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Simultaneous quantification of five phenols in settled house dust using ultra-high performance liquid chromatography-tandem mass spectrometry

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A simple analytical method for the simultaneous determination of five phenols (bisphenol A, triclosan, 4-*tert*-octylphenol, 4-*n*-octylphenol, 4-*n*-nonylphenol) in indoor settled house dust was developed based on ultra-high performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). Analytes were extracted from dust samples using acetone under sonication. The extracts were concentrated and dissolved in 0.2 mL acetonitrile, then analyzed using UPLC-MS/MS in multiple reaction monitoring mode. For quantification, calibration curves of phenol standards in blank dust samples were used. Only 0.025 g of each dust sample was needed for the analysis. Method detection limits were 1.4–192 ng g^{-1}, and absolute recoveries were 79–114% with coefficients of variation <20% for all the analytes (except triclosan, which was at 39.7%). This method was applied to measure the concentration of five phenols in 47 settled house dust samples from urban homes in which pre-school aged children lived. A high frequency of detection for most of the target phenols (except 4-*n*-octylphenol and 4-*n*-nonylphenol) combined with a wide distribution in concentration, supported the notion that indoor dust may represent an important (but widely variable) pathway of exposure to bisphenol A, triclosan and 4-*tert*-octylphenol for toddlers.

Introduction

The concentrations of chemical contaminants, including semi-volatile organic compounds (SVOCs), such as polychlorinated biphenyls, flame retardants and pesticides, are often higher in indoor air than outdoor air.[1] Many indoor contaminants are absorbed by particulate matter that is initially suspended in the air and then later settles as dust. Thus, settled house dust is considered to be a medium of exposure and an indicator of global residential contamination.[2–4] Chemical exposure through settled house dust is very important with respect to infants and toddlers, who are at highest risk because they frequently place their hands in their mouth and ingest dust.

Phenolic compounds, as a type of SVOCs, including bisphenol A (BPA), benzophenone-3 (BP-3), triclosan (TCS), alkylphenols (APs) and chlorophenols, are used in many domestic products. BPA has been used in many plastic consumer products, such as toys, water bottles, spectacle lenses and consumer electronics (*e.g.*, CDs, DVDs, cell phones and personal computers). APs such as 4-*tert*-octylphenol (4-*tert*-OP), 4-*n*-octylphenol (4-*n*-OP) and 4-*n*-nonlyphenol (4-*n*-NP) are major degradation products of the non-ionic surfactant alkylphenol polyoxyethylene ether, which is important in domestic, industrial and agricultural applications.[5] TCS is infused in many consumer products including kitchen utensils, toys, bedding, socks, and trash bags.[6] Therefore, it is reasonable to speculate that high concentrations of these phenolic compounds may be found in settled house dust. Field investigations have confirmed this speculation. Regarding the concentration of BPA: Rudel *et al.*[7] reported ≤17 600 ng g^{-1}; Geens *et al.*[8] reported 9730 ng g^{-1}; and Liao *et al.*[9] noted values of 39 000 ng g^{-1} in Korea and 8000 ng g^{-1} in China. For TCS, concentrations of ≤2200 ng g^{-1} have been observed.[6,10]

BPA, TCS, and APs are endocrine-disrupting chemicals (EDCs).[11,12] Researchers have been investigating the health risks caused by EDCs. BPA[13–16] and TCS[17,18] are reported to be associated with the disruption of the actions of thyroid hormones. BPA has also been associated with attention deficit hyperactivity disorder (ADHD).[19] Given that concentrations of thyroid-stimulating hormone (even within the normal range) have been reported to be associated with lower cognitive function and

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ADHD symptoms in healthy pre-school children,[20] we investigated the possible neurodevelopmental effects of phenols, together with the other main SVOCs in settled house dust, on pre-school children.[21,22]

Gas chromatography-mass spectrometry (GC-MS)[7,23–25] and liquid chromatography-tandem mass spectrometry (LC-MS/MS)[8,26] have been used for the measurement of phenols in settled house dust. LC-MS/MS is a sensitive and specific method that usually requires less sample manipulation than GC-MS. The determination of phenols in dust using LC-MS has been reported, but most studies have focused on only a few types of phenolic compound.[8,26] Therefore, the present study was undertaken to develop a method for the simultaneous determination of BPA, APs (4-*tert*-OP, 4-*n*-OP and 4-*n*-NP) and TCS in indoor settled house dust using ultra-high performance liquid chromatography-electrospray ionization-tandem mass spectrometry (UHPLC-ESI-MS/MS), in order to support the ongoing studies[21,22]. This method involved several hundred dust samples and focused on neurotoxic pollutants. Therefore, a rapid, sensitive and robust analytical method was required for the present study.

