

Supporting Information

Ultrasensitive determination of organotin compounds in plastic food packaging and edible oils by sheathless capillary electrophoresis-electrospray ionization-mass spectrometry

Huiyu He^{a, 1}, Miaomiao Tian^{b, 1}, Lihuan Hu^a, Li Yang^{a, *}

^a *Department of Chemistry, Northeast Normal University, 5268 Renmin Street, Changchun, Jilin Province 130024, PR China*

^b *Institute of Chemical and Industrial Bioengineering, Jilin Engineering Normal University, Changchun, Jilin Province, 130052, China*

*Corresponding author: Li Yang. Tel/Fax: +86-15843035135. E-mail: yangl330@nenu.edu.cn.

¹ These authors contributed equally to this work.

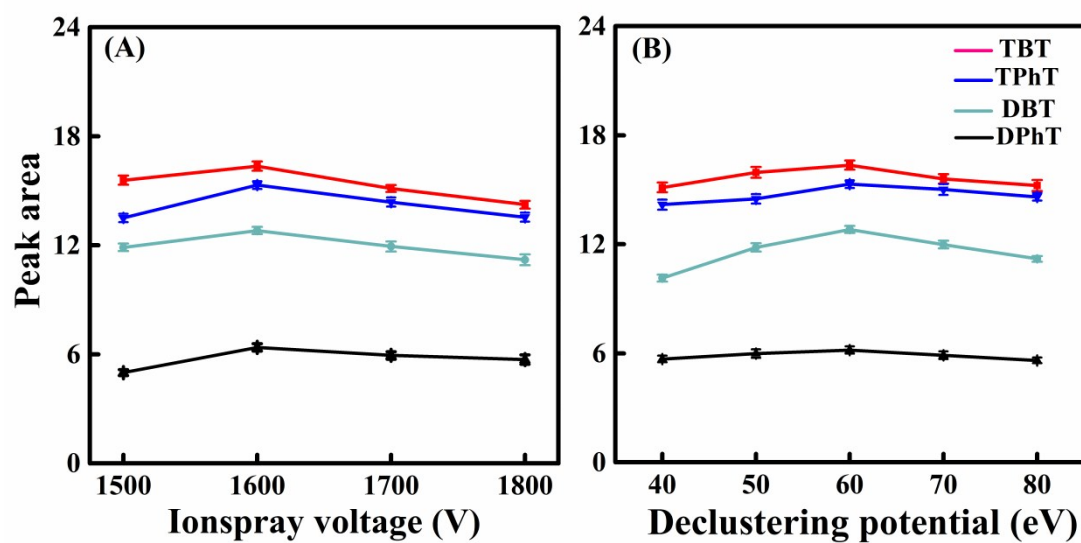


Fig. S1. Effect of ESI ionspray voltage (A) and declustering potential (B) on the sensitivity of four organotin compounds. Sample concentration: TBT (1 $\mu\text{g/mL}$), TPhT (10 $\mu\text{g/mL}$), DBT (10 $\mu\text{g/mL}$), and DPhT (10 $\mu\text{g/mL}$). The other instrument conditions are the same as shown in Fig. 2.

Table S1. Comparison of the proposed method with other methods developed for the preconcentration and determination of organotin in plastic food packaging materials and edible oils.

