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Gas chromatography-electrostatic field Orbitrap high resolution mass spectrometry for screening 70 organic pollutants in infant cereal-based supplementary foods

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ABSTRACT

This study established a method using gas chromatography-electrostatic field Orbitrap high-resolution mass spectrometry (Orbitrap GC-MS) for the simultaneous determination of 70 organic pollutants across 4 categories: organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and phthalates (PAEs) in infant cereal-based supplementary foods. Techniques integrating cryogenic centrifugation and lipid and protein adsorbent (LPAS) purification were employed. The precise mass numbers of target compounds were determined by Orbitrap GC-MS in full-scan mode (Full MS), which effectively minimized matrix interferences in these foods. Method validation on rice flour samples demonstrated that the 70 compounds exhibited excellent linearity within their respective mass concentration ranges, with correlation coefficients all exceeding 0.995. The detection limits for this method ranged 0.10–1.00 μg/kg, while the quantification limits varied 0.3–3.0 μg/kg, meeting the established detection requirements. The average spike recovery of the 70 compounds at 3 spiked levels (5, 20, and 100 μg/kg) ranged 75.3%–119.3%, with relative standard deviations ranging 1.8%–10.8%. Both inter-day and intra-day precision demonstrated relative standard deviation values below 15%. This method was applied to analyze 100 samples of commercial infant cereal-based supplementary food, revealing the presence of PAEs and PAHs in 12.0% of the samples. Notably, no OCPs or PCBs were detected. The detected concentrations of benzo[a]pyrene (BaP) and dibutyl phthalate (DBP) were (4.2 ± 0.1) and (1.8 ± 0.3) μg/kg, respectively. This method is straightforward, highly sensitive, and suitable for the rapid screening and confirmation of 70 organic pollutants in infant cereal-based supplementary foods.

1. Introduction

Adequate nutrition during infancy and early childhood is essential for ensuring healthy growth and optimal development in children. Dietary exposure to potentially harmful substances represents a significant public health concern, particularly because infants and toddlers consume more food per kilogram of body weight than adults.

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Moreover, their metabolic and detoxification systems are not fully developed in the early years, rendering their diets more susceptible to higher concentrations of pollutants[1-2]. Consequently, regulations and standards for infant foods should be stringent to guarantee high safety levels. Despite these regulations, potential contaminants may still be present in these products. Supplementary feeding plays a critical role in transitioning from breastfeeding to a family diet. The World Health Organization (WHO), the European Food Safety Authority (EFSA), and the European Society for Pediatric Gastroenterology, Hepatology, and Nutrition (ESPGHAN) recommend introducing complementary foods after 6 months to prevent nutritional deficiencies[3]. In addition to breast milk and infant formula, infants and toddlers consume a significant portion of conventional and commercial baby foods. Infant cereal-based supplementary foods are an excellent choice for the first complementary food due to their mild flavor, high nutritional content, and accessibility. These foods are not only rich in essential micronutrients such as iron, zinc, and vitamin C[4], but also high in fiber, minimally allergenic, and easy to digest. Moreover, they can help prevent various diseases, including anemia, immune-related diseases, osteoporosis, and rickets. If properly selected, infant cereal-based supplementary foods can become a vital component of a balanced and healthy diet for infants and young children[5-6]. As an essential aspect of nutrient intake in the growth process of infants, monitoring multiple residues of pollutants is crucial for the health of this group and for market regulation. However, current studies predominantly focus on monitoring conventional pollutants, such as mycotoxins and heavy metals[7-11], with high-throughput residue analysis of organic pollutants in infant cereal-based supplementary foods remaining relatively unexplored. Therefore, determining the contamination status of these products is critical for more accurately assessing the dietary exposure of this vulnerable consumer group.

Organic pollutants accumulate in organisms through various mechanisms, and different types of these pollutants can exhibit antagonistic, synergistic, or additive effects. The intake of organic pollutants through infant cereal-based supplementary foods depends on the dosage and frequency of exposure, posing health risks even at low levels. Concurrently, global chemical usage is steadily increasing, with ongoing synthesis of new compounds[12-13]. Certain anthropogenic pollutants, such as pesticides, industrial by-products, pharmaceuticals, and personal care products, are released into the environment, posing potential health threats through dietary intake[14-18], particularly considering the vulnerability of infants, the most susceptible consumer group. Thus, the development of rapid, comprehensive, and precise trace residue screening technologies for organic pollutants has become a critical international research focus. QuEChERS (quick, easy, cheap, effective, rugged, and safe) provides significant advantages for sample pretreatment in analytical determinations, including reduced preparation times, minimal reagent use, and straightforward procedures. However, it is crucial to recognize that the adsorbents typically employed, such as octadecyl silica (C_{18}), primary secondary amine (PSA), and silica gel, may exhibit limited purification capabilities when processing complex samples with high protein and fat content. This limitation arises from their specific physicochemical properties which may not adequately address the challenges presented by such matrices. With the rapid advancement of nanotechnology, innovative adsorbent materials like lipid and protein adsorbent (LPAS) have been developed, offering a viable alternative. LPAS, a polystyrene-based core-shell composite nanomaterial, features an extensive surface area. This configuration not only enhances the mechanical strength and thermal stability of the composite but also improves its biocompatibility. Through targeted covalent modifications, the LPAS incorporates functional groups specifically designed to bind and efficiently remove contaminants such as lipids, phospholipids, and proteins. The robust chemical bonds and superior biocompatibility of LPAS facilitate the rapid capture and release of impurities. This capability effectively prevents the decomposition or structural compromise of target substances within the sample, thereby substantially increasing the efficiency of sample processing. Gas chromatography (GC) and liquid chromatography (LC) coupled with tandem mass spectrometry (MS/MS) are commonly utilized for determining organic pollutants and offer significant advantages in sensitivity and selectivity. However, these methods cannot provide extensive screening to explore a wide range of contaminants[19-21]. High-resolution mass spectrometry (HRMS), specifically the Orbitrap HRMS in full scan mode (Full MS), captures all target compound data, enabling the qualitative identification and quantitative analysis of various organic pollutants in complex matrices. The Orbitrap HRMS system not only matches the quantitative capabilities of gas chromatography-triple quadrupole mass spectrometry but also features high mass resolution, high sensitivity, and high selectivity, essential for both component analysis and quantitative analysis of organics in complex matrices[22-24]. Gas chromatography-electrostatic field Orbitrap high-resolution mass spectrometry (Orbitrap GC-MS) offers mass resolutions up to 120 000 at m/z 200 and mass accuracy below 1 ppm. This provides excellent qualitative and quantitative capabilities for organic pollutants, which facilitates the analysis of trace compounds and reduces sample pre-treatment requirements. Data files collected in Full MS can be used for retrospective data analysis. Currently, Orbitrap GC-MS technology has been applied in analyses of wastewater pollution[25], drug degradation pathways[26], agricultural product pesticide residues[27], and aroma characteristics of sunflower seed oils[28]. To date, there have been no reports on the high-throughput screening of 4 major classes of organic pollutants in infant cereal-based supplementary foods using freeze centrifugation-filtration membrane purification combined with Orbitrap GC-MS technology.