Materials and methods

Materials

BPA, TCS, 4-*tert*-OP, 4-*n*-OP and 4-*n*-NP were obtained from Dr Ehrenstorfer GmbH (purity, 98.5%; Burgermeister-Schlosser, Augsburg, Germany). The chemical structures of the studied compounds are given in Table 1. The acetonitrile, acetone and methanol used were LC-MS grade and supplied by Merck (Darmstadt, Germany). The water used during the LC-MS/MS analyses was pretreated and then purified using an ELGA Purelab Ultra system (Vivendi Water Systems, Buckinghamshire, UK).

Collection of house dust and preparation of blank dust

Dust was collected using a portable commercial vacuum cleaner with a short upholstery nozzle, behind which a paper bag was fixed. The upholstery nozzle was washed with isopropanol before use. Hoses were avoided in case they were difficult to wash and because they could have been contaminated with alkylphenols. The paper bag did not come into contact with any plastic parts of the vacuum cleaner. Simultaneously, butyronitrile gloves were used for all sampling procedures. Dust samples were removed using stainless-steel tweezers and transferred to glass tubes that had previously been cleaned with acetone. The tubes were capped, sealed with polytetrafluoroethylene tape, and stored at −4 °C during transportation.

Sample preparation

Coarse material was removed from the "raw" dust. Particles were separated from fibers by passing through a mesh (size, <150 μm). Dust (25 mg) was placed in a 10 mL glass tube, 1 mL of acetone was added, and the tube was vortex-mixed for 1 min. Extraction was then carried out in an ultrasonic bath for 30 min. After centrifugation at 1500 × *g* for 15 min at 4 °C, 0.5 mL of the supernatant was removed. 1 mL of acetone was then added to the remaining solution and the entire extraction process was repeated. 1 mL of the supernatant was removed and mixed with the 0.5 mL of supernatant obtained from the first extraction. The glass tubes were capped during vortex mixing, sonication and centrifugation, and the supernatant transfer was performed rapidly in order to avoid sample evaporation. Finally, the supernatant was evaporated to dryness at room temperature and dissolved in 0.2 mL of acetonitrile for analysis. All of the prepared samples were centrifuged at 30 000 × *g* for 10 min at 4 °C before UPLC injection. The centrifuge tubes, pipettes and syringes used in the extraction and clean-up steps were made of glass. All glassware was cleaned by ultrasonication in acetone for >30 min, before being rinsed with purified water and dried at 200 °C.

Preparation of standard solutions and blank controls

For the external calibration, 1 mg L^{-1} stock solutions of the five phenols were prepared by dissolving measured amounts of the compounds in acetonitrile. The working standard solutions could be obtained by serial dilution of the stock solutions with acetonitrile. The concentrations of phenol in the working standard solutions were 0.05–1000 ng mL^{-1}.

House dust to be used for the dust blank sample was ashed in a muffle furnace at 800 °C for 1 h in order to destroy all possible traces of phenolic compounds. The dust blank, together with the reagent blank, were prepared in the same manner as that described above for the dust samples.

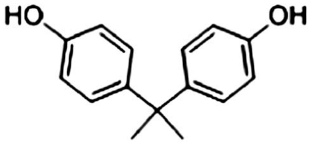
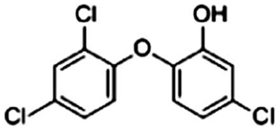
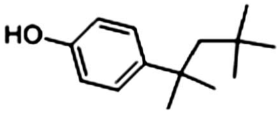
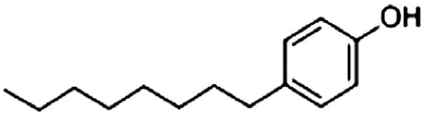
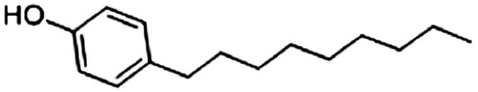
UPLC-MS/MS conditions

The UPLC/MS/MS system comprised an Acquity® UPLC system (Waters, Milford, MA, USA), coupled to a Waters Quattro Premier Mass Spectrometer and was controlled using Masslynx software. The UPLC column was an Acquity UPLC BEH, C18 (1.7 μm, 2.1 mm × 100 mm) equipped with a filter (Frit, 0.2 μm, 2.1 mm; Waters) and a Van Guard BEH, C18 pre-column (1.7 μm). The flow rate was 0.25 mL min^{-1}. Mobile phases A and B were methanol and water, respectively.

