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# Development and validation of a multi-residue method for the simultaneous analysis of brominated and organophosphate flame retardants, organochlorine pesticides, and polycyclic aromatic compounds in household dust†

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Household dust is a sink for multiple toxic chemicals with known or suspected potential health effects. However, most dust exposure studies focus on a few chemicals, which may limit overall understanding of human exposure characteristics because people spend most of their time indoors. This paper describes the development and evaluation of a multi-residue analysis of 20 organochlorine pesticides (OCPs), 15 polycyclic aromatic hydrocarbons (PAHs), 8 polybrominated diphenyl ether congeners (PBDEs), 3 hexabromocyclododecane (HBCDs), 8 synthetic musks (Musks), and 7 organophosphate esters (OPEs) in indoor dusts. After extraction with acetone/hexane (v/v, 1 : 1), all target compounds were fractionated with a Florisil solid-phase extraction (SPE) cartridge into two fractions: PAHs, PBDEs, HBCDs, OCPs and Musks, which were eluted with hexane/dichloromethane, and OPEs eluted with ethyl acetate. Further clean-up using acidified silica 44% cartridges was then performed to enable determination of PBDEs and HBCDs. Instrumental analysis of the target chemicals was performed using gas chromatography (GC) or liquid chromatography (LC) coupled with mass spectrometry (MS) or tandem mass spectrometry (MS/MS). A newly-optimized GC-MS/MS method was employed for the simultaneous determination of PAHs, OCPs, and Musks. The lower limit of quantification (LOQ) values of PAHs, OCPs, and Musks were 0.14–0.92 ng $g^{-1}$, 0.06–0.38 ng $g^{-1}$ and 0.07–0.40 ng $g^{-1}$, respectively. PBDEs were quantified by GC-MS with electron capture negative ionization, and HBCDs and OPEs by LC-MS/MS with electrospray ionization (ESI) in negative and positive ion mode, respectively. Recovery experiments showed that the average recoveries and relative standard deviations were 99–113% and 1–14% for PBDEs, 89–105% and 1–6% for HBCDs, 71–120% and 3–17% for PAHs, 71–112% and 2–17% for OCPs, 77–120% and 2–13% for Musks, and 80–127% and 1–14% for OPEs. Validation experiments showed that the method achieved good accuracy. The developed method was used to analyze SRM 2585 and real indoor dust samples to demonstrate its suitability for routine analysis. The target contaminants were widely detected in SRM 2585 and indoor dust collected from Wuhan of Central China, with PAHs the major species, followed by OPEs, OCPs, and PBDEs.

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## 1 Introduction

The adverse effects of hazardous environmental contaminants, especially on human health and living spaces, have caused increasing concern in recent years.[1,2] Human exposure to environmental contaminants occurs through diverse routes including food ingestion in the case of classical organochlorine pesticides, inhalation in the case of volatile organic compounds, and dust ingestion and dermal absorption in the case of semi-volatile organic compounds.[3] Indoor dust was recently recognized as a significant exposure source for emerging flame retardants (FRs) such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane

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(HBCD),[4,5] and was identified as a major source of environmental contaminants including organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polycyclic musks (Musks) and other chemicals of human health concern.[6] Elevated concentrations of FRs and other contaminants have been widely detected in indoor dust collected from floors and furniture around the world, indicating that indoor dust presents a risk of exposure to hazardous chemicals and adverse health effects.[1,4] Evidence also indicated that organic pollutants in dust compete for human nuclear receptors such as human peroxisome proliferator activated nuclear receptor gamma[7] and estrogen receptor alpha.[8] Given the amount of time people spend in indoor environments,[9] there is a clear and growing need to monitor and evaluate exposure to the diverse pollutants that migrate into indoor dust in order to more comprehensively assess the exposure risks that the indoor microenvironment presents and the associated potential health effects in humans.[10] However, the development of analytical methods for the simultaneous determination of multiple different classes of chemicals found in indoor dust presents a significant challenge.

Studies on the simultaneous analysis of multiple classes of organic contaminants have focused on both characterization and quantification. Hilton *et al.* developed a rapid, non-targeted screening method for the analysis of phthalates, PAHs and their heterocyclic analogs, chlorinated/brominated compounds, and nitro compounds in household dust based on comprehensive two-dimensional gas chromatography coupled to high-resolution mass spectrometry (GC × GC-ToF-MS).[11] However, the loading of the target compounds on the column in this method is limited by the lack of sample fractionation and prior separation of compounds of interest. Some residue analysis methods for the simultaneous determination of multiple classes of organic compounds have been introduced that offer both targeted screening and quantification capabilities. These methods have been applied to vegetation[12] and catfish[13] samples but not to indoor dusts. Although indoor dust is known to present a significant risk of human exposure to several environmental contaminants, most studies on indoor dust have focused on FRs such as PBDEs, hexabromocyclododecane (HBCDs) and organophosphate esters (OPEs).[14–21] Dust is challenging to analyze because it is a complex matrix containing organic contaminants of widely varying polarity.[22] Consequently, direct analysis of 'raw' extracts is impossible without effective separation together with a powerful detection technique. Van den Eede *et al.* developed a fractionation procedure for the determination of several FRs in indoor dust. The fractionation was achieved by Florisil cartridge, which was eluted with hexane and ethyl acetate successively.[23] However, HBCD quantification using this procedure required recombination of the fractions followed by re-solubilization in methanol, which increased the relative standard deviation during liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis by up to 30%. The fractionation of multiple FRs was also achieved on different adsorbents, such as underivatized silica,[24] or self-packed silica gel and alumina cartridge,[25] however, limited to investigate FRs. It is therefore important to develop fractionation procedures that minimize sample complexity and prevent co-elution to enable the simultaneous determination of multiple compound classes using sensitive and selective analytical methods such as GC-MS/MS, GC-MS, or LC-MS/MS. At present, there is no analytical method that uses solid-phase extraction (SPE) to simultaneously clean up and fractionate multiple classes of contaminants in indoor dust (including OCPs, PAHs, Musks, and FRs) prior to determination.

The principal aim of this study was to develop and validate a multi-residue analytical method for indoor dust that would enable simultaneous determination of OCPs, polycyclic aromatic compounds including PAHs and musks, and brominated and organophosphate flame retardants such as PBDEs, HBCDs and OPEs. To enable determination of these compounds at concentrations in the low ppt range, Soxhlet extraction was combined with SPE using Florisil cartridges to fractionate these six target analyte classes into two fractions. In this way, OPEs were separated from the other target compound groups. In addition, a new GC-MS/MS method for the simultaneous determination of OCPs, PAHs and Musks was developed and optimized to expedite the analysis procedure. Finally, the method was applied for the analysis of a certified dust material (NIST SRM2585, "Organic Contaminants in House Dust") and six real dust samples collected in Wuhan.

# 2 Experimental

## 2.1 Chemicals and materials

Standards of PBDE congeners (BDE-28, −47, −99, −100, −153, −154, −183, and −209), α-HBCD, β-HBCD, and γ-HBCD were purchased from AccuStandard Inc. (New Haven, CT, USA). Standards of α-, β-, γ-, δ-BHC, heptachlor, heptachlor epoxide, α-chlordane, γ-chlordane, aldrin, endrin, dieldrin, endosulfan I, endosulfan II, endrin aldehyde, endosulfan sulfate, endrin ketone, *p*,*p*′-DDE, *p*,*p*′-DDD, *p*,*p*′-DDT and methoxychlor, acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]-fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenzo[*a*,*h*]anthracene (DahA), benzo[*g*,*h*,*i*]perylene (BghiP) and indeno[1,2,3-*cd*]pyrene (IcdP) were purchased from Supelco (Bellefonte, PA, USA). Standards of cashmeran (DPMI), celestolide (ADBI), phantolide (AHMI), musk xylene, musk ketone, galaxolide (HHCB), tonalide (AHTN) and traseolide (ATII) were purchased from LGC Promochem GmbH (Mercatorstrasse, Wesel, Germany) (purity > 97%). Standards of tris-(2-chloroethyl)phosphate (TCEP, >97%), tris-(2-chloropropyl) phosphate (TCPP, >99%), tris-(1,3-dichloro-2-propyl)phosphate (TDCPP, >97%), triphenyl phosphate (TPhP, >99%), tributyl phosphate (TBP, >99%), tris-(2-butoxyethyl)phosphate (TBEP, >94%) and tritolyl phosphate (TCP, >90%) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