In this study, a two-step impurity removal process was employed: cryogenic centrifugation and LPAS purification. When combined with Orbitrap GC-MS, this methodology facilitated a high-throughput approach for both the qualitative identification and quantitative analysis of 70 health-risk organic pollutants, including organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and phthalates (PAEs), in infant cereal-based supplementary foods. This method streamlines sample pre-treatment, reduces analysis time, enhances extraction efficiency, and minimizes matrix effects (MEs). It is highly effective for non-target screening and precise quantification of organic contaminants in these foods, providing essential technical support for food safety risk assessments.

2. Materials and methods

2.1 Materials and reagents

Select infant cereal-based supplementary foods with high detection rates of organic pollutants. Samples of cereal-based

products (including 54 rice flour, 90 biscuits, and 56 noodles) used in the experiment, totaling 3 categories, were purchased from local supermarkets and online platforms in China. They were stored at room temperature in a sealed condition for later use.

Acetonitrile (HPLC grade, Merck, Germany); sodium chloride (chromatography grade, Kermel Chemical Reagents Co., Ltd., Tianjin, China); PSA (40–60 μm), C_{18} (40–60 μm), 44% acidic silica gel packing (75–250 μm, Anpel Scientific Instrument Co., Ltd., Shanghai, China); LPAS (20–40 μm, Beijing Kodnosi Technology Co., Ltd., Beijing, China).

The 21 PAHs standards (mixed standard solution of 1 000 μg/mL in dichloromethane): naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), 5-methylchrysene (5-Mchr), benzo[b]fluoranthene (BbFlu), benzo[k]fluoranthene (BkFlu), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), benzo[g,h,i]perylene (BghiP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBahA), dibenzo[a,e]pyrene (DBaeP), dibenzo[a,i]pyrene (DBaiP), dibenzo[a,h]pyrene (DBahP) were purchased from Dr. Ehrenstorfer (Augsburg, Germany).

The 17 PAEs standards (mixed standard solution of 1 000 μg/mL in *n*-hexane): dimethyl phthalate (DMP), diethyl phthalate (DEP), diallyl phthalate (DAP), diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), bis(2-methoxyethyl) phthalate (DMEP), bis(4-methyl-2-pentyl) phthalate (BMPP), bis(2-ethoxyethyl) phthalate (DEEP), dipentyl phthalate (DPP), dihexyl phthalate (DHXP), benzyl butyl phthalate (BBP), bis(2-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), bis(2-ethylhexyl) phthalate (DEHP), diphenyl phthalate (DPhP), dioctyl phthalate (DNOP), dinonyl phthalate (DNP) were purchased from Dr. Ehrenstorfer (Augsburg, Germany).

The 8 PCBs standards (mixed standard solution of 100 μg/mL in *n*-hexane): 2,4,4′-trichlorobiphenyl (PCB 28), 2,2,5,5-tetrachlorobiphenyl (PCB 52), 2,2,4,5,5-pentachlorobiphenyl (PCB 101), 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB 153), pentachlorobiphenyl (PCB 118), 2,2,3,4,4,5-hexachlorobiphenyl (PCB 138), 2,2,3,4,4,5,5-heptachlorobiphenyl (PCB 180), decachlorobiphenyl (PCB 209) were purchased from Tianjin Alta Technology Co., Ltd. (Tianjin, China).

The 24 OCPs standards (mixed standard solution of 100 μg/mL in *n*-hexane): *α*-chlordane, *γ*-chlordane, aldrin, dieldrin, endrin, *β*-endosulfan, quintozene, hexachlorobenzene, heptachlor, heptachlor epoxide, *α*-endosulfan, 4,4′-DDD, 4,4′-DDT, 2,4′-DDT, *γ*-HCH, *δ*-HCH, 4,4′-DDE, *α*-BHC, *β*-HCH, *cis*-Nonachlor, Mirex, 2,4′-DDD, 2,4′-DDE, *trans*-nonachlor were purchased from Tianjin Alta Technology Co., Ltd. (Tianjin, China).

2.2 Commercial infant cereal-based supplement samples

Infant cereal-based supplements, designed for infants aged 6 months and older (6–12 months) and toddlers (12–36 months), are primarily composed of one or more types of grains, such as wheat, rice, barley, oats, rye, and corn, with grains constituting over 25% of the dry matter. Additionally, these products include appropriate nutritional enhancers and/or other additives. Tailored for consumption starting from the age of 6 months, these processed foods are critical for early dietary needs. A total of 100 samples of infant cereal-based supplements were acquired from regional supermarkets and online platforms across China, encompassing various commercial brands and types. All samples were maintained in their original packaging and stored at room temperature before analysis.

2.3 Instruments and equipment

The instrumental setup includes a Thermo Scientific™ GC-Orbitrap mass spectrometer (equipped with a TRACE 1310 gas chromatograph and a TriPlus RSH™ autosampler, Thermo Fisher Scientific, USA); an MS104S electronic balance (accuracy of 0.1 mg, Mettler Toledo, Switzerland); a 3K15 high-speed refrigerated centrifuge (Sigma, Germany); a Milli-Q ultra-pure water system (Merck Millipore, Germany); a Reax Control vortex mixer (Heidolph, Germany); and a Hitachi S-3400N scanning electron microscope (SEM) (Hitachi, Japan). Additional equipment includes a DC-12 nitrogen blowdown concentrator (Shanghai Ampu, China); a refrigerator (Haier, Qingdao, China); and 0.22 μm microporous filter membranes (Tianjin Aijiren, Tianjin, China).

2.4 Chromatographic conditions

A TG-5 SilMS column (30 m × 0.25 mm × 0.25 μm, 5% phenyl-95% methylpolysiloxane, Thermo Fisher Scientific, USA) was used. The inlet temperature was set to 280 ℃. The temperature program began at 80 ℃, held for 2 min, then increased at a rate of 8 ℃/min to 260 ℃ and held for 5 min, followed by an increase at 8 ℃/min to 310 ℃, where it was held for 10 min. The carrier gas was helium (purity ≥ 99.999%) at a flow rate of 1.0 mL/min. The injection mode was splitless with an injection volume of 1 μL.

2.5 Mass spectrometry conditions

The ionization mode was electron ionization (EI) with electron energy set at 70 eV. The ion source temperature was 280 ℃, and the transfer line temperature was 300 ℃. Helium (purity ≥ 99.999%) served as the protective gas. The automatic gain control (AGC Target) setting was 1×10^6. The solvent delay was set to 5 min, and the acquisition mode was set to Full MS. The mass resolution was 60 000 FWHM at *m*/*z* 200. The scanning range was *m*/*z* 50 to 550. External mass calibration was performed prior to each sequence using perfluorotributylamine, with fragment ions at *m*/*z* 68.994 6, 99.993 0, 130.991 4, 196.983 0, 218.984 9, 263.986 4, 413.976 7, and 501.970 3 (Fig. 1). The mass error tolerance was ± 1×10^{-6} (± 0.2 mDa). Internal mass calibration used 3 background ions from column bleed as lock masses ($C_5H_{15}O_3Si_3^+$, *m*/*z* 207.032 36; $C_7H_{21}O_4Si_4^+$, *m*/*z* 281.051 15; $C_9H_{27}O_5Si_5^+$, *m*/*z* 355.069 94), with a search window set to ± 2×10^{-6} (± 1 mDa). If the exact masses of the specified background ions were not detected within ± 2×10^{-6} in a scan, internal lock mass correction was not applied. The instruments were controlled using Tune 2.8 and TraceFinder 5.1 (Thermo Scientific).

