

Multiwalled carbon nanotubes-poly (vinyl alcohol) composite cryogel used in microcolumn liquid chromatography to separate various herbicides

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Supporting Information

Table S1 The retention time (t_R) and the resolution (R_s) of atrazine, diuron and 2,4-D at various percentages of acetonitrile in eluent (n=3)

Acetonitrile (% v/v)	t_R (min)			R_s	
	Atrazine	Diuron	2,4-D	R_{s_1}	R_{s_2}
10	1.33	3.02	4.94	0.80	0.83
20	2.27	4.37	6.11	1.14	0.91
30	3.01	5.23	7.56	1.20	1.22
35	3.29	6.02	8.91	1.33	1.52
40	4.95	9.48	14.28	2.75	2.97
45	5.38	10.53	15.01	3.32	3.09
50	6.61	14.75	24.59	6.26	7.87
60	8.84	16.21	26.85	7.02	9.67
70	9.75	23.01	34.76	18.94	15.67
80	14.65	28.23	42.51	19.40	21.97

R_{s_1} is the resolution of atrazine and diuron, R_{s_2} is the resolution of diuron and 2,4-D

Table S2 The peak area and peak asymmetry factor (A_s) for atrazine, diuron and 2,4-D using various sample volumes (n=3)

Sample volume (μ l)	Peak area (V·s)			Peak asymmetry factor (A_s)		
	Atrazine	Diuron	2,4-D	Atrazine	Diuron	2,4-D
20	0.1767±0.0058	0.1667±0.0041	0.1573±0.0065	0.712±0.058	0.637±0.023	0.724±0.051
40	0.3433±0.0063	0.2833±0.0052	0.2033±0.0042	0.972±0.063	0.815±0.047	0.953±0.048
80	0.5067±0.0049	0.4067±0.0044	0.3467±0.0037	1.097±0.048	1.041±0.035	1.106±0.047
100	0.5767±0.0035	0.5167±0.0035	0.5651±0.0033	1.137±0.051	1.103±0.029	1.159±0.031
150	1.151±0.0034	1.0807±0.0047	0.8918±0.0035	1.193±0.036	1.153±0.032	1.197±0.053
200	1.200±0.0039	1.267±0.0032	0.9867±0.037	1.438±0.039	1.323±0.041	1.482±0.033
300	1.5867±0.0092	1.4467±0.0039	1.3533±0.0082	1.637±0.056	1.439±0.036	1.740±0.067

Table S3 Chromatographic performances of the developed system for the separation of atrazine, diuron and 2,4-D

Compound	Retention time (t_R)	Capacity factor (k')	Resolution (R_s)	Peak asymmetry factor (A_s)	Plate number ($N \times 10^3$)
Atrazine	3.843±0.015	3.3467±0.0057	–	1.000±0.034	2.2200±0.0020
Diuron	7.570±0.010	8.236±0.012	5.6236±0.0032	0.750±0.031	3.1260±0.0017
2,4-D	12.540±0.010	14.290±0.010	6.7127±0.0064	0.937±0.035	7.9960±0.0010

Table S4 The concentration of atrazine, diuron and 2,4-D of water samples spiked at various concentration

Sample	Recoveries (spiked concentration $\mu\text{g L}^{-1}$) (n = 5)								
	Atrazine			Diuron			2,4-D		
	2	10	100	2	10	100	2	10	100
1	89.9±5.4	99.2±4.0	99.2±3.7	87.5±4.2	92.1±6.2	96.5±7.1	87.4±3.5	96.7±4.9	99.2±8.3
2	87.5±6.2	97.9±5.4	105.7±3.9	83.4±4.8	95.5±3.9	97.9±4.1	86.9±3.2	89.9±4.3	94.9±3.5
3	89.7±5.7	96.5±7.2	98.3±5.8	94.4±3.9	98.9±6.3	107.3±6.1	88.9±5.9	96.8±4.8	99.5±5.4
4	86.5±6.2	89.2±7.1	92.2±5.3	92.5±5.1	94.5±3.6	99.9±5.5	86.2±4.5	93.5±3.2	95.3±4.2
5	86.3±3.5	92.5±3.6	96.5±4.1	93.3±6.2	98.1±3.4	99.1±2.9	88.1±3.4	92.5±4.2	98.4±3.7
6	90.2±3.2	92.2±5.6	99.1±5.7	91.4±3.5	96.8±6.3	98.3±5.2	90.4±3.9	94.8±3.9	94.8±4.1
7	89.5±3.8	95.1±5.8	99.4±4.9	88.5±4.8	90.9±3.6	95.1±4.7	88.3±4.8	93.2±5.7	96.4±3.8
8	89.3±5.1	93.6±3.2	102.7±3.8	86.5±3.7	95.8±3.9	101.2±3.9	90.9±3.7	92.5±3.1	99.3±5.4

Table S5 A comparison of the developed method with other methods

Analytical method	Column	Sample preparation	LOD ($\mu\text{g L}^{-1}$)			LOQ ($\mu\text{g L}^{-1}$)			Sample volume (mL)	Analysis time* (min)	Reference
			Atrazine	Diuron	2,4-D	Atrazine	Diuron	2,4-D			
HPLC-UV	C18 monolithic	On-line SPE	22	-	57	73	-	190	3.0	10	[23]
HPLC-UV	Zorbax StableBondC18	SPE	0.050	0.10	0.15	-	-	-	500	-	[30]
GC-MS	ZB-5	SPE	-	-	-	0.0043	-	-	1000	27	[31]
LC-ESI-MS/MS	XTerra® MS C18	SPE	0.002	0.02	0.02	0.02	0.04	0.04	250	10	[32]
LC-MS/MS	Kinetex® 2.6 μm C18	Mixed mode anion exchange SPE	0.001	0.007	0.004	0.007	0.010	0.010	250	15	[33]
Simple-LC-UV	MWCNTs-PVA composite cryogel	-	1.00	1.00	1.50	3.00	3.00	6.50	0.15	14	This Work

* not including the sample preparation time

HPLC-UV = High-performance liquid chromatography with UV detector, LC-ESI-MS-MS = Liquid chromatography coupled to electrospray ionization tandem mass spectrometry, GC-MS = Gas chromatography-mass spectrometry, LC-MS/MS = Liquid chromatography coupled to tandem mass spectrometry, SPE = Solid phase extraction