For use as volumetric internal standards, $^{13}$C-BDE-209 and $^{13}$C-PCB-208 were purchased from Cambridge Isotope Laboratories (Andover, MA, USA); pentachloronitrobenzene (PCNB) was purchased from AccuStandard Inc. (New Haven, CT, USA); hexamethylbenzene (HMB) was purchased from Dr

 

Ehrenstorfer-Schäfer. Bgm-Schlosser (Augsburg, Germany); $^{13}C_{12}$-α, β, and γ-HBCD were purchased from Wellington Laboratories (Guelph, Ontario, Canada); and $d_{21}$-tripropyl phosphate ($d_{21}$-TPrP) was purchased from C/D/N Isotopes Inc (Pointe-Claire, Quebec, Canada). For use as surrogates, 2,4,5,6-tetrachloro-*m*-xylene (TMX), $d_{10}$-Ace, $d_{10}$-Phen, $d_{12}$-Chry and $d_{12}$-Pery were purchased from Supelco (Bellefonte, PA, USA); $d_{18}$-α, β, γ-HBCD were purchased from Wellington Laboratories (Guelph, Ontario, Canada); and $d_{12}$-TCEP (>99%), $d_{15}$-TPhP (>99%) and $d_{27}$-TBP (>99%) were purchased from C/D/N Isotopes Inc (Pointe-Claire, Quebec, Canada).

Reagents and materials used for sample analysis were: dichloromethane (DCM, pesticide grade, J&K Chemical Ltd., USA); ethyl acetate (EtAc), *n*-hexane (Hex) and methanol (MeOH) (HPLC grade, CNW, Germany); acetone (Ace, HPLC grade, Honeywell Burdick & Jackson, USA). Empty polypropylene filtration tubes (6 mL) SPE cartridges (CNW, Germany); Supelclean™ ENVI™-Florisil® (1 g/6 mL) cartridges (Supelco, Bellefonte, USA); silica gel (63–200 μm, activated at 180 °C for 12 hours, Merck, Germany); and sulfuric acid (98%, Sigma-Aldrich, Germany).

### 2.2 Sample collection

Indoor dust samples ($n = 6$) were randomly collected during May 2013 from urban residential houses in Wuhan, which is the capital of Hubei province in Central China. A full detail description of the sample collection is described elsewhere.[26] Indoor dust was collected from the surfaces of furniture, floors, and household appliances by sweeping, using the sampling procedure described in the VDI 4300-8 standard (the VDI is the German Association of Engineers). In brief, dust samples were swept onto aluminum foil using clean paint brushes, sealed in polyethylene zip bags, and brought back to the laboratory. The samples were then sieved using stainless steel 60-mesh (250 μm) testing sieves to remove large debris, and hair was removed from the dust using clean tweezers. Finally, the dust was transferred onto clean aluminum foil, sealed in a polyethylene zip bag, and stored at −20 °C until analysis. To prevent cross-contamination, the paint brushes, tweezers, and sieves were cleaned between samples by ultrasonic rinsing in water for 5 min, followed by rinsing three times with deionized water three times, air drying to remove bound dust, and scrubbing with acetone and hexane.

### 2.3 Sample extraction and clean up

Samples (500 mg) were weighed and spiked with surrogate internal standards (20 ng of TMX and HBCD; 200 ng of PAHs and OPEs), and then Soxhlet extracted for 48 h with 200 mL Ace/Hex mixture (v/v, 1 : 1). Activated copper powder was added to remove sulfur, then the extract was evaporated and redissolved in 1 mL of Hex. Prior to fractionation, a Florisil SPE cartridge was prewashed with 8 mL EtAc and 12 mL Hex sequentially. The extracts were fractionated by eluting first with 10 mL of Hex/DCM (v/v, 8 : 2) to obtain fraction 1 (F1) and then with 10 mL

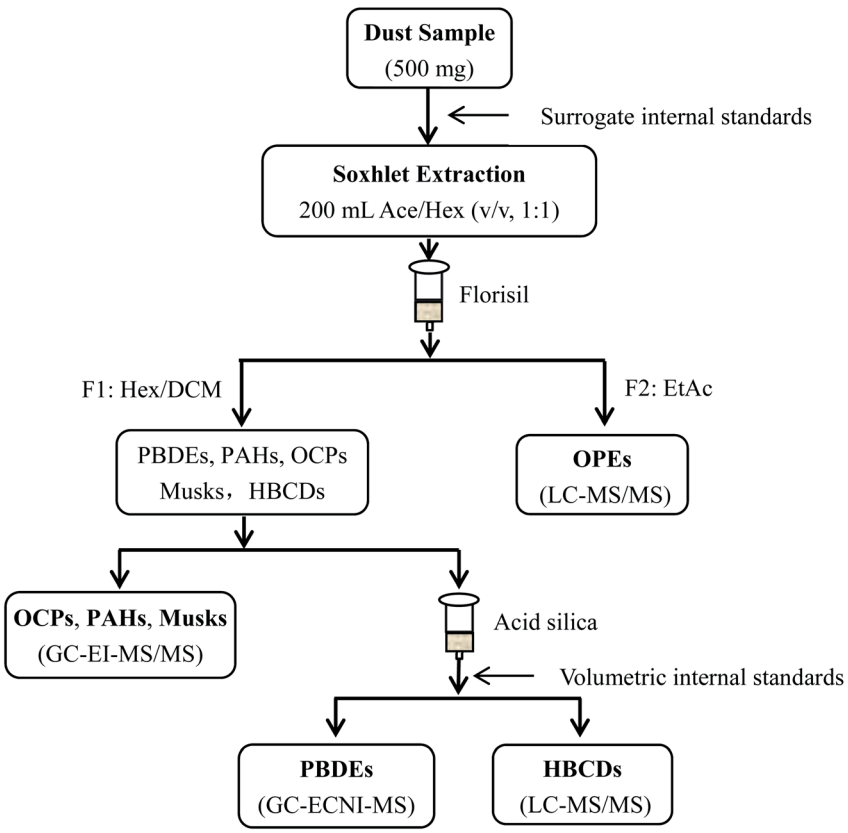


Fig. 1 Schematic representation of the dust sample preparation procedure.

of EtAc to obtain fraction 2 (F2). F1 was split into two equal aliquots. One aliquot was concentrated under $N_2$ flow and reconstituted in 200 μL Hex for the simultaneous analysis of OCPs, PAHs and Musks by GC-MS/MS. The other aliquot was transferred onto an acidified silica gel cartridge (44% sulfuric acid, w/w, prewashed with 6 mL Hex) for further clean-up. Elution was performed with 10 mL of Hex/DCM (v/v, 1 : 1), and the eluate was evaporated to dryness under a gentle nitrogen flow before reconstitution in 200 μL Hex for analysis of PBDEs using GC-MS in electron capture negative ionization (ECNI) mode. The Hex solvent was then evaporated to dryness, and reconstituted in 200 μL MeOH for determination of HBCDs by LC-MS/MS. Finally, F2 was concentrated under an $N_2$ flow and reconstituted in 200 μL MeOH for determination of OPEs by LC-MS/MS. Before instrumental analysis, the following volumetric internal standards were added: PCNB and HMB for OCPs, PAHs and Musks; $^{13}C$-PCB-208 for PBDEs; $^{13}C_{12}$-α, β, γ-HBCD for HBCDs, and $d_{21}$-TPrP for OPEs. A schematic representation of the sample preparation procedure is shown in Fig. 1.