2.6 Preparation of standard solutions

Mixed standard solution: due to the immiscibility of *n*-hexane and acetonitrile, after blowing the mixture nearly dry with nitrogen, it is redissolved in acetonitrile. A specified volume of various pollutant mixed standard solutions is transferred into a 100 mL volumetric flask and diluted with acetonitrile to prepare a mixed reserve solution at a concentration of 10 μg/mL. This solution is stored in a brown

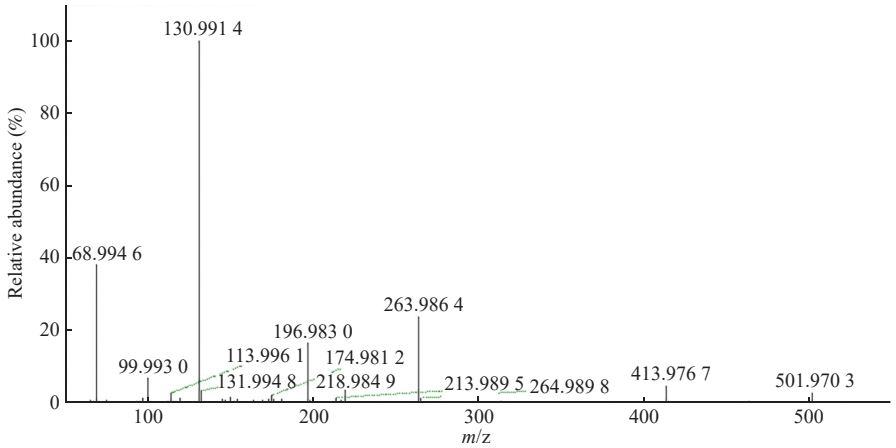

Fig. 1 Spectral mass calibration.

storage bottle at –20 ℃ and allowed to stand at room temperature for 30 min before use. The reserve solution is further diluted with acetonitrile to obtain mixed standard intermediate working solutions at concentrations of 1.0 and 0.1 μg/mL, respectively. These solutions are used for spike recovery experiments and to prepare a series of standard working solutions.

Blank matrix standard solution: an appropriate volume of the mixed standard solution is accurately measured and combined with the extract from the blank sample to prepare a series of standard solutions. These solutions are prepared and used immediately.

2.7 Sample pretreatment method

Accurately weigh 3 g homogeneously mixed sample (to a precision of 0.001 g) into a 40 mL glass tube. Add 7 mL water and vortex to mix (adjust the amount of water based on the moisture content of the sample), then allow it to stand for 20 min. Add 10 mL acetonitrile, shake vigorously for 1 min, then add 6 g of sodium chloride until the aqueous phase is saturated and vortex again for 1 min. Centrifuge at 9 000 r/min for 3 min. Transfer the supernatant to another 40 mL glass tube and freeze at –70 ℃ for 20 min. Transfer 6 mL supernatant to a 15 mL glass tube containing 200 mg LPAS, vortex for 1 min, then centrifuge at 9 000 r/min for 3 min. Accurately transfer 3 mL of the supernatant to a 15 mL glass tube, and evaporate to near dryness under nitrogen at 40 ℃. Reconstitute in 1 mL acetonitrile, filter through a 0.22 μm pore-size filter, and analyze by Orbitrap GC-MS. Perform identical steps for the reagent blank, omitting the sample addition.

2.8 Quality assurance

Before analysis, all materials used in the sample preparation process, including disposable glass pipettes and centrifuge tubes, are sequentially cleaned with acetone, *n*-hexane, and acetonitrile, all of chromatographic grade. Blank experiments are conducted according to the procedures outlined in Section 2.7, without adding any samples, to monitor potential contamination from laboratory materials and chemicals. PAEs, particularly DEHP, DBP, and DIBP, detected in the blanks have their mean absolute values subtracted from the concentrations found in the infant cereal-based supplementary samples. Consequently, samples are reported as positive for these compounds only if the PAE signals are at least twice as high as those detected in the procedural blanks. Acetonitrile is injected as a solvent blank before and after each batch of samples to confirm the absence of target analytes in these solvent blanks.

2.9 Data analysis

The software used for data processing was TraceFinder 5.1 (Thermo Scientific, Waltham, MA, USA). For target purposes, the database contained retention time, the target ion's accurate experimental mass, and 2 confirming ions' accurate experimental masses. European Commission SANTE guideline was also followed foridentification purposes: a positive was confirmed based on a target ion and 2 confirmingions from the EI spectra with mass accuracy $\leq 5 \times 10^{-6}$ and an retention time tolerance ≤ 0.1 min. The absolute difference in the ion ratio of the same compound should be kept within ± 20%.

3. Results and discussion

3.1 Construction of the compound database

Given that the mixed standard solution comprises multiple target compounds, numerous ion peaks with identical relative molecular masses but differing structures may be observed. These peaks are calibrated using *n*-alkanes for the retention index (RI) and differentiated using a deconvolution plug-in. The resultant mass spectra are compared against high-resolution mass spectrometry databases and the National Institute of Standards and Technology (NIST) library. By analyzing the fragment ions' *m*/*z* values and their molecular formulas, it is possible to identify the target compounds, determine their retention times, and characterize their primary fragment ions. In this study, 70 standard solutions of organic pollutants at a concentration of 200 ng/mL were subjected to Full MS scans, simultaneously collecting the retention times of *n*-alkanes (C_7 to C_{40}). Deconvolution technology was employed to generate mass spectra, selecting the most intense ions as quantitative ions and 2 to 5 fragment ions as characteristic fragment ions. The retention

time and fragment ion information were consolidated into a compound database file to create a high-resolution mass spectral database for these compounds. The data were imported into TraceFinder 5.1 software to establish a database of the precise mass numbers for the 70 organic pollutants, as shown in Table 1. This screening database includes each compound's name, CAS number, molecular formula, molecular weight, retention time, and precise relative molecular mass. The mixed standard data were analyzed and processed to facilitate accurate qualitative screening and quantitative analysis of the 70 compounds simultaneously.

Table 1
Formula, retention time and mass spectrometric of the 70 compounds.