The gradient of mobile phase A was programmed as follows: 80% A at 0.0–1.5 min, then the percentage of A was increased linearly up to 100% between 1.5–3.0 min; 100% A between 3.0–4.5 min, then the percentage of A was decreased to 80% from 4.5–7 min. The temperature of the chromatography column was maintained at 35 °C in a column oven. The injection volume was 5 μL in a partial loop using a needle overfill injection mode. The sample chamber temperature was maintained at 4 °C.

The MS/MS detector was equipped with an ESI interface and operated in negative ionization mode. The quantitative analyses were carried out in multiple reaction monitoring (MRM) mode. The conditions for the MS/MS detector were set as follows: source temperature, 120 °C; desolvation temperature, 400 °C; cone gas flow, 50 L h^{-1}; flow of desolvation gas (nitrogen), 800 L h^{-1}; capillary voltage, 2.50 kV; extractor voltage, 6 V; and RF lens, 0.5 V. The other parameters are presented in Table 1.

Table 1 Elemental composition and ions monitored for phenols[a]

Phenol	Structure	CAS No.	Elemental composition	RT (min)	Transition	Cone voltage (V)	Collision energy (eV)
Bisphenol A		80-05-7	$C_{15}H_{16}O_2$	1.27	227 > 212	35	20
Triclosan		3380-34-5	$C_{12}H_7Cl_3O_2$	2.82	287 > 35	20	10
4-*tert*-Octylphenol		140-66-9	$C_{14}H_{22}O$	3.00	205 > 133	37	20
4-*n*-Octylphenol		1806-26-4	$C_{14}H_{22}O$	3.73	205 > 106	33	20
4-*n*-Nonylphenol		104-40-5	$C_{15}H_{24}O$	4.00	219 > 106	35	22

[a] RT: retention time.

Method validation

A recovery efficiency study was conducted ($n = 6$) using blank dust spiked with different concentrations of each phenolic compound according to their different detection limits and possible concentration range in dust samples, for intra-day variation. Inter-day variation was carried out over four days with 2.4 μg g^{-1} added to the blank dust using four samples. The instrumental detection limits (IDLs) were determined on the basis of the responses at a signal-to-noise ratio (S/N) of 3. The method detection limits (MDLs) under the chromatographic conditions described above were calculated using the IDLs, the volume of the extracts and the sample weights using the following formula:

$$\text{MDL} = \text{IDL (ng mL}^{-1}) \times 0.2 \text{ (final volume, mL)} \times 6 \text{ (dilution factor)}/0.025 \text{ (sample mass, g)}.$$

Results and discussion

Quality control and method performance

Indoor settled house dust is a heterogeneous mixture of fibers and inorganic particles characterized by a high content of organic carbon. This composition implies that the extraction and determination of target compounds will be difficult. Using larger dust samples can help to achieve a lower detection limit, but this often introduces excessive interference in the sample preparation and instrumental analysis from the complex matrices in house dust. Several classes of SVOC were simultaneously analyzed during our study, so the mass of the dust sample for each analysis was limited. Therefore, only a 0.025 g dust sample is used (often dust samples of >0.1 g are reported for such analyses).[7,26,27] Due to the small size of the dust sample,

Table 2 Linear range, regression coefficients, IDLs, MDLs and the daily variation of the calibration curve slopes and intercepts[a]

Analyte	Linear range (ng mL^{-1})	Regression coefficient	IDL (ng mL^{-1})	MDL (ng g^{-1})	Slope CV (%)	Intercept CV (%)
Bisphenol A	0.1–500	$r = 0.9997$	0.09	4.8	8	9
Triclosan	5.0–1000	$r = 0.9995$	4.00	192.0	19	25
4-*tert*-Octylphenol	0.5–200	$r = 0.9996$	0.49	24.0	12	21
4-*n*-Octylphenol	0.05–200	$r = 0.9986$	0.03	1.4	11	30
4-*n*-Nonylphenol	0.05–200	$r = 0.9995$	0.03	1.4	15	28

[a] IDL: instrumental detection limit; MDL: method detection limit; CV: coefficient of variation.