Organotins	Pretreatment method	Analysis technique	Linear range (ng/mL)	LOD (ng/mL)	Matrices	Ref.
DBT	SPME	GC-MS	25.6-76.8	0.0015	Wine	1
TBT			27.4-82.2	0.0011		
TPhT			32.4-97.2	0.0003		
DBT	SPME	GC-AED	25.6-76.8	0.0064	Wine	1
TBT			27.4-82.2	0.0041		
TPhT			32.4-97.2	0.0016		
DBT	HS-SDME	GC-ICP-MS	0.02-5	0.0018	Shellfish	2
TBT				0.0008		
DBT	HS-LPME	GC-Et-AAS	0.005-0.25	0.0005	PVC	3
TBT			0.002-0.17	0.00017		
DBT	HS-SPME	GC-FPD	0.9-152.3	0.3	PVC plastics	4
DBT	UE-SPE	HPLC-MS/MS	1-50	0.3	Plastic packaging Materials	5
TBT				0.1		
DPhT				0.8		
TPhT				0.6		
DBT	LLE	GC-MS	10-1000	0.29	Plant oil	6
TBT				0.19		
TPhT				0.31		
DBT	LTFE-MSPD	HPLC-ICP-MS	0.5-100	0.59	Edible vegetable oil	7
TBT				0.28		
DPhT				0.52		
TPhT				0.41		
DBT	UE-SPE	CE-ESI-MS (sheathless)	0.1-500	0.017	Plastic packaging	This work
TBT			0.01-50	0.002		
DPhT			0.1-400	0.016		
TPhT			0.1-500	0.050		
DBT	LTFE-SPE	CE-ESI-MS (sheathless)	0.1-500	0.021	Edible vegetable oils	This work
TBT			0.01-50	0.009		
DPhT			0.1-400	0.011		
TPhT			0.1-500	0.032		

SPME: solid-phase microextraction; HS-LPME: Headspace liquid phase microextraction; Et-AAS: electrothermal atomic absorption spectrometry; HS-SPME: Headspace solid-phase microextraction; UE: ultrasonic extraction; SPE: solid phase extraction; LLE: Liquid-liquid extraction; LTFE: low-temperature freezing extraction; MSPD: matrix solid-phase dispersion; HG-AAS: hydride generation atomic absorption spectrometry.

Table S2. Organotin contents determined in five edible oils and five plastic food packaging materials (n=3).

Samples	Content (ng/g)			
	DBT	TBT	DPhT	TPhT
Edible oil bottles	-	-	-	-
Plastic cake packaging	-	-	0.123±0.025	-
Milk packaging boxes	-	0.258±0.008	-	-
Baked goods kraft paper	-	0.483±0.005	-	-
Food preservation film	-	-	-	-
Corn oil	0.971±0.026	-	-	-
Sesame oil	-	-	-	-
Olive oil	-	-	-	-
Soybean oil	0.958±0.013	0.068±0.006	-	-
Peanut oil	0.769±0.032	-	-	-

^{a)} Content ± SD (ng/g).

Table S3. Validation parameters of recoveries at three levels for four organotin detected by sheathless CE-ESI-MS.

