Supporting information

A novel magnetic multi-walled carbon nanotubes-based magnetic solid-phase extraction combined with dispersive liquid-liquid microextraction method for determination of four phenoxy carboxylic acid herbicides in food crops by using ultra-high performance liquid chromatography-tandem mass spectrometry

Xucan Yuan, Chu Liu, Jing Zhao, Pengfei Zhao, Longshan Zhao*

School of Pharmacy, Shenyang Pharmaceutical University, Shenyang, Liaoning Province, 110016, China

***Correspondence:** Longshan Zhao, Department of Pharmaceutical Analysis, School of Pharmacy, Shenyang Pharmaceutical University, Shenyang, Liaoning Province, 110016, P. R. China.

E-mail address: longshanzhao@163.com. Tel./Fax.: +86-24-43520571.

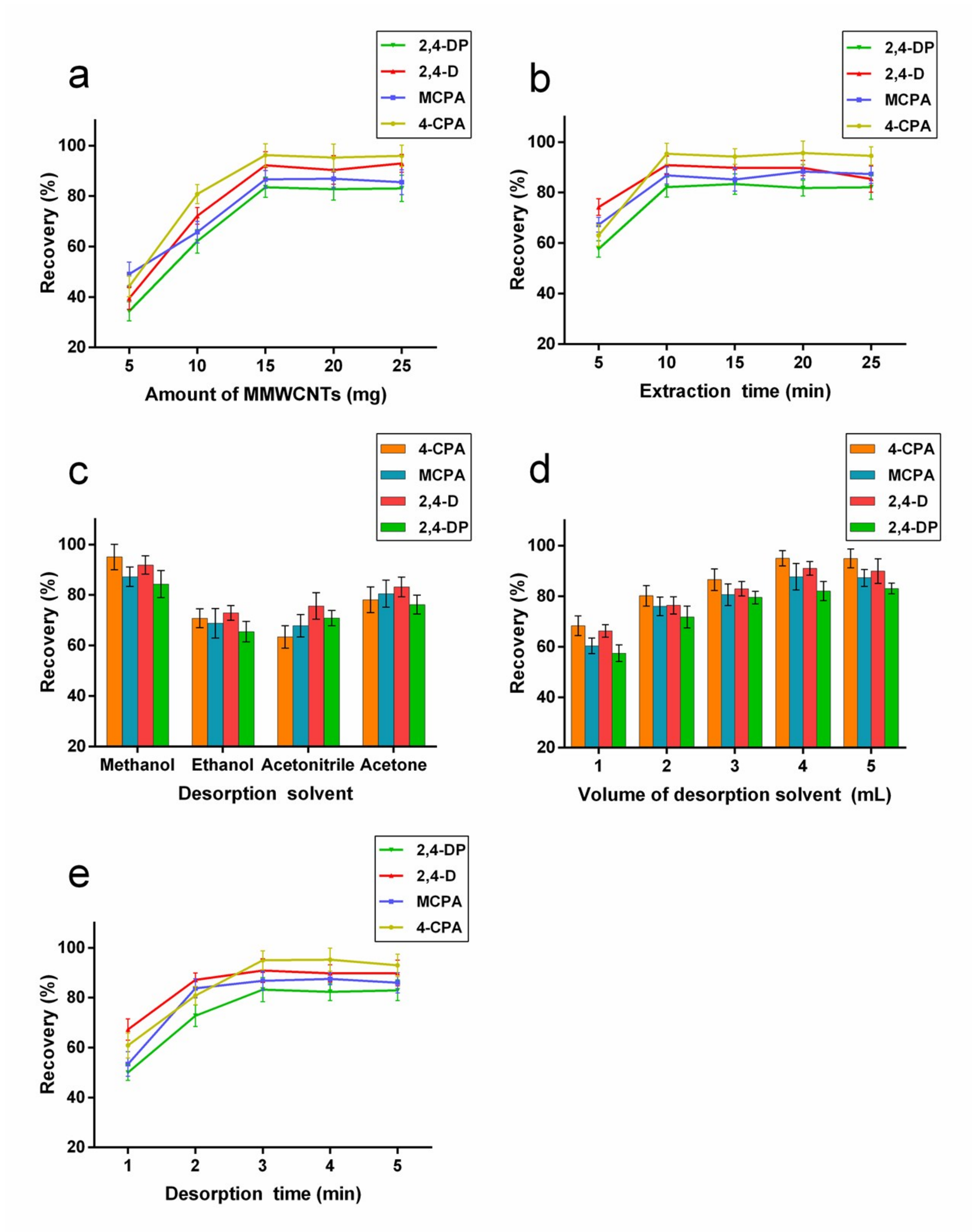

Fig. S1 Effect of the amount of sorbent (a), extraction time (b), the type of desorption solvent (c), the volume of desorption solvent (d), desorption time (e) on the extraction efficiency of the analytes for MSPE.