Table 1 Optimized conditions, limits of detection (mLOD) and limit of quantification (mLOQ) of the method obtained by GC-MS/MS analysis for PAHs, OCPs and Musks

| Name | $R_t$/min | Quantifier *m*/*z* (collision energy/eV) | Qualifier *m*/*z* (collision energy/eV) | mLOD (ng $g^{-1}$) | mLOQ (ng $g^{-1}$) |
|---|---|---|---|---|---|
| **PAHs** | | | | | |
| Acenaphthene | 10.82 | 152 > 151(10) | 152 > 126(10) | 0.05 | 0.17 |
| Acenaphthylene | 11.28 | 154 > 153(10) | 154 > 152(10) | 0.05 | 0.15 |
| Fluorene | 12.77 | 166 > 165(10) | | 0.04 | 0.14 |
| Phenanthrene | 16.02 | 178 > 152(30) | 178 > 176(30) | 0.06 | 0.20 |
| Anthracene | 16.21 | 178 > 152(30) | 178 > 176(30) | 0.07 | 0.22 |
| Fluoranthene | 20.82 | 202 > 201(10) | 202 > 200(10) | 0.07 | 0.23 |
| Pyrene | 21.74 | 202 > 201(10) | 202 > 100(10) | 0.07 | 0.23 |
| Benz[*a*]anthracene | 27.21 | 228 > 226(20) | 228 > 202(20) | 0.09 | 0.31 |
| Chrysene | 27.35 | 228 > 226(20) | 228 > 202(20) | 0.16 | 0.55 |
| Benzo[*b*]fluoranthene | 31.82 | 252 > 250(30) | 252 > 226(30) | 0.19 | 0.64 |
| Benzo[*k*]fluoranthene | 31.91 | 252 > 250(30) | 252 > 226(30) | 0.13 | 0.44 |
| Benzo[*a*]pyrene | 33.03 | 252 > 250(30) | 252 > 226(30) | 0.23 | 0.76 |
| Indeno[1,2,3-*cd*]pyrene | 37.78 | 276 > 274(35) | 276 > 250(35) | 0.18 | 0.59 |
| Dibenz[*a*,*h*]anthracene | 38.07 | 278 > 276(35) | 276 > 274(35) | 0.27 | 0.92 |
| Benzo[*g*,*h*,*i*]perylene | 39.07 | 276 > 274(35) | 278 > 276(35) | 0.19 | 0.63 |
| **OCPs** | | | | | |
| α-BHC | 14.46 | 219 > 183(10) | 256 > 183(10), 219 > 183(10) | 0.02 | 0.07 |
| β-BHC | 15.24 | 219 > 183(10) | 256 > 183(10), 254 > 183(10) | 0.03 | 0.11 |
| γ-BHC | 15.52 | 219 > 183(10) | 256 > 183(10), 254 > 183(10) | 0.02 | 0.07 |
| δ-BHC | 16.46 | 219 > 183(10) | 256 > 183(10), 254 > 183(10) | 0.04 | 0.15 |
| Heptachlor | 17.95 | 272 > 237(20) | 374 > 237(15), 372 > 237(15) | 0.02 | 0.07 |
| Aldrin | 19.19 | 263 > 193(10) | 329 > 293(5), 293 > 220(5) | 0.04 | 0.14 |
| Heptachlor epoxide | 20.55 | 353 > 263(10) | 390 > 353(5) | 0.08 | 0.27 |
| γ-Chlordane | 21.39 | 373 > 266(10) | 410 > 375(8), 241 > 206(10) | 0.04 | 0.13 |
| α-Chlordane | 21.84 | 373 > 266(10) | 410 > 375(8), 241 > 206(10) | 0.06 | 0.18 |
| Endosulfan I | 21.84 | 241 > 206(10) | 339 > 160(10), 195 > 159(5) | 0.06 | 0.19 |
| *p*,*p*′-DDE | 22.70 | 246 > 176(45) | 318 > 248(20), 316 > 246(20) | 0.03 | 0.10 |
| Dieldrin | 22.80 | 277 > 241(10) | | 0.06 | 0.19 |
| Endrin | 22.80 | 281 > 245(12) | 265 > 230(8), 263 > 228(8) | 0.12 | 0.38 |
| Endrin aldehyde | 23.53 | 279 > 243(12) | 345 > 243(12), 209 > 174(10) | 0.07 | 0.24 |
| Endosulfan II | 23.93 | 241 > 206(10) | 197 > 159(5), 195 > 159(5) | 0.07 | 0.23 |
| *p*,*p*′-DDD | 24.20 | 235 > 165(15) | 318 > 235(15), 320 > 237(15) | 0.02 | 0.06 |
| Endosulfan sulfate | 25.31 | 272 > 237(10) | 272 > 237(10) | 0.04 | 0.14 |
| *p*,*p*′-DDT | 25.54 | 235 > 165(10) | 354 > 235(5) | 0.08 | 0.26 |
| Endrin ketone | 26.93 | 317 > 101(10) | 281 > 245(10), 319 > 101(10) | 0.08 | 0.27 |
| Methoxychlor | 27.58 | 227 > 169(20) | 310 > 227(8) | 0.08 | 0.28 |
| **Musks** | | | | | |
| DPMI | 11.45 | 206 > 191(10) | 191 > 163(10) | 0.07 | 0.22 |
| ADBI | 14.67 | 244 > 229(10) | 229 > 187(8) | 0.04 | 0.15 |
| AHMI | 15.35 | 244 > 229(10) | 229 > 187(8) | 0.05 | 0.18 |
| ATII | 16.88 | 215 > 173(8) | 258 > 215(8) | 0.06 | 0.20 |
| HHCB | 16.97 | 258 > 243(8) | | 0.02 | 0.07 |
| Musk xylene | 17.01 | 282 > 265(8) | 297 > 282(5) | 0.08 | 0.29 |
| AHTN | 17.10 | 258 > 243(8) | | 0.05 | 0.16 |
| Musk ketone | 19.06 | 279 > 191(10) | 294 > 279(10) | 0.12 | 0.40 |

 

### 2.4 Instrumental analysis

The instrumental analysis of PBDEs[27] and HBCDs[28] has been described previously; details of the analytical procedures and instrumental analysis conditions are given in the ESI (Sections 1 and 2†).

For multi-determination of OCPs, PAHs and Musks, GC-EI-MS/MS analysis was performed using an Agilent 7890A GC unit coupled to an Agilent 7000A triple quadrupole mass spectrometer and a 7693 autosampler. The column used was a DB-5MS with dimensions of 30 m × 0.25 mm × 0.25 μm (J&W Scientific, USA). The GC oven temperature program was set as follows: held at 70 °C for 5 min, ramped at 10 °C $min^{-1}$ to 160 °C and then at 5 °C $min^{-1}$ to 280 °C, held for 5 min, ramped at 20 °C $min^{-1}$ to 300 °C, and finally held for 5 min. Helium (purity 99.999%) was used as the carrier gas with a constant flow of 1.2 mL $min^{-1}$. A pulsed splitless injection with a volume of 1 μL was used. The total run time was 41 min. The injector, quadrupole, and transfer line temperatures were 260, 150, and 300 °C, respectively. The triple quadrupole mass spectrometer (QqQ) was operated in multiple reaction monitoring (MRM) mode with an emission current of 50 μA and electron impact ionization at 70 eV. The ionization source temperature was set to 230 °C. The optimized MS/MS transitions for OCPs, PAHs, and Musks are presented in Table 1.

OPEs analysis was performed using an Agilent 1100 series liquid chromatograph (Agilent Technologies, Palo Alto, CA) coupled to an AB SCIEX API 4000 QqQ mass spectrometer (AB SCIEX, Foster City, CA). The Analyst 1.5 software was used for data acquisition and processing. The injection volume was 10 μL and the flow rate was 0.5 mL $min^{-1}$. A Zorbax SB-C18 reversed-phase column (4.6 × 250 mm, 5 μm, Agilent) was used to separate target analytes. The electrospray ionization (ESI) source conditions were identical for all analytes, with an ion spray voltage of +4000 V in positive ion mode and a source temperature of 500 °C. The nebuliser gas and desolvation gas pressures were 40.00 psi, while the curtain gas and collision gas pressures were 15.00 psi. Analyte quantitation was performed using mass transition ion-pairs of 284.5 > 98.8 for TCEP, 326.7 > 98.8 for TCPP, 430.6 > 98.8 for TDCPP, 326.7 > 151.9 for TPhP, 398.8 > 198.8 for TBEP, 368.7 > 90.8 for TCP, and 266.8 > 98.8 for TBP. The mobile phase gradient was established using water (A)/MeOH (B)/acetonitrile (C). The eluent composition was initially 30 : 70 A/B (v/v), and was changed to 100% B over 15 minutes, held for 7 minutes, then changed to 50 : 50 B/C over 1 min, held for 7 min, and finally returned to 30 : 70 A/B over 3 min.