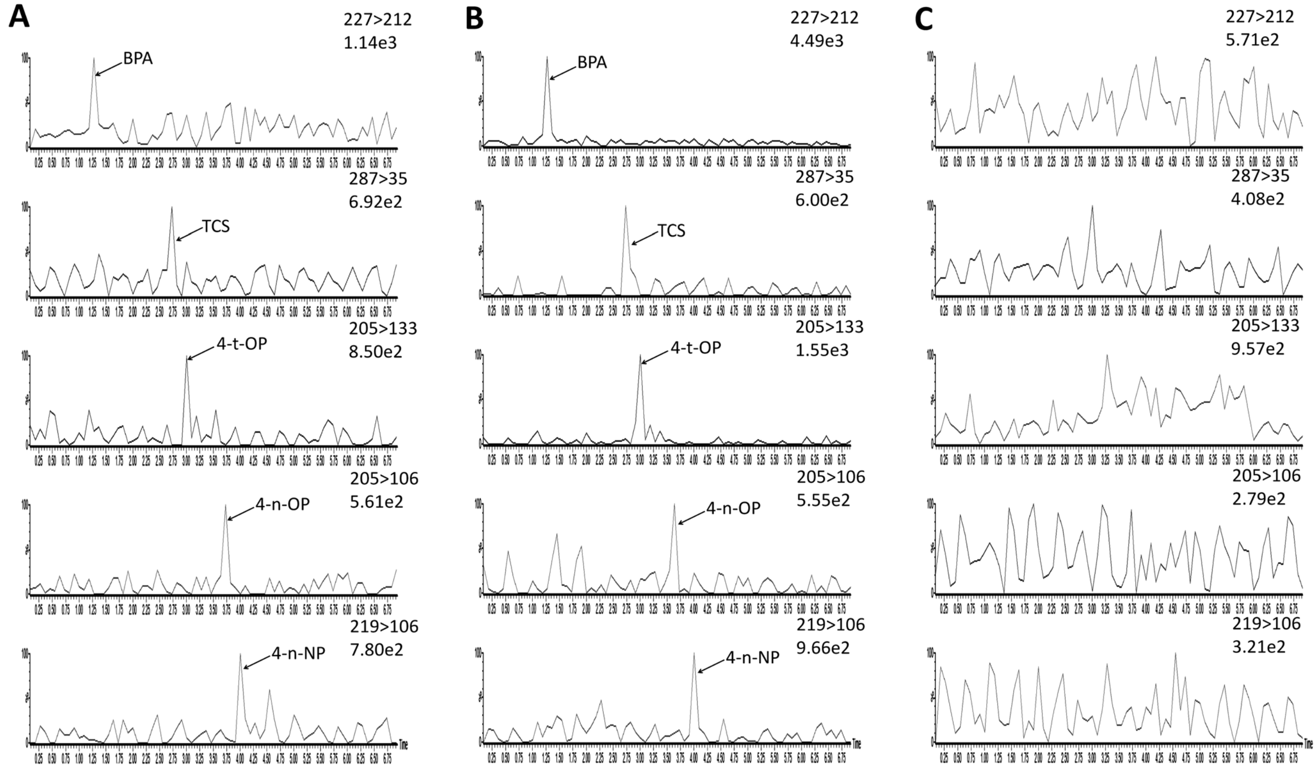


Fig. 1 Chromatograms of the extracted ions: (A) a fortified dust blank with low concentrations of phenols, BPA (0.2 ng mL^{-1}), TCS (10 ng mL^{-1}), 4-*t*-OP (1 ng mL^{-1}), 4-*n*-OP (0.1 ng mL^{-1}), 4-*n*-NP (0.1 ng mL^{-1}). (B) Dust samples with detectable phenols, whose concentrations are close to the median levels. (C) Blank house dust sample.

after extraction, other purification steps were not carried out. The purification steps extend the time needed for analysis and involve considerable consumption of organic solvent. Moreover, the risk of loss of the analytes during purification may be high, particularly for commonly found substances.