Compound	CAS	Chemical formula	Molecular weigh	Retention time (min)	*m/z*		
					Quantitative ion	Qualitative ion 1	Qualitative ion 2
Nap	91-20-3	$C_{10}H_8$	128.17	7.46	128.062 05	129.065 41	102.046 40
DMP	131-11-3	$C_{10}H_{10}O_4$	194.18	11.91	163.038 97	133.028 41	135.044 06
Acy	208-96-8	$C_{12}H_8$	152.19	11.92	152.062 05	153.065 41	126.046 40
Ace	83-32-9	$C_{12}H_{10}$	154.21	12.47	154.077 70	152.062 05	153.069 88
Fl	86-73-7	$C_{13}H_{10}$	166.22	13.96	166.077 70	165.069 88	139.054 23
DEP	84-66-2	$C_{12}H_{14}O_4$	222.24	14.03	149.023 32	121.028 41	176.046 80
α-HCH	319-84-6	$C_6H_6Cl_6$	290.83	15.61	180.937 30	145.968 45	218.911 03
Hexachlorobenzene	118-74-1	C_6Cl_6	284.78	15.82	281.812 57	285.806 67	248.840 76
DAP	131-17-9	$C_{14}H_{14}O_4$	246.26	16.19	149.023 32	132.020 58	76.030 75
β-HCH	319-85-7	$C_6H_6Cl_6$	290.83	16.35	180.937 30	145.968 45	218.911 03
γ-HCH	58-89-9	$C_6H_6Cl_6$	290.83	16.49	180.937 30	145.968 45	218.911 03
Quintozene	82-68-8	$C_6NO_2Cl_5$	295.33	16.63	213.871 91	248.840 76	294.833 66
Phe	85-01-8	$C_{14}H_{10}$	178.22	16.74	178.077 70	152.062 05	179.081 06
Ant	120-12-7	$C_{14}H_{10}$	178.22	16.87	178.077 70	176.062 05	152.062 05
δ-HCH	319-86-8	$C_6H_6Cl_6$	290.83	17.13	180.937 30	145.968 45	218.911 03
DIBP	84-69-5	$C_{16}H_{22}O_4$	278.34	17.75	149.023 32	223.096 48	167.033 88
PCB 28	7012-37-5	$C_{12}H_7Cl_3$	257.54	18.03	255.960 78	186.023 08	257.957 83
Heptachlor	76-44-8	$C_{10}H_5Cl_7$	373.32	18.33	269.812 57	100.007 42	336.848 74
PCB 52	35693-99-3	$C_{12}H_6Cl_4$	291.99	18.81	289.921 81	291.918 86	219.984 11
DBP	84-74-2	$C_{16}H_{22}O_4$	278.34	18.93	149.023 32	150.026 67	121.028 41
Aldrin	309-00-2	$C_{12}H_8Cl_6$	364.91	19.19	260.859 36	290.929 63	326.906 31
DMEP	117-82-8	$C_{14}H_{18}O_6$	282.29	19.41	149.023 25	176.046 80	59.049 14
Heptachlor epoxide	1024-57-3	$C_{10}H_5Cl_7O$	389.32	20.17	352.843 66	350.846 61	236.840 76
Flu	206-44-0	$C_{16}H_{10}$	202.25	20.26	202.077 70	200.062 05	101.038 58
BMPP	146-50-9	$C_{20}H_{30}O_4$	334.45	20.31, 20.36	149.023 32	167.033 88	85.101 18
γ-Chlordane	5103-74-2	$C_{10}H_6Cl_8$	409.78	20.73	372.825 42	376.819 52	374.822 47
DEEP	605-54-9	$C_{16}H_{22}O_6$	310.35	20.76	149.023 32	193.049 54	104.025 67
2,4'-DDE	3424-82-6	$C_{14}Cl_4H_8$	354.49	20.86	245.999 76	317.934 51	247.996 81
Pyr	129-00-0	$C_{16}H_{10}$	202.25	20.89	202.077 70	200.062 05	203.081 06
PCB 101	37680-73-2	$C_{12}H_5Cl_5$	326.43	20.92	323.882 84	253.945 13	325.879 89
β-Endosulfan	33213-65-9	$C_9H_6O_3SCl_6$	406.93	21.03	236.840 76	169.968 46	159.984 11
α-Chlordane	5103-71-9	$C_{10}H_6Cl_8$	409.78	21.10	372.825 42	376.819 52	374.822 47
DPP	131-18-0	$C_{18}H_{26}O_4$	306.4	21.15	149.023 32	104.025 67	237.112 14
trans-Nonachlor	39765-80-5	$C_{10}Cl_9H_5$	444.22	21.21	408.783 50	236.840 76	404.789 40
4,4'-DDE	72-55-9	$C_{14}H_8Cl_4$	318.03	21.60	315.937 46	247.996 81	245.999 76
Dieldrin	60-57-1	$C_{12}H_8Cl_6O$	380.91	21.65	262.856 41	81.033 49	260.859 36
2,4'-DDD	53-19-0	$C_{14}Cl_4H_{10}$	354.49	21.80	235.007 58	165.069 88	237.004 63
Endrin	72-20-8	$C_{12}H_8Cl_6O$	380.91	22.16	242.952 95	280.926 68	316.903 36
α-Endosulfan	959-98-8	$C_9H_6O_3SCl_6$	406.93	22.37	236.840 76	169.968 46	159.984 11
PCB 118	31508-00-6	$C_{12}H_5Cl_5$	326.43	22.43	323.882 84	325.879 89	253.945 13
4,4'-DDD	72-54-8	$C_{14}H_{10}Cl_4$	320.04	22.58	235.007 58	199.030 90	165.069 87
2,4'-DDT	789-02-6	$C_{14}H_9Cl_5$	354.49	22.65	235.007 58	165.069 87	237.004 63

Table 1 (*Continued*)

Compound	CAS	Chemical formula	Molecular weigh	Retention time (min)	*m/z*		
					Quantitative ion	Qualitative ion 1	Qualitative ion 2
cis-Nonachlor	5103-73-1	$C_{10}Cl_9H_5$	444.22	22.68	408.783 50	236.840 76	404.789 40
PCB 138	35065-28-2	$C_{12}H_4Cl_6$	360.88	22.90	357.843 87	359.840 92	287.906 16
DHXP	84-75-3	$C_{20}H_{30}O_4$	334.45	23.22	149.023 32	251.127 78	233.117 22
BBP	85-68-7	$C_{19}H_{20}O_4$	312.36	23.33	206.093 75	123.044 06	105.033 49
4,4'-DDT	50-29-3	$C_{14}H_9Cl_5$	354.49	23.43	235.007 58	199.030 90	165.069 87
PCB 153	35065-27-1	$C_{12}H_4Cl_6$	360.88	23.54	357.843 87	287.906 16	359.840 92
BaA	56-55-3	$C_{18}H_{12}$	228.29	24.51	228.093 25	226.077 70	209.096 69
DBEP	117-83-9	$C_{20}H_{30}O_6$	366.45	24.56	149.023 32	193.049 54	85.064 79
Chr	218-01-9	$C_{18}H_{12}$	228.29	24.61	228.093 35	226.077 70	113.038 58
PCB 180	35065-29-3	$C_{12}H_3Cl_7$	395.32	25.08	391.804 90	393.801 94	323.864 24
DCHP	84-61-7	$C_{20}H_{26}O_4$	330.42	25.08	149.023 32	167.033 88	249.112 14
DEHP	117-81-7	$C_{24}H_{38}O_4$	390.56	25.29	149.023 32	167.033 88	279.159 08
DPhP	84-62-8	$C_{20}H_{14}O_4$	318.33	25.41	225.054 62	104.025 67	77.038 58
Mirex	2385-85-5	$C_{10}Cl_{12}$	545.54	25.80	271.809 62	269.812 57	166.903 06
5-Mchr	3697-24-3	$C_{19}H_{14}$	242.32	26.14	242.109 00	241.101 18	226.077 70
DNOP	117-84-0	$C_{24}H_{38}O_4$	390.56	27.71	149.023 32	279.159 08	261.148 52
BbFlu	205-99-2	$C_{20}H_{12}$	252.31	28.50	252.093 35	250.077 70	125.038 58
BkFlu	207-08-9	$C_{20}H_{12}$	252.31	28.61	252.093 35	250.077 70	126.046 40
BeP	192-97-2	$C_{20}H_{12}$	252.31	29.79	252.093 35	250.077 70	113.038 58
BaP	50-32-8	$C_{20}H_{12}$	252.31	30.02	252.093 35	250.077 70	126.046 40
PCB 209	2051-24-3	$C_{12}Cl_{10}$	498.66	30.51	493.687 98	495.685 03	427.744 37
DNP	84-76-4	$C_{26}H_{42}O_4$	418.61	31.13	149.023 32	293.174 74	167.033 88
BghiP	191-24-2	$C_{22}H_{12}$	276.33	34.34	276.093 35	274.077 70	138.046 40
IP	193-39-5	$C_{22}H_{12}$	276.33	34.48	278.108 95	276.093 35	274.077 70
DBahA	53-70-3	$C_{22}H_{14}$	278.35	35.06	276.093 35	274.077 70	138.046 40
DBaeP	192-65-4	$C_{24}H_{14}$	302.38	39.80	302.108 86	300.093 32	225.042 92
DBaiP	189-55-9	$C_{24}H_{14}$	302.38	40.33	302.108 86	300.093 32	281.051 21
DBahP	189-64-0	$C_{24}H_{14}$	302.38	40.58	302.108 86	300.093 32	253.016 78