### 2.5 Calibration, validation, and quality control

Internal standard multipoint calibration was performed for PAHs, OCPs, and Musks by performing analyses at six or more different concentration levels and then applying least-squares linear regression. The final method was validated by performing spiking experiments using three concentration levels designated $Q_{low}$, $Q_{middle}$ and $Q_{high}$, with three replicates per level. The spiking concentrations were chosen based on the concentration ranges expected in real dust samples. Specifically, the concentration of 5, 10, and 100 ng $g^{-1}$ were selected to represent $Q_{low}$, $Q_{middle}$ and $Q_{high}$ for PBDEs and HBCD, the concentration of 10, 50, and 500 ng $g^{-1}$ were used for OCPs, and 50, 500,2500 ng $g^{-1}$ were set for OPEs, PAHs and Musks, respectively. Dust samples that had already undergone organic pollutant extraction were reused as matrix blanks for the spiking experiments. In addition, a reagent blank with a matrix of anhydrous sodium sulfate was included in every analytical series. The matrix effect was evaluated by comparing the slopes of the calibration curves obtained in solvent and in the matrix. The limit of detection (mLOD) and limit of quantification (mLOQ) of the method were determined by injecting analytes at various concentrations in spiked blank dust extracts to find the concentrations yielding peak signals of 3 times and 10 times the background noise of the chromatogram, respectively. To determine the method's accuracy and precision (expressed in relative standard deviations, or RSDs), recovery experiments by spiking pre-extracted matrix with three replicates per level were performed. To test the analytical method's suitability, it was used to quantify compounds belonging to six classes in three replicate 500 mg samples of a certified dust material (SRM2585). The levels of target contaminations reported in our study were not corrected for recoveries.

## 3 Results and discussion

### 3.1 Optimization of the SPE procedure

Extracts containing multiple compounds of interest are commonly subjected to clean-up and fractionation by SPE prior to instrumental analysis. Various sorbents including Florisil and silica gel can be used to separate the compounds of interest from interfering co-extractants.[29] To analyze compound classes with very different polarities, we performed an initial separation using Florisil because it is a moderately polar magnesium silicate-based material that offers strong retention of polar compounds and generates only a weak background signal in chromatograms.[23,30] Elution solvents were chosen based on the principle of similarity, *i.e.*, the idea that substances with the same polarity (either polar or non-polar) dissolve one-another. Hexanes were chosen as the eluent for non-polar compounds such as PAHs and PBDEs, while more polar solvents were needed for compounds such as OCPs, Musks and OPEs. Unfortunately, there was little published data on the elution behavior of the targeted compound classes from Florisil SPE cartridges when eluting with solvents of different polarities. Therefore, to identify appropriate elution solvents and optimize the SPE method, we first investigated the elution behavior of mixtures containing 8 PBDEs, 3 HBCDs, 20 OCPs, 15 PAHs, 8 Musks, and 7 OPEs from Florisil SPE cartridges. Elution was performed using four different solvents including the nonpolar Hex, the moderately polar DCM, and the relatively polar EtAc. Details of this experiment are presented in the ESI (Section 3†). As expected, changing the polarity of the eluent affected the recovery of the different compounds (Fig. S1†). For non-polar analytes such as PAHs and PBDEs, Hex was the optimal solvent, achieving complete recovery from the cartridge after eluting with a reasonable volume of solvent. For slightly polar

compounds such as OCPs, Musks, and HBCDs, complete recovery was not achieved after elution with Hex. Therefore, a more polar solvent was needed. It was found that complete recovery of these compounds could be achieved by eluting with Hex/DCM (v/v, 1 : 1), DCM, or EtAc. For OPEs, recovery increased with solvent polarity, and complete recovery was achieved when eluting with EtAc. These results are consistent with previous reports.[32]

Having established the elution behavior of the targeted compounds, it was necessary to identify effective separation conditions. We therefore conducted fractionation experiments using Florisil SPE cartridges using 3 different elution conditions (A, B and C), as shown in Fig. 2. Elution conditions A (F1: 10 mL Hex, F2: 10 mL EtAc) did not separate HBCDs, OCPs, and Musks effectively because some slightly polar compounds such as heptachlor, endosulfan II, endrin aldehyde, DPMI, HHCB, ADBI and β-HBCD were eluted in both F1 and F2; a key objective was to avoid the elution of one compound class in two fractions. Because it was apparent that slightly polar solvents would fully elute HBCDs, OCPs, and Musks, it was necessary to increase the solvent polarity of the first fraction (F1) while limiting the elution volume to avoid elution of OPEs. Satisfactory separation was achieved using the B conditions (F1: 10 mL Hex/DCM (v/v, 8 : 2), F2: 10 mL EtAc); all compound classes other than OPEs were eluted in F1, and OPEs were fully eluted in F2. However, the recovery of some compounds including heptachlor (75%) and ADBI (78%) were unsatisfactory. To increase the recovery of these compounds, we tested elution conditions C (F1: 10 mL Hex/DCM (v/v, 7 : 3), F2: 10 mL EtAc). While PBDEs, HBCDs, PAHs, OCPs and Musks were completely eluted with good recoveries under these conditions, some OPEs (mainly TPhP and TCP) were also found in F1. Consequently, these conditions did not provide adequate separation. However, the B conditions provided adequate retention of both non-polar and polar compounds, allowing the compounds of interest to be separated into distinct fractions without undesired co-elution.

When attempting to detect HBCDs by LC-MS/MS, the effect of co-eluting residual matrix components on the ionization of target analytes can cause either signal suppression or enhancement, which is a limitation of the ESI interface.[33] Special cares must therefore be taken to eliminate potential interferences by optimizing the sample preparation protocol. It is worth noting that the protocol developed in this work isolates HBCDs in a single fraction, which should simplify the treatment of troublesome matrix effects during subsequent LC-MS analysis.[23] Matrix effects were further suppressed by subjecting the HBCD fraction to an additional purification step using silica-supported sulfuric acid. It was thus possible to selectively separate six compound classes using a Florisil 1 g/6 mL SPE cartridge, eluting with 10 mL of Hex/DCM (v/v 8 : 2) and then 10 mL of EtAc.

### 3.2 Optimization of GC-EI-MS/MS

Low detection limits for all the analytes of interest were achieved using gas chromatography coupled with a triple quadrupole mass spectrometer, enabling successful assignment and confirmation of peak identities. Compounds were identified based on their MRM transitions and retention times.[12] To achieve good separation, a range of temperature programs were tested. The final GC operating conditions and optimized oven temperature programs are described fully in the "Instrumental analysis" section. Using the optimized conditions, a chromatogram of the mixture of 43 contaminants with good analytical

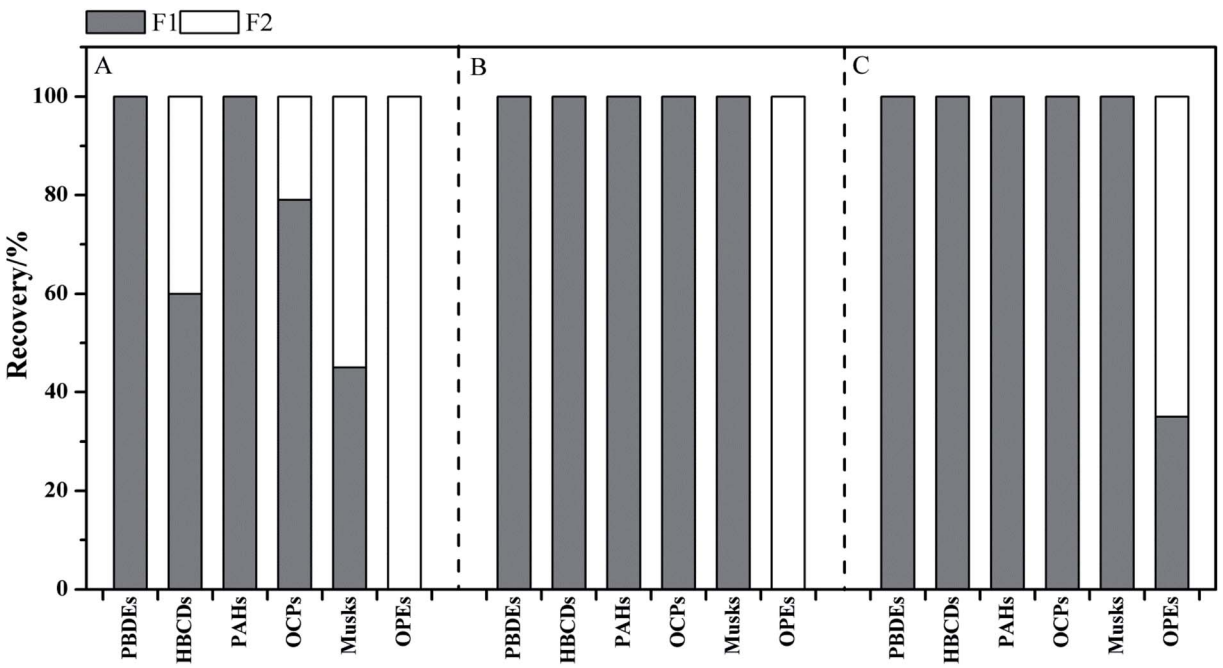


Fig. 2 The separation of PBDEs, HBCDs, PAHs, OCPs, Musks and OPEs on a 1 g/6 mL Florisil cartridge under three different elution conditions ((A) F1-10 mL Hex + F2-10 mL EtAc; (B) F1-10 mL Hex/DCM (v/v 8 : 2) + F2-10 mL EtAc; (C) F1-10 mL Hex/DCM (v/v 7 : 3) + F2-10 mL EtAc).