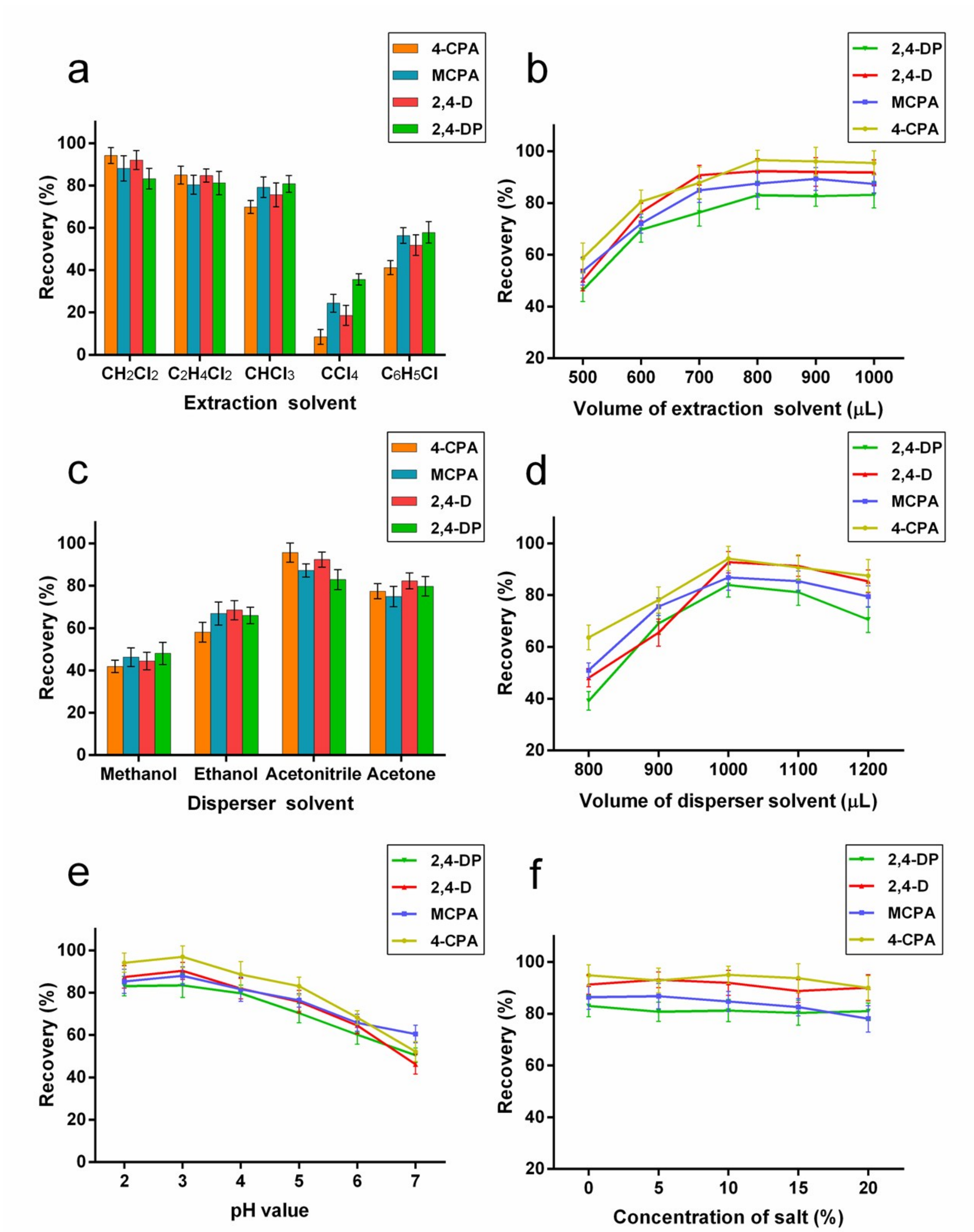

Fig. S2 Effect of the type of extraction solvent (a), the volume of extraction solvent (b), the type of disperser solvent (c), the volume of disperser solvent (d), pH of sample solution (e), the concentration of salt (f) on the extraction efficiency of the analytes for DLLME.

Table S1 Matrix effect (ME) and overall process efficiency (PE) of the proposed method in different matrices

Analyte	Rice				Millet				Soy				Oatmeal				Barley			
	ME[a]	ME[b]	PE[a]	PE[b]	ME[a]	ME[b]	PE[a]	PE[b]	ME[a]	ME[b]	PE[a]	PE[b]	ME[a]	ME[b]	PE[a]	PE[b]	ME[a]	ME[b]	PE[a]	PE[b]
4-CPA	94.7	83.2	89.4	80.7	90.6	83.2	86.3	81.0	98.6	121.3	93.6	117.3	88.5	75.2	85.3	73.7	90.6	78.2	87.1	76.4
MCPA	86.4	78.5	74.1	70.5	88.5	67.2	76.7	61.4	92.4	78.6	82.1	72.7	92.7	83.9	81.4	76.5	86.5	85.7	76.3	78.6
2,4-D	91.6	72.8	84.5	69.8	80.4	63.5	75.2	62.3	86.2	87.4	81.2	84.8	82.9	68.4	76.8	65.2	104.3	130.4	97.9	128.3
2,4-DP	90.2	88.4	75.8	75.6	97.8	114.3	80.4	96.1	108.2	124.5	90.7	129.7	100.2	113.6	83.4	97.7	95.8	90.2	80.5	77.6

[a] : Samples were pretreated with MSPE-DLLME.