3.2 Selection of extraction conditions

The pervasive presence of certain PAEs in the environment poses a major challenge in developing multi-residue methods for these contaminants. Specifically, several laboratory sources of PAEs, such as sample containers, organic solvents, and chemicals, affect the background levels in Orbitrap GC-MS analyses and could potentially contaminate the samples. Therefore, this study focuses on a simplified sample preparation method that requires fewer steps. The moisture content in grains typically ranges from 11% to 14%. In this method, 7 mL of water is added to the pre-weighed samples and allowed to stand for 20 min to activate the grains, fully moistening them and facilitating subsequent extraction with an organic solvent. Given that OCPs, PAHs, PAEs, and PCBs are lipophilic compounds, and infant cereal-based supplements contain fats, sugars, and pigments, these organic compounds are co-extracted, resulting in analytical interferences. Consequently, the extracts must be purified. The choice of extraction solvent and purification method significantly impacts extraction efficiency. The study compared the recovery of 70 compounds (added at 10 μg/kg) using dichloromethane, hexane, petroleum ether, and acetonitrile as solvents, as shown in Fig. 2. The results indicated that dichloromethane exhibited the poorest extraction performance, with 55 compounds having a recovery rate of less than 70%; lipid-soluble substances caused significant interferences in hexane and petroleum ether, with recoveries ranging from 51.5%–132.7% and 62.9%–138.4%, respectively; acetonitrile effectively precipitated proteins in infant cereal-based supplementary foods and exhibited low solubility for lipids and other impurities, thereby significantly reducing the contamination of sample impurities on the instrument. The recovery rates for all compounds were between 70% and 120%, meeting the detection requirements.

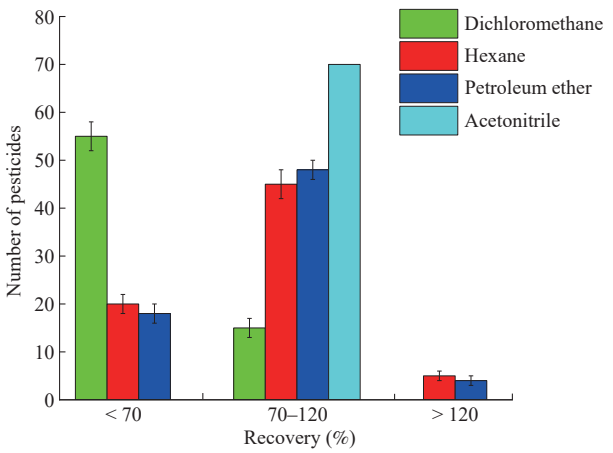

Fig. 2 Recovery results for different extraction solvent.

In contemporary methodologies, the pretreatment of organic pollutants in infant biscuit samples predominantly relies on solid-phase extraction (SPE) or gel permeation chromatography (GPC). These methods complicate the process, typically leading to significant sample loss and increased workload. Consequently, samples initially undergo cryogenic centrifugation at –70 ℃, followed by dispersive solid-phase extraction (d-SPE). Although cryogenic centrifugation succeeds in partially removing lipophilic and macromolecular substances, it falls short of achieving effective impurity removal, thus necessitating further purification. We examined the effects of C_{18}, PSA, 44% acidic silica gel adsorbents, and LPAS adsorbents, each added at a concentration of 50 μg/kg, on the recovery rates of target substances. Then, 200 mL of each adsorbent were incorporated into the extraction liquids for purification. The results revealed varied recovery rates for 70 organic pollutants: 54.5%–126.8% for C_{18}, 21.7%–97.5% for PSA, 59.3%–116.9% for acidic silica gel, and 67.1%–118.6% for LPAS. The respective relative standard deviations (RSD) were recorded at 3.1%–9.7%, 2.3%–7.7%, 4.2%–8.7%, and 2.5%–8.5%. The number of compounds with recovery rates between 70% and 120% were 54, 45, 62, and 68, respectively, indicating that the purification effects of 44% acidic silica gel and LPAS were significantly superior to those of C_{18} and PSA. PSA functions as a weak anion-exchange filler, utilized for the extraction of pigments, organic acids, and sugars *via* hydrogen bonding. C_{18} primarily targets the removal of certain lipids from the extraction liquid, albeit with limited purification capacity. Acidic silica gel, merging the characteristics of sulfonation and silica gel column chromatography, effectively removes lipids and pigments from the extracts through oxidation and hydrolysis with concentrated sulfuric acid. Modified with specific functional groups, LPAS demonstrates robust adsorption capabilities, effectively binding lipids, phospholipids, and proteins without reacting chemically with the target substances. SEM images (Fig. 3) before and after LPAS purification show numerous impurities adhering to the surface of LPAS post-adsorption. The SEM analysis was conducted using an electron beam accelerated at 15 kV, observing the sample across a 1 mm field at 157× magnification, complemented by a 300-micrometer reference scale for precise dimensional assessment. Fig. 4 displays the total ion current chromatograms of the samples post-cryogenic centrifugation, with and without LPAS purification, respectively. The TIC response of the LPAS-purified sample significantly surpasses that of the non-purified sample, evidenced by a notable reduction in interference peaks, thereby reducing the background values for instrumental analysis. Fig. 5 illustrates the presence of compounds at retention times of 18.83 and 20.89 min in the supernatant subjected solely to cryogenic centrifugation; these compounds, identified as pentadecanoic acid and *α*-linolenic acid, are both lipid substances. Their identification was confirmed through deconvolution analysis and a NIST search, coupled with retention indices. This provides further evidence of the efficacy of LPAS in removing additional lipid and similar interferences. Given the observed recovery rates, purification effects, and pretreatment efficiency, LPAS has been selected for further experimental purification.