 

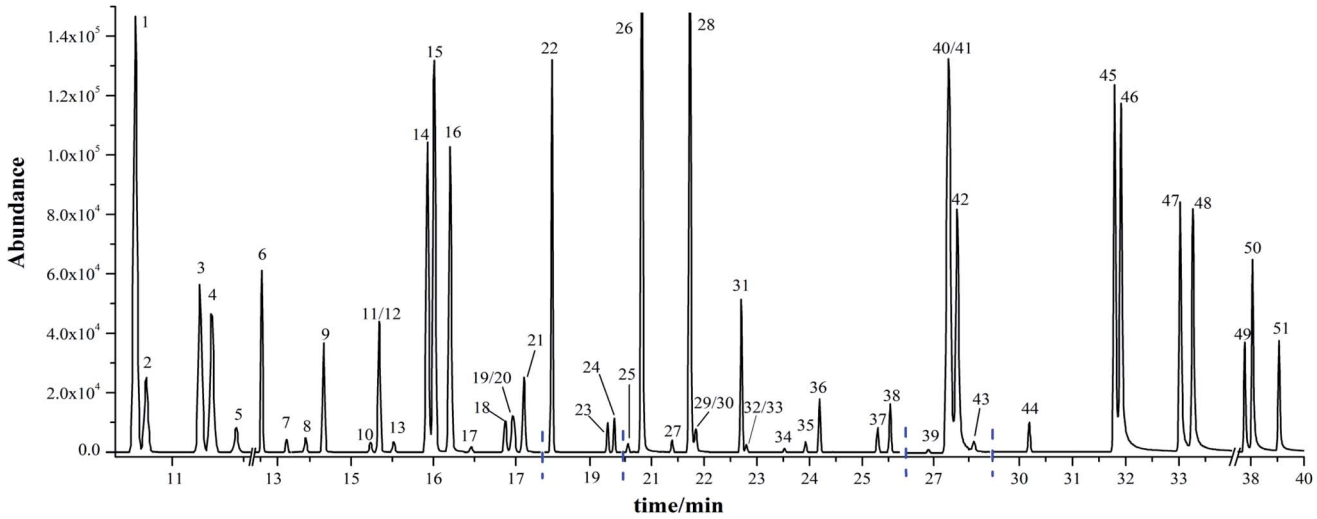


Fig. 3 Total ion chromatogram of a mixture of PAHs (500 ppb), OCPs (100 ppb) and Musks (500 ppb) prepared in Hex by GC-EI-MS/MS analysis. (1) HMB (2) acenaphthene (3) $d_{10}$-Ace (4) acenaphthylene (5) DPMI (6) fluorene (7) TMX (8) α-BHC (9) ADBI (10) β-BHC (11) PCNB (12) AHMI (13) γ-BHC (14) $d_{10}$-Phen (15) phenantrene (16) anthracene (17) δ-BHC (18) ATII (19) HHCB (20) musk xylene (21) AHTN (22) heptachlor (23) musk ketone (24) aldrin (25) heptachlor epoxide (26) fluoranthene (27) γ-chlordane (28) pyrene (29) α-chlordane (30) endosulfan I (31) *p*,*p*′-DDE (32) dieldrin (33) endrin (34) endrin aldehyde (35) endosulfan II (36) *p*,*p*′-DDD (37) endosulfan sulfate (38) *p*,*p*′-DDT (39) endrin ketone (40) benz[*a*]anthracene (41) $d_{12}$-Chry (42) chrysene (43) methoxychlor (44) $^{13}$C-PCB208 (45) benzo[*a*]fluoranthene (46) benzo[*k*]fluoranthen (47) benzo[*a*]pyrene (48) $d_{12}$-Pery (49) indeno[1,2,3-*cd*]pyrene (50) dibenz[*a*,*h*]anthracene (51) benzo[*g*,*h*,*i*]perylene.

separation was obtained in 41 min (Fig. 3). Variables considered when optimizing the triple quadrupole MS/MS conditions were the choices of precursor ions and product ions as well as the optimization of the collision energies to maximize the response from each target compound. After obtaining full scan spectra, the precursor ion for each analyte was selected and subjected to a range of collision energy voltages (*i.e.*, different potentials on the second quadrupole) to generate MS/MS product ions. Collision energies ranging from 5 to 45 eV were tested. Finally, two or three product ions were chosen for each analyte based on their selectivity and sensitivity (Table 1). For the most of OCPs, the ions obtained from the loss of the 1–3 chlorine atoms in the collision cell were monitored as product ions. For some congeners of PAHs, the parent-to-parent MRM transitions (for example, fluoranthene, 202 > 202) also shows high sensitivity, however, a third transition (202 > 201) may be more appropriate, since the parent-to-parent transitions may not always offer adequate selectivity in the presence of a complex matrix. There were some compound pairs (*i.e.*, phenanthrene–anthracene and fluoranthene–pyrene) that had the same quantifier and qualifier mass transitions but could be successfully distinguished because they eluted at different times. Additionally, there were several pairs of co-eluting compounds (*i.e.*, transition 258 > 243 for HHCB and 282 > 265 for musk xylene, and transition 373 > 266 for α-chlordane and 241 > 206 for endosulfan I, respectively) that had different MRM transitions, allowing both compounds to be unambiguously identified despite their co-elution. The shapes of the compounds' chromatographic peaks correlated strongly with their scan times, dwell times, scan rates, and number of monitored transitions.[34,35] To obtain low detection limits and well-shaped chromatographic peaks, the dwell time was adjusted to allow at least 5 cycles per second throughout the chromatographic run, providing a sufficient number of chromatographic points (>15 points) for all compounds. The final MS/MS conditions used in this study are detailed in Table 1. A key advantage of the high selectivity and sensitivity of QqQ methods is that only a small quantity of dust extract is introduced into the instrument during each run, which reduces the potential for matrix interference and increases the method's long-term reliability.

### 3.3 Method validation

PAHs, OCPs, and Musks were identified based on their retention times and precursor and selected daughter ions. The detector response was linear at concentrations of 50–2500 ng

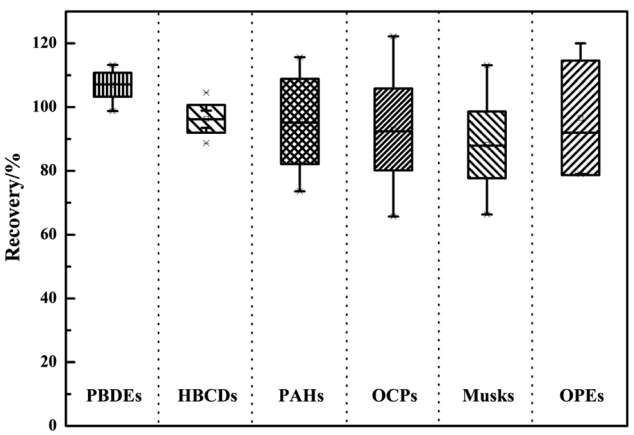


Fig. 4 Box plots representing average recoveries ($n$ = 9) and relative standard deviations (RSD) for six classes of analytes under the optimized SPE method at three different concentration levels.