[b]: Samples were pretreated with the MSPE only.

Table S2 Linearity range, correlation coefficients, instrument detection and quantification limits and method detection and quantification limits for 4-CPA, MCPA, 2,4-D, 2,4-DP

Analyte	Linearity range (ng g^{-1})	IDL (ng mL^{-1})	IQL (ng mL^{-1})	r^2					MDL (ng g^{-1})					MQL (ng g^{-1})				
				Rice	Millet	Soy	Oatmeal	Barley	Rice	Millet	Soy	Oatmeal	Barley	Rice	Millet	Soy	Oatmeal	Barley
4-CPA	1.5-500	1.5	5.0	0.9965	0.9982	0.9949	0.9970	0.9943	0.34	0.35	0.32	0.35	0.34	1.12	1.16	1.07	1.17	1.15
MCPA	1.5-500	0.8	2.5	0.9987	0.9952	0.9974	0.9956	0.9990	0.22	0.21	0.19	0.20	0.21	0.67	0.65	0.61	0.61	0.66
2,4-D	3.0-500	3.0	10.0	0.9975	0.9948	0.9952	0.9961	0.9954	0.71	0.80	0.74	0.78	0.61	2.37	2.66	2.46	2.60	2.04
2,4-DP	1.5-500	1.5	5.0	0.9946	0.9978	0.9991	0.9953	0.9985	0.40	0.37	0.33	0.36	0.37	1.32	1.24	1.10	1.20	1.24

Table S3 Accuracy and precision of the proposed method in different matrices

Analyte	Matrix: Spiked (ng g^{-1})	Rice: Accuracy (%)	Rice: Precision (RSD%) Intra-day	Rice: Precision (RSD%) Inter-day	Millet: Accuracy (%)	Millet: Precision (RSD%) Intra-day	Millet: Precision (RSD%) Inter-day	Soy: Accuracy (%)	Soy: Precision (RSD%) Intra-day	Soy: Precision (RSD%) Inter-day	Oatmeal: Accuracy (%)	Oatmeal: Precision (RSD%) Intra-day	Oatmeal: Precision (RSD%) Inter-day	Barley: Accuracy (%)	Barley: Precision (RSD%) Intra-day	Barley: Precision (RSD%) Inter-day
4-CPA	10	95.7	4.6	4.0	97.9	2.8	5.5	95.1	4.4	4.9	90.6	4.2	3.9	92.8	5.8	5.3
	200	89.3	5.2	5.1	93.6	4.5	6.7	88.7	3.0	4.1	101.2	10.9	7.0	88.3	3.0	4.5
	400	92.6	3.7	4.0	90.8	2.5	5.2	94.3	2.6	5.1	95.5	6.3	3.0	96.7	3.5	5.6
MCPA	10	96.3	3.1	4.3	96.4	3.3	6.3	92.9	3.7	5.8	87.7	2.8	3.9	94.0	5.0	4.0
	200	92.7	4.6	6.7	94.8	7.0	4.3	85.9	4.4	4.3	94.5	3.3	4.8	91.2	1.5	5.0
	400	91.4	1.6	2.8	88.2	6.5	5.4	90.5	4.9	5.0	93.1	4.1	4.3	102.7	2.2	5.3
2,4-D	10	92.7	5.0	3.9	94.4	1.5	3.3	92.6	3.4	5.1	92.3	3.5	2.5	89.1	6.0	7.3
	200	86.0	3.2	6.0	92.0	4.0	7.2	87.1	6.4	6.7	97.8	7.1	5.6	87.5	2.7	4.8
	400	89.5	2.9	4.6	89.8	2.8	4.3	85.7	3.3	4.5	93.6	5.7	2.5	95.7	7.6	4.0
2,4-DP	10	94.3	4.4	3.8	95.3	3.4	5.4	90.2	3.9	3.4	83.9	2.9	3.2	90.5	4.3	6.0
	200	87.7	3.2	5.1	90.9	5.3	4.6	84.8	2.5	3.2	95.8	3.4	3.0	84.7	2.8	4.3
	400	91.8	7.5	6.7	87.6	2.7	5.3	89.4	4.2	4.7	92.4	4.7	3.8	92.4	3.2	4.9