3.3 Determination of mass spectrometric parameters

Orbitrap GC-MS high-resolution mass spectrometry differs from the qualitative and quantitative methods used in triple quadrupole systems. This technology leverages a full-scan mode to determine exact mass numbers, thereby simplifying the optimization of GC-MS parameters. This advancement reduces the necessary time for sample pretreatment and enables rapid screening coupled with precise quantitative analysis, thus markedly enhancing both efficiency and accuracy. When employing a resolution of R = 60 000 or greater during sample analysis, the system achieves a scan rate exceeding 7 spectra per second. This capability ensures that sufficient scan points are collected, and the mass error is maintained within 1 ppm, reinforcing data stability and reliability. Such high resolution substantially mitigates matrix interference, improving the accuracy of screening and facilitating the clear differentiation of target analytes from matrix constituents. According to the qualitative and quantitative analysis database presented in Table 1, it becomes feasible to rapidly screen and accurately quantify 70 organic pollutants, as depicted in the total ion chromatogram shown in Fig. 6. During searches utilizing the spectral library detailed in Table 1, critical factors influencing qualitative determination include discrepancies in exact mass numbers, retention times, isotope distribution patterns, and isotope abundance ratios. According to EU guidelines SANTE/11312/2021[29], high-resolution mass spectrometry confirmation necessitates the presence of at least one ion with an exact mass number and a corresponding fragment ion. Table 1 enumerates the precise masses of 3 fragment ions for the 70 pollutants, calculated to 5 decimal places. One ion is designated as the quantitative ion, while the other 2 serve as qualitative ions, ensuring effective and accurate discrimination against interfering substances. This database also incorporates isotopic details, such as chlorine isotopes ^{35}Cl and ^{37}Cl with an approximate abundance ratio

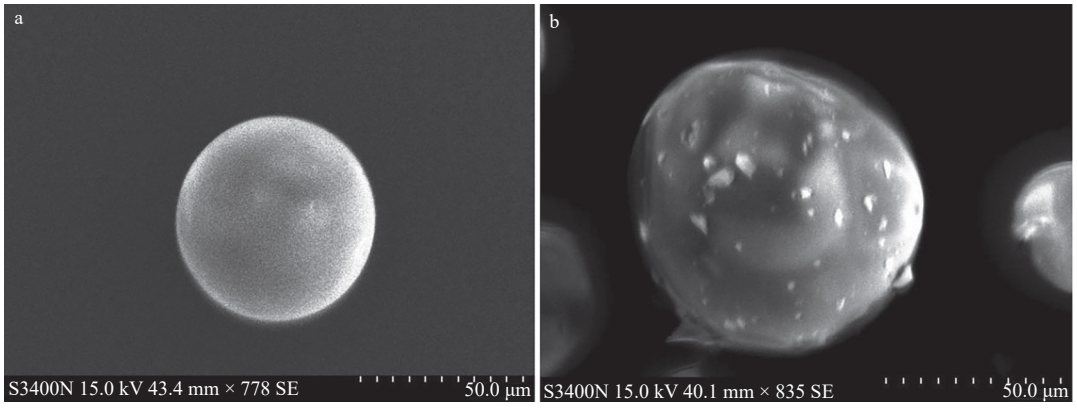

Fig. 3 SEM images of LPAS (a) before and (b) after adsorption.

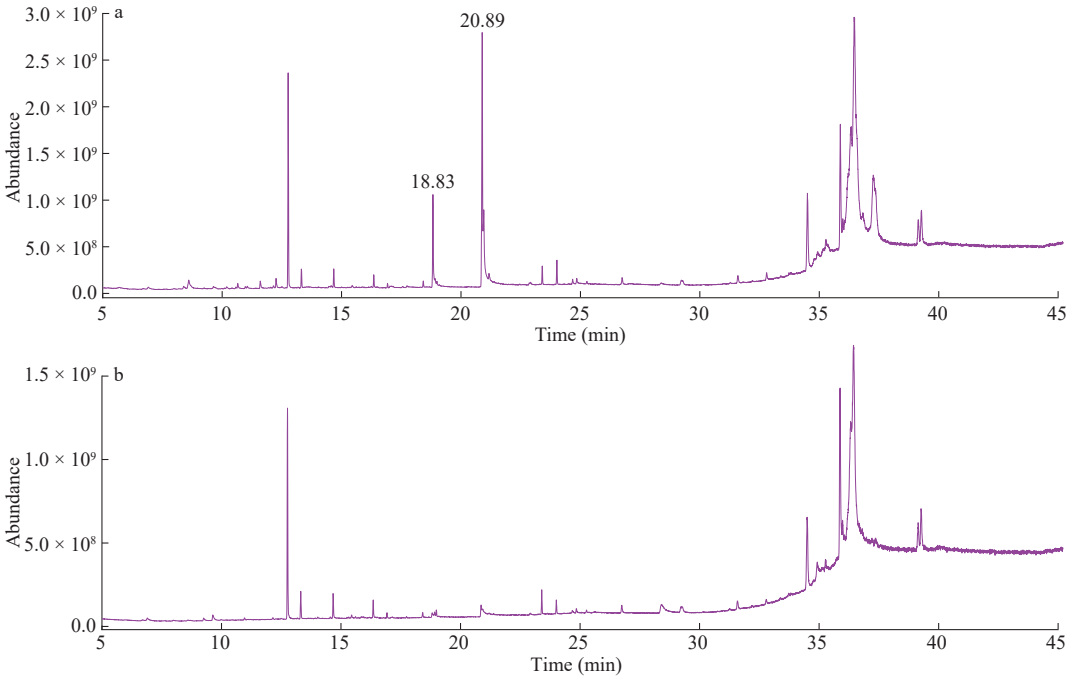

Fig. 4 Total ion chromatogram of the infant and toddler biscuit sample (a) without and (b) with LPAS purification.

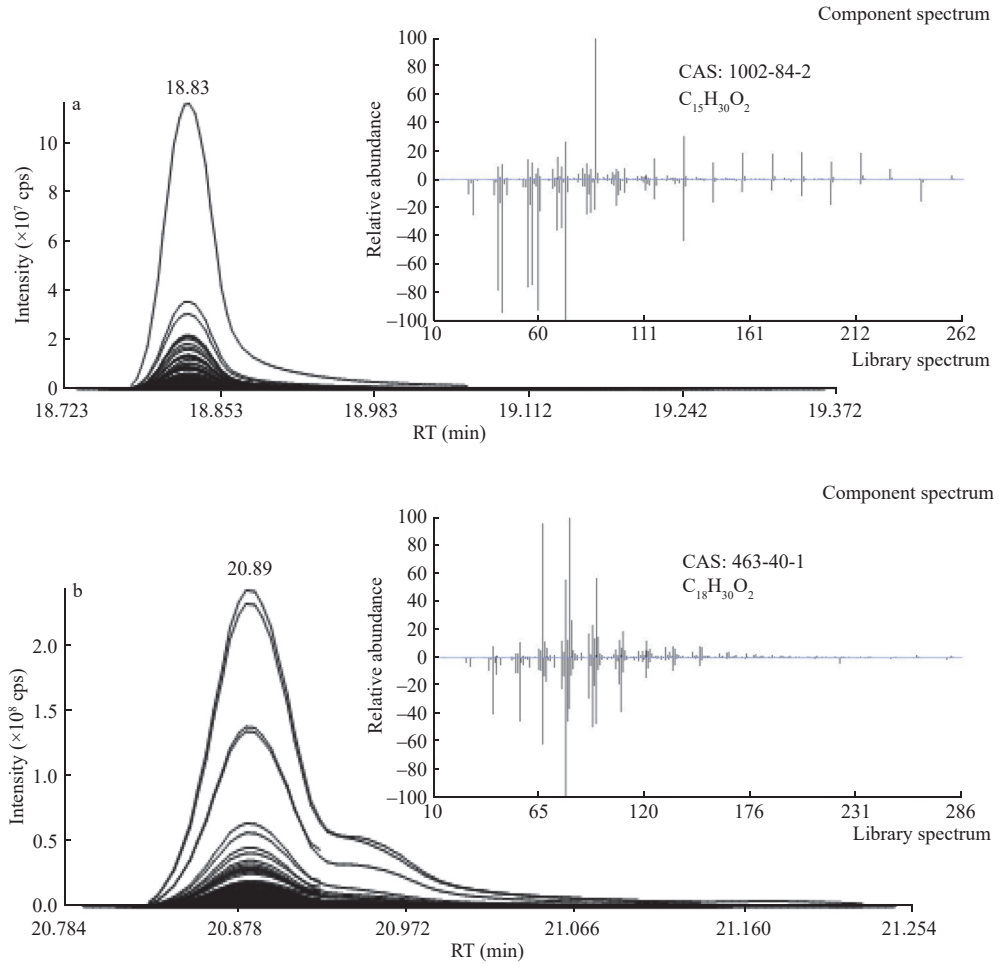

Fig. 5 Ion overlay and mass spectrogram of (a) *n*-pentadecanoic acid and (b) *α*-linolenic acid.