Table 2 Concentrations (ng $g^{-1}$ dust) of six classes of analytes measured in SRM 2585 ($n = 3$) and dust samples ($n = 6$) from Wuhan dwellings[a]

| | | SRM 2585 ($n = 3$, mean ± SD) | | | Dust samples ($n = 6$) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Name | Measured | Certified or indicative[31] | Measured/certified or indicative (%) | S1 | S2 | S3 | S4 | S5 | S6 |
| PBDEs | BDE-28 | 50.9 ± 5.1 | 46.9 ± 4.4 (ref. 32) | 108 | nd | nd | 4.4 | 4.7 | 6.9 | 2.2 |
| | BDE-47 | 499 ± 39 | 497 ± 46 (ref. 32) | 100 | nd | nd | 6.9 | 23.8 | 27.9 | 2.2 |
| | BDE-100 | 151 ± 13 | 145 ± 11 (ref. 32) | 104 | nd | 0.6 | nd | 1.0 | 1.6 | nd |
| | BDE-99 | 937 ± 40 | 892 ± 53 (ref. 32) | 105 | nd | 3.6 | 6.1 | 18.0 | 11.2 | 1.4 |
| | BDE-154 | 90.6 ± 3.8 | 83.5 ± 2.0 (ref. 32) | 109 | nd | 0.5 | nd | 1.8 | 1.1 | nd |
| | BDE-153 | 121 ± 8 | 119 ± 1 (ref. 32) | 102 | nd | 2.5 | nd | 9.3 | 3.3 | 0.4 |
| | BDE-183 | 41.9 ± 3.7 | 43.0 ± 3.5 (ref. 32) | 98 | nd | nd | nd | nd | nd | nd |
| | BDE-209 | 2870 ± 60 | 2510 ± 190 (ref. 32) | 114 | 56.3 | 298 | 622 | 493 | 3210 | 263 |
| HBCDs | α-HBCD | 20.4 ± 2.2 | 19.0 ± 3.7 (ref. 33) | 107 | 3.0 | 12.1 | 26.3 | 15.2 | 17.6 | 6.6 |
| | β-HBCD | 4.8 ± 0.3 | 4.3 ± 1.1 (ref. 33) | 112 | 0.3 | 7.4 | 4.6 | 2.5 | 3.8 | 0.9 |
| | γ-HBCD | 115 ± 9.6 | 120 ± 22 (ref. 33) | 96 | 0.7 | 9.8 | 5.8 | 10.3 | 11.5 | 1.8 |
| Musks | ADBI | 123 ± 9.4 | 150 ± 15.7 (ref. 34) | 81 | nd | nd | nd | nd | nd | nd |
| | AHMI | 239 ± 18.9 | 202 ± 5.2 (ref. 34) | 118 | nd | nd | nd | nd | nd | nd |
| | ATII | 147 ± 8.4 | 139 ± 5.8 (ref. 34) | 106 | nd | nd | nd | nd | nd | nd |
| | HHCB | 1460 ± 26 | 1460 ± 67 (ref. 34) | 100 | 34.4 | 11.3 | 77.1 | 7.9 | 49.9 | 149 |
| | Musk xylene | 910 ± 6.9 | 895 ± 7.2 (ref. 34) | 102 | nd | nd | 15.0 | nd | 49.2 | nd |
| | AHTN | 1700 ± 11 | 1650 ± 88 (ref. 34) | 103 | 31.7 | 5.6 | 27.1 | 8.0 | 14.8 | 71.0 |
| | Musk ketone | 545 ± 9.2 | 477.0 ± 29.7 (ref. 34) | 114 | 154 | nd | 87.6 | nd | 72.5 | 815 |
| OPEs | TBP | 187 ± 9 | 180 ± 20 (ref. 35) | 104 | 21.5 | 7.7 | 28.0 | 14.5 | 7.9 | 26.1 |
| | TCEP | 743 ± 98 | 700 ± 170 (ref. 35) | 106 | 283 | 262 | 578 | 80.8 | 1510 | 1110 |
| | TCPP | 846 ± 65 | 820 ± 100 (ref. 35) | 103 | 65.0 | 105 | 1020 | 71.7 | 138 | 211 |
| | TPhP | 860 ± 80 | 990 ± 70 (ref. 38) | 87 | 177 | 45.9 | 58.0 | 93.9 | 4.3 | 640 |
| | TDCPP | 2230 ± 136 | 2020 ± 260 (ref. 35) | 103 | 46.7 | 86.5 | 799 | 95.1 | 111 | 229 |
| | TBEP | 49 200 ± 4000 | 49 000 ± 9600 (ref. 35) | 109 | 70.4 | 24.8 | 227 | 153 | nd | 93.1 |
| | TCP | 1170 ± 112 | 1070 ± 110 (ref. 35) | 110 | 15.5 | 8.8 | 0.0 | 12.0 | nd | 87.6 |
| OCPs | α-BHC | 0.4 ± 0.1 | — | — | 2.7 | nd | 16.5 | 0.5 | 0.7 | 2.9 |
| | β-BHC | 2.9 ± 0.3 | — | — | 9.3 | nd | 20.2 | 6.4 | 1.2 | 23.0 |
| | γ-BHC | 6.5 ± 0.3 | — | — | 2.0 | nd | 11.0 | nd | 0.6 | 4.7 |
| | δ-BHC | 3.87 ± 1.34 | 4.06 ± 0.55 (ref. 32) | 95 | 1.6 | nd | 13.9 | 0.3 | 0.3 | 7.3 |
| | Heptachlor | 113 ± 6 | 166 ± 34 (ref. 32) | 68 | nd | nd | nd | nd | nd | nd |
| | Aldrin | 42.1 ± 5.1 | — | — | nd | nd | nd | nd | nd | nd |
| | Heptachlor epoxide | 10.2 ± 1.3 | 11.3 ± 0.6 (ref. 32) | 90 | nd | nd | nd | nd | nd | nd |
| | γ-Chlordane | 171 ± 6 | 174 ± 45 (ref. 32) | 98 | nd | nd | nd | nd | nd | nd |
| | α-Chlordane | 303 ± 9 | 277 ± 96 (ref. 32) | 109 | nd | nd | nd | nd | nd | nd |
| | Endosulfan I | 43.8 ± 3.6 | — | — | nd | nd | nd | nd | 2.0 | nd |
| | *p,p′*-DDE | 283 ± 6 | 261 ± 2 (ref. 32) | 109 | 18.8 | 3.1 | 107 | 2.8 | 4.4 | 48.1 |
| | Dieldrin | 97 ± 7 | 88 ± 21 (ref. 32) | 110 | nd | nd | nd | nd | nd | nd |
| | Endrin | 111 ± 4.1 | — | — | nd | nd | nd | nd | nd | nd |
| | Endrin aldehyde | 6.3 ± 1.2 | — | — | nd | nd | nd | nd | nd | nd |
| | Endosulfan II | 7.9 ± 1.6 | — | — | nd | nd | nd | nd | 5.5 | nd |
| | *p,p′*-DDD | 26.4 ± 7.6 | 27.3 ± 0.8 (ref. 32) | 97 | 36.1 | 9.1 | 196 | 7.9 | 8.7 | 174 |
| | *p,p′*-DDT | 129 ± 5 | 111 ± 23 (ref. 32) | 117 | 71.8 | 20.7 | 1570 | 10.6 | 15.0 | 600 |
| | Endrin ketone | 2.8 ± 1.7 | — | — | nd | nd | nd | nd | nd | nd |
| | Methoxychlor | 361 ± 30.7 | — | — | nd | nd | nd | nd | nd | nd |
| PAHs | Ace | 52.1 ± 2.0 | — | — | 44.1 | 33.2 | 82.1 | 28.9 | 77.7 | 58.2 |
| | Acy | 83.5 ± 4.9 | — | — | 43.7 | 5.9 | 26.8 | 6.2 | 34.8 | 59.6 |
| | Flu | 245 ± 12.9 | — | — | 156 | 88.3 | 271 | 39.4 | 202 | 379 |
| | Phen | 1795 ± 8 | 1920 ± 20 (ref. 32) | 93 | 1110 | 1180 | 1690 | 670 | 1000 | 4930 |
| | Ant | 93.2 ± 4.1 | 96.0 ± 5.2 (ref. 32) | 97 | 47.6 | 41.1 | 90.7 | 42.2 | 54.7 | 265 |
| | Fluo | 3810 ± 6 | 4380 ± 100 (ref. 32) | 87 | 1030 | 967 | 1510 | 670 | 996 | 3940 |
| | Pyr | 2860 ± 9 | 3290 ± 30 (ref. 32) | 87 | 637 | 552 | 904 | 427 | 602 | 2720 |
| | BaA | 1150 ± 5 | 1160 ± 54 (ref. 32) | 99 | 112 | 193 | 358 | 178 | 197 | 731 |
| | Chry | 2360 ± 6 | 2260 ± 60 (ref. 32) | 104 | 1730 | 551 | 900 | 585 | 1090 | 7600 |
| | BbF | 2770 ± 8 | 2700 ± 90 (ref. 32) | 102 | 689 | 847 | 1110 | 741 | 1070 | 4310 |
| | BkF | 1290 ± 3 | 1330 ± 70 (ref. 26) | 97 | 195 | 181 | 210 | 161 | 156 | 575 |
| | BaP | 1330 ± 2 | 1140 ± 10 (ref. 32) | 117 | 116 | 368 | 429 | 282 | 220 | 418 |
| | IcdP | 2060 ± 6 | 2080 ± 100 (ref. 32) | 99 | 141 | 506 | 566 | 417 | 403 | 945 |
| | BghiP | 2160 ± 5 | 2280 ± 40 (ref. 32) | 95 | 224 | 458 | 478 | 399 | 417 | 983 |
| | DahA | 336 ± 9 | 301 ± 50 (ref. 32) | 112 | 36.0 | 97.1 | 127 | 86.1 | 91.8 | 256 |

