DCBAA
TCAA
Acetone-to-methanol ratio (v/v)
Volume of eluent (mL)
Sample volume (mL)
pH
GO-RNH2/Al2O3(g)
Acetone-to-methanol ratio (v/v)
Volume of eluent (mL)
Sample volume (mL)
MCAA
TCAA
Desirability

Fig. S1. Contour plots showing the effects of five factors on the relative response of (A) MCAA, (B) TCAA, and (C) the global desirability of ten HAAs. Conditions: GO-RNH_2 /Al_2O_3 mass of 0.1-0.5 g, acetone-to-methanol volume ratio of 1-5, volume of eluent 1-5 mL, sample volume of 5-15 mL and sample pH 2-10. The red portion of the graphs indicates that the effects of factors on extraction are highly significant, and the green portion shows the lack of influences.

References

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