of 3:1 and an atomic weight difference of 1.997 05 Da, further enabling qualitative analysis[30]. For qualitative confirmation of target compounds in samples, the criteria are as follows: 1) the measured value of the exact mass number (*m*/*z*) for both quantitative and qualitative ions must fall within a maximum error margin of ≤ 5×10^{-6}; 2) the retention time window deviation for quantitative ions should not exceed ± 0.025 min, and the retention time deviation for qualitative ions relative to quantitative ions should be within ± 0.1 min; 3) the absolute difference in the peak area ratio of qualitative to quantitative ions for the same compound must remain within ± 20%. TraceFinder 5.1 software significantly streamlines the process of qualitative confirmation and quantitative measurement of target compounds.

3.4 Retrospective analysis

Non-target HRMS full-scan data facilitates the rapid and cost-effective screening of newly identified contaminants from previously collected HRMS datasets, or compounds not initially considered during the analysis, a process known as retrospective analysis. Orbitrap GC-MS, with its superior resolution and mass accuracy, provides robust technical support for the precise detection of trace substances within complex sample matrices. While triple quadrupole mass spectrometry is also utilized for targeted screening, its main limitation lies in the finite number of selective reaction monitoring (SRM) channels, which typically max out at several hundred. Moreover, once data collection concludes, the scope of screening targets is fixed, precluding the inclusion of additional compounds at a later stage. Orbitrap GC-MS, however, captures data across the entire mass range without the constraints of SRM channel numbers and does not necessitate pre-defining the fragmentation ions of the compounds under investigation. This feature renders it exceptionally suited for multi-residue analysis of pollutants. In Full MS mode, theoretically, there is no upper limit to the number of compounds that can be screened, and data collection remains independent of the number of compounds in the database. During the screening process, simply updating the target list suffices to screen for new targets within the existing data. Thus, after data collection, the information can be retrospectively analyzed and reanalyzed to broaden the scope of targets. For instance, when analyzing samples, additional information such as retention time, molecular formula, exact mass number of fragment ions, and ion ratios of emerging compounds like dibenzo[a,l]pyrene (DBalP) can be integrated into a database of 70 substances for reanalysis. This methodology not only expands the analysis of target compounds without the need to recollect real-time data but also enhances flexibility, facilitates retrospective and suspect screening of organic pollutants, and probes the emergence of new contaminants. This approach holds significant promise for advancing risk-monitoring technologies in infant cereal-based supplementary foods.

3.5 ME

MEs are evaluated using the formula: ME (%) = (B–A)/A × 100, where A represents the signal peak area of the pesticide target in pure solvent, and B represents the signal peak area of the same concentration of the target added to the sample matrix. An ME of 0% indicates no matrix effect, values above 0% suggest signal enhancement, and values below 0% indicate signal suppression[31]. Matrix effects are classified based on their intensity: a high matrix effect is characterized by ME values less than –50% or greater than 50%; a medium matrix effect by ME values between –50% and –20% or between 20% and 50%; and a low matrix effect by ME values between –20% and 20%[32]. In this experiment, matrix effects were assessed across 3 typical matrices: rice flour, biscuits, and noodles. It was observed that 92.9% of the compounds exhibited low ME (–20.0% < ME < 20.0%), and 7.1% exhibited medium ME (–50.0% < ME < –20.0% or 20.0% < ME < 50.0%), specifically DEHP, DBaeP, DBaiP, DBahP, and PCB 209; no compounds displayed high ME (ME < –50.0% or ME > 50.0%). Moreover, the

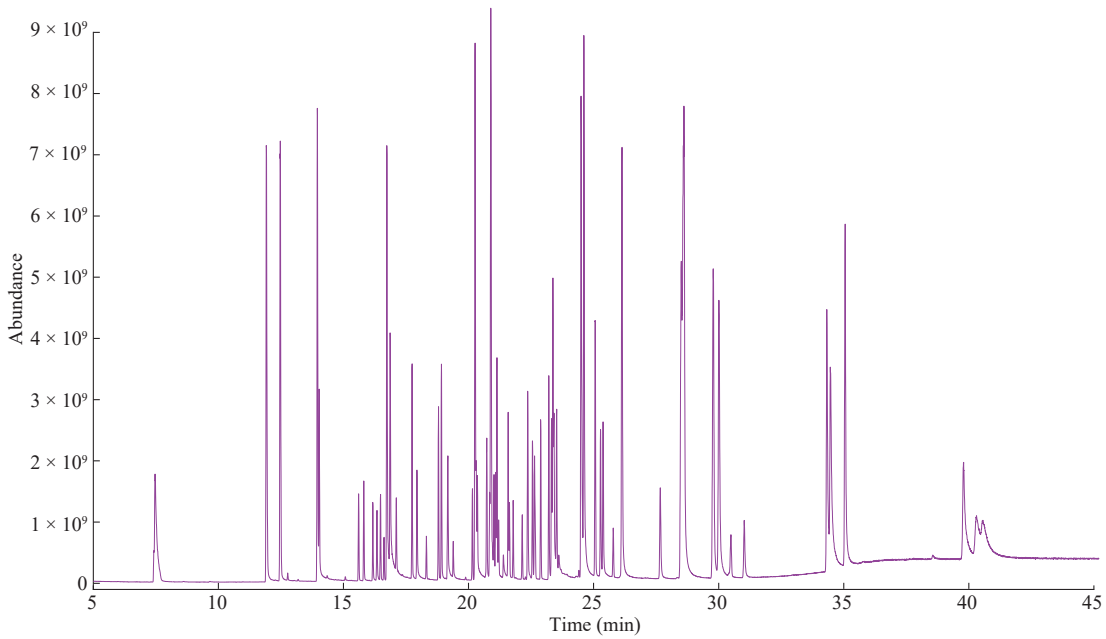

Fig. 6 Total ion chromatogram of 70 organic pollutants in standard solution (200 ng/mL) according to the established qualitative and quantitative database.

magnitude of ME across 70 compounds was found to vary with matrix complexity: biscuits > rice flour > noodles. This variation is likely because the more components present in the sample, the more pronounced the ME may be. Multiple components in a complex matrix can compete with the target analyte and affect the detection process. Biscuits, which contain vegetable oil, milk powder, syrup, and other substances, present a more complex matrix than rice flour and noodles, leading to greater interference with organic compounds. It was demonstrated that the sample preparation method used in this experiment is characterized by high efficiency in removing matrix co-extractives. Compared to traditional purification techniques, the freeze centrifugation-filtration membrane purification technique used here is characterized by a lower ME. The magnitude of ME is also influenced by factors including the nature of the matrix, the ratio of analyte to matrix, and the systemic conditions of the Orbitrap GC-MS, as well as the physicochemical properties of the compounds themselves. Given the significant impact of ME on the accuracy, detectability, and reproducibility of the analytical method, which in turn affects quantitative analysis, a matrix-matched calibration curve was employed to compensate for the matrix effect in this experiment.