[a] "—"-no values for this compound; nd means non-detectable.

 

$g^{-1}$ for PAHs and Musks and 5 to 100 ng $g^{-1}$ for OCPs, and the correlation coefficients for the studied compounds ranged from 0.997 to 1.000, indicating good linearity of the analytical curve. The calculated mLOD and mLOQ for each target compound are presented in Table 1. The LOQ ranged from 0.14 to 0.92 ng $g^{-1}$ for PAHs, 0.06 to 0.38 ng $g^{-1}$ for OCPs and 0.07 to 0.40 ng $g^{-1}$ for Musks, respectively. The LOQ for PAHs was one order of magnitude lower than those reported by Ruan *et al.* (1.57 to 6.58 ng $g^{-1}$).[17] The LOQ for some congeners of Musks, OCPs and PAHs were also lower than that reported by Mercier *et al.*[14] The low LOQ values obtained for PAHs, OCPs and Musks demonstrate the high sensitivity of the new GC-MS/MS method.

The final method was validated by performing spiking experiments based on pre-extracted matrix blank at three concentration levels ($Q_{low}$, $Q_{middle}$ and $Q_{high}$), with three replicates per level, full detail was given in ESI (Section 4†). For PAHs, Musks and OPEs, the low, middle, and high levels were 50, 500, and 2500 ng $g^{-1}$ respectively. For OCPs, they were 10, 100, and 500 ng $g^{-1}$. For HBCDs, the spiking levels were 5, 50, and 100 ng $g^{-1}$. For PBDEs, the spiking levels were 5, 20, and 100 ng $g^{-1}$. As shown in Fig. 4, all compounds exhibited good recoveries and reproducibility. Accuracy was generally acceptable and ranged between 81 and 120%. Recovery experiments showed that the mean recoveries and relative standard deviations (RSDs) for the different compound classes were 99–113% and 1–14% for PBDEs, 89–105% and 1–6% for HBCDs, 71–120% and 3–17% for PAHs, 71–112% and 2–17% for OCPs, 77–120% and 2–13% for Musks, and 80–127% and 1–14% for OPEs (see the ESI Table S1†). Good recoveries were achieved for all six compound groups at the middle and high levels, but the recoveries of some OCPs, Musks and OPEs were less stable at the low level than at the middle and high levels. Losses of BHC and musk xylene occurred mostly during evaporation may be attributed to their high volatility. The method's accuracy was poor for TCEP (>120%) at the low level (50 ng $g^{-1}$) probably due to interfering compounds that may have eluted from the Florisil cartridges. A typical chromatogram was added in ESI (Fig. S3†). Similar results for TCEP have been reported previously.[23]

To verify the method's performance and suitability for the analysis of residential dust, the standard reference material (SRM) 2585 ("Organic contaminants in house dust") was analyzed using the developed procedure. Six classes of compounds were quantified in three samples of 500 mg of SRM 2585; Table 2 compares the measured concentrations of each compound to their certified or indicative concentrations in SRM 2585. Overall, the measured concentrations agreed quite well with the certified values for PBDEs, PAHs, and OCPs, ranging from 87% (Fluo and Pyr) to 117% (*p*,*p*′-DDT and BaP) of the certified concentrations. However, the measured concentration of heptachlor was only 68% of the certified value, possibly due to losses caused by its volatility. The measured concentrations of HBCDs, Musks, and OPEs ranged from 81% (ADBI) to 118% (AHMI) of the indicative concentrations reported by Abdallah *et al.*,[36] Peck *et al.*[37] and Van den Eede *et al.*[38] Unfortunately, no certified or indicative values exist for eleven OCPs (α-, β-, γ-BHC, aldrin, endosulfan I, endosulfan II, endrin, endrin aldehyde, endosulfan sulfate, endrin ketone and methoxychlor), three PAHs (Ace, Acy and Flu). We also compared the measured concentrations to values previously reported in the literature for SRM 2585 (see the ESI Table S2†). Overall, while the measured concentrations diverged slightly from the literature values, they were generally close to the certified or indicative values for SRM 2585. In addition, the results of the spiking experiments showed that co-eluting matrix components from the dust samples did not affect the ionization of the target analyte during LC-ESI-MS/MS for HBCDs and OPEs, which is consistent with the results obtained in the analysis of the SRM.

### 3.4 Application of the method to non-reference samples

Recoveries of surrogate standards were satisfactory for each sample, with average recoveries of 101% for PBDEs, 98% for d-HBCDs, 96% for d-PAHs, 93% for OCPs, and 88% for d-OPEs (the corresponding RSDs were 11, 19, 17, 19 and 24%, respectively). Results for the 59 targeted compounds are presented in Table 2. Of these compounds, 15 were not detected above their mLOQ in any of the six dust samples: one PBDE (BDE-183), eleven OCPs (heptachlor, aldrin, heptachlor epoxide, γ-chlordane, α-chlordane, dieldrin, endrin, endrin aldehyde, endosulfan II, endrin ketone and methoxychlor) and three Musks (ADBI, AHMI and ATII). Two compounds were not detected above their mLOD in any of the six dust samples: endosulfan sulfate and DPMI. These results confirm the presence of the following hazardous environmental contaminants in Wuhan dust samples: (i) PBDEs (BDE-28, −47, −99, −100, −154, −153 and −209 at concentrations of several to several hundreds ng $g^{-1}$); (ii) HBCDs (several ng $g^{-1}$ of α, β, γ-HBCD); (iii) PAHs (several tens to several thousands ng $g^{-1}$ of Ace, Acy, Flu, Phen, Ant, Fluo, Pyr, BaA, Chry, BbF, BkF, BaP, DahA, BghiP and IcdP); (iv) OCPs (several ng $g^{-1}$ to several thousands ng $g^{-1}$ of α, β, γ, δ-BHC, endosulfan I, *p*,*p*′-DDE, endosulfan II, *p*,*p*′-DDD and *p*,*p*′-DDT); (v) Musks (several to several hundreds ng $g^{-1}$ of HHCB, musk xylene, AHTN and musk ketone); and (vi) OPEs (several tens to several thousands ng $g^{-1}$ of TBP, TCEP, TCPP, TPhP, TDCPP, TBEP and TCP). Moreover, BDE-209, three HBCDs, fifteen PAHs, three OCPs (*p*,*p*′-DDE, *p*,*p*′-DDD and *p*,*p*′-DDT), two Musks (HHCB and AHTN) and five OPEs (TBP, TCEP, TCPP, TPhP and TDCPP) were detected in all samples. The highest concentrations of Phen (4930 ng $g^{-1}$), Fluo (3940 ng $g^{-1}$), Chry (7600 ng $g^{-1}$), BbF (4310 ng $g^{-1}$), HHCB (149 ng $g^{-1}$) and musk ketone (815 ng $g^{-1}$) were observed in S6 (the old town in JiangAn). S5 (the new town in CaiDian) had the highest concentrations of BDE-209 (3210 ng $g^{-1}$) and TCEP (1510 ng $g^{-1}$). S3 was taken from CaiDian and had elevated levels of *p*,*p*′-DDT (1570 ng $g^{-1}$), TCPP (1020 ng $g^{-1}$) and TDCPP (799 ng $g^{-1}$). In conclusion, PAHs were the most concentrated contaminants in these samples, followed by OPEs, OCPs, and PBDEs. However, due to the limited dust sample size, more analysis is needed to clarify their distribution characteristics and possible sources.