Given the common mesh size of steel screens in the Chinese market and the quantity of dust used for the analysis, a mesh size of 150 μm was chosen. For most pollutants in settled house dust, their concentration increases progressively as the size of the dust particles decreases and their specific surface area increases.[28] Particles less than 100–200 μm in diameter are retained most efficiently for absorption in the digestive tract or skin.[28,29]

Due to the large number of samples, ultrasonic extraction was used to batch-process samples in order to save time and solvent. Acetone and dichloromethane were tested as extraction solvents. The supernatant seemed slightly turbid after centrifugation when dichloromethane was used, when compared with acetone. Acetone also provided greater recoveries than dichloromethane, therefore, acetone was chosen as the extraction solvent.

A 100 mm C18 UPLC column was used instead of a 50 mm column for better separation. Gradient A was developed and demonstrated excellent separating capacity. Chromatograms of the phenols showed good peak separation in negative ion mode with the ESI source, which allowed for the sensitive and

Table 3 Intra- and inter-day precision values and recoveries of the phenols

	Intra-day ($n = 6$)						Inter-day ($n = 4$)	
	$0.007^{ad}/0.48^{b}/0.048^{c}$ μg g^{-1} added		$0.48^{acd}/2.4^{b}$ μg g^{-1} added		$24^{a}/48^{b}/9.6^{cd}$ μg g^{-1} added		2.4 μg g^{-1} added	
Analyte	AR (% ± CV)	RR (% ± CV)	AR (% ± CV)	RR (% ± CV)	AR (% ± CV)	RR (% ± CV)	AR (% ± CV)	RR (% ± CV)
Bisphenol A	99.0 ± 8.5	90.2 ± 10.9	91.2 ± 10.4	101.2 ± 6.5	88.2 ± 8.8	101.6 ± 8.4	95.4 ± 17.9	99.3 ± 17.2
Triclosan	111.9 ± 39.7	98.9 ± 20.9	94.3 ± 8.1	103.0 ± 11.0	95.7 ± 6.6	99.0 ± 5.9	93.7 ± 11.0	98.9 ± 12.5
4-*tert*-Octylphenol	91.8 ± 11.4	85.0 ± 9.9	114.2 ± 11.5	100.0 ± 5.9	78.9 ± 5.7	99.8 ± 6.2	88.1 ± 15.7	96.8 ± 15.3
4-*n*-Octylphenol	85.2 ± 15.3	84.3 ± 16.9	101.4 ± 19.8	101.4 ± 7.5	94.0 ± 5.3	100.9 ± 7.5	93.3 ± 11.3	100.0 ± 11.3
4-*n*-Nonylphenol	78.9 ± 19.3	80.6 ± 18.9	99.2 ± 9.7	99.4 ± 7.7	87.3 ± 9.6	100.3 ± 10.0	95.1 ± 15.1	100.4 ± 12.4

[a] For bisphenol A. [b] For triclosan. [c] For 4-*tert*-octylphenol. [d] 4-*n*-Octylphenol and 4-*n*-nonylphenol; AR: absolute recovery; RR: relative recovery; CV: coefficient of variation.

Table 4 Comparison of the concentrations determined in the present study and those in the literature[a]

Analyte	*n*	DR (%)	Sieve size	Median (range) (ng g^{-1})	Location	Reference
Bisphenol A	18	100	<500 μm	1460 (535–9730)	Belgium	27
	12	100	<63 μm	553 (117–1486)	Germany	30
	118	86	<150 μm	820 (nd–17600)	USA	7
	38	100	<2 mm	1600 (200–9380)	USA	9
	44	NR	<425 μm	*(nd–2320)	USA	31
	22	100	<2 mm	2700 (500–21800)	Japan	9
	41	100	<2 mm	3260 (980–39100)	Korea	9
	55	96	<2 mm	630 (nd–8350)	China	9
	47	100	<150 μm	290 (20–2390)	China	Present study
Triclosan	18	100	<500 μm	220 (25–1830)	Belgium	27
	10	100	<60 μm	525 (240–2200)	Spain	6
	10	100	<60 μm	880 (25–2444)	Spain	10
	63	100	<80 μm	378 (82–4090)	Canada	23
	47	96	<150 μm	570 (nd–42220)	China	Present study
4-*tert*-Octylphenol	47	85	<150 μm	80 (nd–530)	China	Present study
4-*n*-Octylphenol	47	51	<150 μm	5 (nd–20)	China	Present study
4-*n*-Nonylphenol	47	51	<150 μm	3 (nd–9)	China	Present study

[a] *n*: number of samples analyzed; DR: detection rate; *: median concentration was not reported; NR: not reported; nd: not detected.

selective determination of these phenols in MRM mode. The MRM approach was developed by optimizing the cone voltage and collision energy to induce the highest possible intensities of the characteristic fragment ions. Based on the relationships between the MS-MS ions, the fragmentation pathways of collision-induced dissociation for generating daughter ions for quantitation are listed in Table 1.