Samples	Added (ng/g)	DBT		TBT		DPhT		TPhT	
		Recovery	RSD (%)	Recovery	RSD (%)	Recovery	RSD (%)	Recovery	RSD (%)
		(%)	(n=5)	(%)	(n=5)	(%)	(n=5)	(%)	(n=5)
Edible oil bottles	0.4 (4.0)	83.44	5.28	87.87	4.42	83.38	6.56	81.25	6.90
	4.0 (40)	81.03	4.81	83.74	5.52	87.48	3.01	88.05	5.00
	40.0 (400.0)	88.62	5.93	86.24	7.53	88.11	6.31	87.42	4.04
Plastic cake packaging	0.4 (4.0)	89.69	6.4	85.03	3.23	83.34	5.85	81.34	4.60
	4.0 (40)	85.75	3.98	85.25	4.66	87.11	6.78	88.31	3.93
	40.0 (400.0)	83.46	6.06	86.71	3.49	88.83	7.89	87.17	7.56
Milk packaging boxes	0.4 (4.0)	85.76	4.41	80.6	5.7	83.51	5.43	84.05	7.23
	4.0 (40)	87.56	4.98	86.02	6.37	81.41	6.87	85.04	3.86
	40.0 (400.0)	86.88	4.02	96.98	4.08	81.95	6.66	95.62	4.10
Baked goods kraft paper	0.4 (4.0)	84.22	3.11	80.54	5.44	83.59	5.26	85.1	5.58
	4.0 (40)	83.19	3.75	81.8	2.56	93.35	6.01	88.57	4.42
	40.0 (400.0)	86.43	3.23	87.56	4.86	101.56	4.75	88.75	3.03
Food preservation film	0.4 (4.0)	95.92	7.78	82.52	4.95	80.27	3.82	87.35	5.35
	4.0 (40)	86.99	6.74	80.66	2.67	83.45	5.83	80.82	7.52
	40.0 (400.0)	88.98	6.91	86.25	5.21	81.4	5.88	86.71	4.32
Corn oil	0.4 (4.0)	85.3	3.83	87.03	3.76	87.79	4.88	88.84	6.58
	4.0 (40)	87.75	4.52	86.78	3.17	87.92	4.32	83.26	4.48
	40.0 (400.0)	96.46	4.04	98.28	5.47	93.27	5.89	89.67	3.01
Sesame oil	0.4 (4.0)	88.02	5.67	84.78	4.96	84.35	3.92	88.39	5.24
	4.0 (40)	95.43	5.73	96.98	3.42	89.22	5.16	95.23	4.21
	40.0 (400.0)	97.95	4.07	108.52	3.35	92.02	6.26	99.58	4.88
Olive oil	0.4 (4.0)	83.73	6.43	88.17	4.28	85.03	4.56	88.55	4.04
	4.0 (40)	90.32	3.98	98.57	3.07	88.64	5.27	96.76	4.22
	40.0 (400.0)	86.49	3.61	104.14	5.19	88.4	5.6	88.98	3.88
Soybean oil	0.4 (4.0)	86.23	5.13	80.85	5.44	86.68	6.09	88.53	4.71
	4.0 (40)	101.88	3.78	85.98	3.12	87.52	5.55	83.98	6.01
	40.0 (400.0)	85.89	8.47	88.42	3.52	81.85	6.72	92.46	8.53
Peanut oil	0.4 (4.0)	87.19	3.67	87.35	6.63	85.94	5.44	86.14	5.74
	4.0 (40)	95.81	8.71	86.63	2.66	88.09	6.49	80.7	5.42
	40.0 (400.0)	96.36	5.37	88.49	2.15	101.91	7.58	82.13	6.25

The three spiked concentrations of TBT were 0.4 ng/g, 4 ng/g, and 40 ng/g;

The three spiked concentrations of TPhT, DBT and DPhT were 4 ng/g, 40 ng/g, and 400 ng/g.

References

1. N. Campillo, P. Viñas, R. Peñalver, J. I. Cacho and M. Hernández-Córdoba, Solid-phase microextraction followed by gas chromatography for the speciation of organotin compounds in honey and wine samples: a comparison of atomic emission and mass spectrometry detectors, *J. Food Compos. Anal.*, 2012, **25**, 66-73.
2. Q. Xiao, B. Hu and M. He, Speciation of butyltin compounds in environmental and biological samples using headspace single drop microextraction coupled with gas chromatography-inductively coupled plasma mass spectrometry, *J. Chromatogr. A*, 2008, **1211**, 135-141.
3. M. Kaykhani and A. Khatibi, Determination of butyltin stabilizers in PVC using liquid-phase microextraction with electrothermal atomic absorption spectrometry, *J. Iran Chem. Soc.*, 2011, **8**, 374-381.
4. Q. R. Ou and C. W. Whang, Determination of butyltin and octyltin stabilizers in poly(vinyl chloride) products by headspace solid-phase microextraction and gas chromatography with flame-photometric detection, *Anal. Bioanal. Chem.*, 2006, **386**, 376-381.
5. T. Li, Y. She, M. Wang, G. Liu, H. Yu, J. Wang, S. Wang, F. Jin, M. Jin and H. Shao, Simultaneous determination of four organotins in food packaging by high-performance liquid chromatography-tandem mass spectrometry, *Food Chem.*, 2015, **181**, 347-353.
6. Y. Liu, Y. Ma, G. Lan, A. Yan, X. Mao and Y. Wan, Low-temperature precipitation for the determination of residual organotin compounds in plant oil using dispersive-solid phase extraction and gas chromatography-mass spectrometry, *Anal. Methods*, 2015, **7**, 3685-3691.
7. Y. Liu, Y. Ma, Y. Wan, L. Guo and X. Wan, Fast and effective low-temperature freezing extraction technique to determine organotin compounds in edible vegetable oil, *J. Sep. Sci.*, 2016, **39**, 2380-2387.