## 4 Conclusions

A multi-class method for the simultaneous determination of OCPs, PAHs, PBDEs, HBCDs, Musks and OPEs in indoor dusts

was developed and validated. To enable simultaneous analysis of all six analyte classes, a comprehensive clean-up and fractionation procedure was needed. Therefore, samples were subjected to Soxhlet extraction with acetone/hexane, then the extracts were cleaned-up and fractionated on a Florisil SPE cartridge with optimized conditions. This one-step fractionation/clean-up process generates two fractions, one containing OCPs, PAHs, Musks, PBDEs, and HBCDs, and another containing OPEs. This both speeds up the analysis and reduces solvent consumption. A further purification step using silica-supported sulfuric acid also reduce matrix effects for the analysis of PBDEs and HBCD. Multiple mass spectrometric methods were used to determine the concentrations of the target compounds in the dust extracts, including GC-ECNI-MS for PBDEs and LC-ESI-MS/MS for HBCDs and OPEs. Notably, a newly-optimized method using gas chromatography electron impact ionization tandem mass spectrometry (GC-EI-MS/MS) was used to simultaneously determine PAHs, OCPs and Musks in indoor dust. The optimized MS/MS method enable simple, sensitive, and robust detection of multi-class of target organics in complex dust extracts. The low LOQ values achieved for PAHs (0.14–0.92 ng $g^{-1}$), OCPs (0.06–0.38 ng $g^{-1}$) and Musks (0.07–0.40 ng $g^{-1}$) demonstrate the high sensitivity of this method. The measurements of the concentrations of six classes of environmental contaminants in indoor dusts may clarify the risks posed by exposure to these chemicals, supporting future risk assessments and the development of improved regulations.

## Conflicts of interest

The authors declare that they have no conflicts of interest.

## Acknowledgements

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## References

1 E. Malliari and O. I. Kalantzi, *Environ. Int.*, 2017, **108**, 146–169.
2 C. D. Kassotis, K. Hoffman and H. M. Stapleton, *Environ. Sci. Technol.*, 2017, **51**, 8735–8745.
3 F. Mercier, P. Glorennec, O. Thomas and B. L. Bot, *Environ. Sci. Technol.*, 2011, **45**, 6716–6727.
4 L. Bramwell, S. V. Glinianaia, J. Rankin, M. Rose, A. Fernandes, S. Harrad and T. Pless-Mulolli, *Environ. Int.*, 2016, **92–93**, 680–694.
5 L. Lucattini, G. Poma, A. Covaci, J. de Boer, M. H. Lamoree and P. E. G. Leonards, *Chemosphere*, 2018, **201**, 466–482.
6 J. W. Roberts, L. A. Wallace, D. E. Camann, P. Dickey, S. G. Gilbert, R. G. Lewis and T. K. Takaro, *Rev. Environ. Contam. Toxicol.*, 2009, **201**, 1–39.
7 M. Fang, T. F. Webster and H. M. Stapleton, *Environ. Sci. Technol.*, 2015, **49**, 10057–10064.
8 G. Suzuki, N. M. Tue, G. Malarvannan, A. Sudaryanto, S. Takahashi, S. Tanabe, S. Sakai, A. Brouwer, N. Uramaru, S. Kitamura and H. Takigami, *Environ. Sci. Technol.*, 2013, **47**, 2898–2908.
9 N. Bonvallot, C. Mandin, F. Mercier, B. Le Bot and P. Glorennec, *Indoor Air*, 2010, **20**, 458–472.
10 S. M. Clifford, J. Zhang, T. Sigsgaard, J. Matti, P. J. Lioy, S. Robert and M. H. Karol, *Environ. Health Perspect.*, 2007, **115**, 958–964.
11 D. C. Hilton, R. S. Jones and A. Sjödin, *J. Chromatogr. A*, 2010, **1217**, 6851–6856.
12 K. Banerjee, S. Utture, S. Dasgupta, C. Kandaswamy, S. Pradhan, S. Kulkarni and P. Adsule, *J. Chromatogr. A*, 2012, **1270**, 283–295.
13 Y. Sapozhnikova and S. J. Lehotay, *Anal. Chim. Acta*, 2013, **758**, 80–92.
14 F. Mercier, E. Gilles, G. Saramito, P. Glorennec and B. Le Bot, *J. Chromatogr. A*, 2014, **1336**, 101–111.
15 W. Weathers, M. Colon, A. Hines and E. M. Ulrich, *J. Chromatogr. A*, 2014, **1356**, 266–271.
16 D. Lankova, A. Svarcova, K. Kalachova, O. Lacina, J. Pulkrabova and J. Hajslova, *Anal. Chim. Acta*, 2015, **854**, 61–69.
17 X. Ruan, Q. Lu and Z. Yang, *Anal. Methods*, 2016, **8**, 1690–1698.
18 C. Christia, B. Tang, S. S. Yin, X. J. Luo, B. X. Mai, G. Poma and A. Covaci, *Anal. Bioanal. Chem.*, 2019, **411**, 7015–7025.
19 B. B. Du, Y. Zhang, H. Chen, M. J. Shen, W. Zhou and L. X. Zeng, *J. Chromatogr. A*, 2019, **1603**, 199–207.
20 F. Mercier, E. Gilles, P. Soulard, C. Mandin, C. Dassonville and B. Le Bot, *J. Chromatogr. A*, 2020, **1615**, 460768.
21 F. Dubocq, A. Karrman, J. Gustavsson and T. Wang, *Environ. Pollut.*, 2021, **276**, 116701.
22 W. Butte and B. Heinzow, *Rev. Environ. Contam. Toxicol.*, 2002, **175**, 1–46.
23 N. Van den Eede, A. C. Dirtu, N. Ali, H. Neels and A. Covaci, *Talanta*, 2012, **89**, 292–300.
24 A. C. Ionas and A. Covaci, *Int. J. Environ. Anal. Chem.*, 2013, **93**(10), 1074–1083.
25 C. He, X. Wang, P. Thai, J. F. Mueller, C. Gallen, Y. Li and C. Baduel, *Talanta*, 2017, **164**, 503–510.
26 X. Zeng, Y. Wu, Z. Liu, S. Gao and Z. Yu, *Environ. Toxicol. Chem.*, 2018, **37**, 345–352.
27 W. Zhang, Y. Lu, S. Gao, X. Jia, Z. Yu, X. Zeng, G. Sheng and J. Fu, *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*, 2015, **50**, 1316–1323.
28 S. Gao, J. Wang, Z. Yu, Q. Guo, G. Sheng and J. Fu, *Environ. Sci. Technol.*, 2011, **45**, 2093–2099.
29 S. P. J. van Leeuwen and J. de Boer, *J. Chromatogr. A*, 2008, **1186**, 161–182.
30 N. Ali, S. Harrad, D. Muenhor, H. Neels and A. Covaci, *Anal. Bioanal. Chem.*, 2011, **400**, 3073–3083.

 

31 National Institute of Standards & Technology Certificate of Analysis, *Standard Reference Material 2585*, 2018.
32 S. Brommer, S. Harrad, N. Van den Eede and A. Covaci, *J. Environ. Monit.*, 2012, **14**, 2482–2487.
33 A. I. García-Valcárcel and J. L. Tadeo, *J. Sep. Sci.*, 2009, **32**, 3890–3897.
34 S. Walorczyk, *J. Chromatogr. A*, 2007, **1165**, 200–212.
35 A. Rashid, S. Nawaz, H. Barker, I. Ahmad and M. Ashraf, *J. Chromatogr. A*, 2010, **1217**, 2933–2939.
36 M. Abou-Elwafa Abdallah, E. Tilston, S. Harrad and C. Collins, *J. Environ. Monit.*, 2012, **14**, 3276–3283.
37 A. M. Peck, J. R. Kucklick and M. M. Schantz, *Anal. Bioanal. Chem.*, 2007, **387**, 2381–2388.
38 N. Van den Eede, A. C. Dirtu, H. Neels and A. Covaci, *Environ. Int.*, 2011, **37**, 454–461.