The calibration curve was linear over the concentration range 0.1–1000 ng mL^{-1} for each target analyte. After adjustment of the concentrations using a pilot analysis of the samples and the levels reported in the literature, the concentration ranges were chosen (Table 2). Good linearity was achieved for all analytes with coefficients of correlation >0.998 (Table 2). The inter-day variability of the calibration curve slopes was excellent for all analytes with coefficients of variation (CV) < 20%. The values of the IDLs and MDLs are summarized in Table 2. Phenols are ubiquitous in the environment, so the blank house dust sample and the reagent blank were analyzed (which were prepared and determined in the same manner used for the dust samples). Typical chromatograms of the five phenols and blank house dust sample are shown in Fig. 1.

The validation results for the proposed method are presented in Table 3. The mean absolute and relative recoveries of the target compounds in the blank dust control samples for intra-day variation ranged from 78.9% to 114.2% and from 80.6% to 103.0%, respectively, with CV ≤ 21% (except for a low concentration of TCS with 39.7%) for the absolute recoveries. For the inter-day variation, the mean absolute and relative recoveries were >88%, and CV was <18%. The intra- and inter-day precision and recoveries of the target compounds suggest good reproducibility and accuracy during both sample preparation and determination.

Method application

BPA, TCS, 4-*tert*-OP, 4-*n*-OP and 4-*n*-NP were analyzed simultaneously in indoor settled dust samples obtained from 47 urban homes in which pre-school aged children lived (Table 4). The most frequently identified phenols were BPA and TCS, which were detected in 100% and 96% of the dust samples, respectively. 4-*tert*-OP was detected in ∼85% of the dust samples, while 4-*n*-OP and 4-*n*-NP had the lowest detection prevalence (50%). The BPA levels reported in the present study were lower than those reported in China by Liao *et al.* even though the sieve size used in our study was smaller than the one used in their study.[9] This difference might be explained by the influence of higher BPA levels in some of the laboratory dust samples used in the study by Liao *et al.* The dust samples of Liao *et al.* were from houses, student dormitories, offices, and laboratories. Higher concentrations of BPA in floor dust from offices than in homes have been reported, and these have been attributed to the use of more electronic equipment and furniture in offices and laboratories than in homes.[8,26] The maximum BPA level in the present study was similar to that reported in Murray and Albany in the USA,[26] higher than that reported in Germany,[30] but far lower than those reported in Belgium,[8] Japan,[9] Korea[9] and other places in the USA.[7,9] The median level of TCS was similar to those reported in Belgium,[27] Spain[6,10] and Canada,[23] but the maximum level was more than tenfold higher.

Studies on the occurrence of 4-*tert*-OP, 4-*n*-OP and 4-*n*-NP in indoor dust samples are very limited. The median and maximum levels of these three phenols were all far lower than those of BPA and TCS. In the present study, the concentration ranges of all of the targeted compounds varied widely from home to home, suggesting that exposure to these chemicals is dependent on individual activities and consumer preferences.

Conclusion

A simple and robust analytical method has been developed for the simultaneous measurement of five different phenols (Bisphenol A, TCS, 4-*tert*-OP, 4-*n*-OP and 4-*n*-NP) in indoor settled house dust based on UPLC-MS/MS. Analytes were extracted from the dust samples by sonication, and only a small amount of the dust sample was used. The method developed here provided adequate recoveries with good repeatability and reproducibility for the target compounds under investigation using as little as 0.025 g of dust mass. A high frequency of detection for most of the target phenols (except 4-*n*-OP and 4-*n*-NP) combined with a wide distribution in concentration, supports the notion that indoor dust may represent a potentially important (but widely variable) pathway of exposure to BPA, TCS and 4-*tert*-OP for toddlers.

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