3.6 Method validation

The sensitivity, linearity, accuracy, and precision of this method were evaluated and are detailed in Table 2. Qualitative and quantitative analyses of 70 organic pollutants were conducted using Orbitrap GC-MS. A mixed standard storage solution was progressively diluted with acetonitrile to prepare a series of working standard solutions. Chromatographic peak areas (Y) were plotted as the ordinate against the mass concentration (X) of the control solution on the abscissa. Standard solutions were added to a blank matrix to determine the limit of detection (LOD) and quantification (LOQ), which were established when the analyte response was approximately 3 times and 10 times the noise level, respectively. The results demonstrated a strong linear relationship for the 70 compounds ($R^2 > 0.995$), with LOD ranging from 0.1 to 1.0 μg/kg and LOQ from 0.3 to 3.0 μg/kg, meeting the requirements for detection. A recovery study was conducted to examine the accuracy of this method, utilizing 3 spiking concentrations (5, 20, and 100 μg/kg) in rice flour. Each spiking level was replicated 6 times, and the average recovery and relative standard deviation (RSD) were calculated. The results indicated that except for DBaeP, DBaiP, and DBahP, where the average recovery rates ranged from 75.1% to 79.6%, slightly below the desired level, other compounds had recovery rates ranging from 80.1% to 119.3%, with RSD values between 1.8% and 10.8%. The precision of this method was determined by assessing the intra-day and inter-day repeatability at the spiked concentration of 20 μg/kg, expressed as RSDs, with values lower than 11.2%. Generally, the inter-day precision exceeded the intra-day precision. Upon completion of all validation steps, the accuracy and precision of the proposed method were confirmed to be excellent, suggesting that this method is well-suited for analyzing trace residues of organic pollutants in infant cereal-based supplementary foods.

Table 2
Method validation results of the 70 compounds in rice flour.

Compound	LOD (μg/kg)	LOQ (μg/kg)	Linear range (ng/mL)	R^2	Recoveries (RSDs (%))			Intra-day RSD (%) (n = 6)	Inter-day RSD (%) (n = 6)
					5 μg/kg	20.0 μg/kg	100 μg/kg		
Nap	0.5	1.5	5–100	0.999 8	85.3 (9.1)	88.5 (10.8)	102.4 (9.6)	1.1	5.5
DMP	0.1	0.3	1–100	0.999 3	86.6 (7.1)	94.2 (4.5)	96.5 (7.4)	1.3	2.9
Acy	0.1	0.3	1–100	0.999 6	90.2 (8.2)	95.6 (9.7)	98.4 (7.2)	0.6	2.3
Ace	0.1	0.3	1–100	0.999 1	89.4 (6.1)	87.4 (8.2)	88.4 (9.1)	2.7	6.8
Fl	0.5	1.5	5–100	0.999 5	91.8 (7.2)	92.7 (4.8)	94.2 (9.5)	1.4	3.1
DEP	0.5	1.5	5–100	0.997 7	95.2 (6.1)	85.1 (9.7)	92.8 (9.2)	3.2	6.3
α-HCH	0.1	0.3	1–100	0.999 5	92.2 (7.2)	94.4 (6.3)	90.4 (9.5)	2.1	3.2
Hexachlorobenzene	0.1	0.3	1–100	0.998 0	93.3 (9.2)	88.5 (8.1)	101.3 (4.2)	1.9	4.0
DAP	0.1	0.3	1–100	0.999 5	97.1 (8.2)	97.1 (4.4)	92.3 (8.7)	0.8	1.7
β-HCH	0.1	0.3	1–100	0.999 3	94.2 (7.1)	93.5 (5.3)	93.5 (8.9)	1.4	4.6
γ-HCH	0.1	0.3	1–100	0.997 3	91.2 (6.2)	102.4 (9.4)	97.2 (7.7)	5.5	5.0
Quintozene	0.1	0.3	1–100	0.998 2	101.1 (7.1)	96.5 (7.1)	108.4 (6.5)	2.6	4.1
Phe	0.1	0.3	1–100	0.998 3	107.3 (1.2)	98.4 (7.2)	103.4 (8.2)	0.7	2.8
Ant	0.3	1.0	3–100	0.999 1	103.1 (7.1)	103.4 (9.1)	80.1 (2.4)	2.2	3.1
δ-HCH	0.3	1.0	3–100	0.996 1	86.1 (7.1)	97.2 (9.4)	88.3 (9.5)	0.9	3.6
DIBP	0.3	1.0	3–100	0.999 2	86.2 (5.2)	102.8 (9.2)	93.5 (5.2)	1.5	5.2
PCB 28	0.3	1.0	3–100	0.998 4	85.9 (5.1)	90.4 (9.5)	105.2 (4.4)	1.6	3.1
Heptachlor	0.3	1.0	3–100	0.999 1	89.2 (9.1)	80.3 (4.3)	95.6 (4.5)	1.1	2.3
PCB 52	0.5	1.5	5–100	0.999 0	93.2 (1.8)	92.3 (8.5)	91.2 (9.5)	4.8	4.7
DBP	0.5	1.5	5–100	0.995 1	89.3 (8.2)	93.5 (8.6)	90.4 (4.2)	9.3	10.7
Aldrin	0.5	1.5	5–100	0.995 2	92.2 (6.1)	97.2 (7.4)	94.2 (4.5)	0.8	2.6
DMEP	0.5	1.5	5–100	0.996 1	92.8 (7.2)	108.4 (6.3)	105.6 (9.7)	0.6	2.1

Table 2 (*Continuted*)

Compound	LOD (μg/kg)	LOQ (μg/kg)	Linear range (ng/mL)	R^2	Recoveries (RSDs (%))			Intra-day RSD (%) (n = 6)	Inter-day RSD (%) (n = 6)
					5 μg/kg	20.0 μg/kg	100 μg/kg		
Heptachlor epoxide	0.5	1.5	5–100	0.999 8	105.1 (5.1)	87.8 (6.4)	94.5 (2.4)	1.1	2.9
Flu	0.1	0.3	1–100	0.999 3	92.2 (6.6)	93.1 (6.7)	101.5 (5.6)	0.5	4.5
BMPP	0.1	0.3	1–100	0.999 6	87.2 (7.2)	99.1 (8.3)	81.5 (7.7)	1.2	3.6
γ-Chlordane	0.1	0.3	1–100	0.999 1	95.4 (5.1)	87.6 (5.1)	95.2 (3.9)	1.5	6.5
DEEP	0.3	1.0	3–100	0.999 5	103.1 (6.1)	101.5 (4.6)	91.7 (5.3)	1.1	3.2
2,4'-DDE	0.3	1.0	3–100	0.997 7	82.4 (4.2)	93.4 (4.1)	101.4 (4.3)	2.6	7.0
Pyr	0.1	0.3	1–100	0.999 5	89.5 (9.4)	80.5 (7.7)	82.55 (6.1)	1.4	2.7
PCB 101	0.1	0.3	1–100	0.998 0	102.1 (9.3)	95.5 (6.1)	81.0 (7.3)	1.0	1.1
β-Endosulfan	1.0	3.0	10–100	0.999 5	95.1 (6.3)	98.4 (7.5)	107.2 (5.8)	1.1	1.3
α-Chlordane	1.0	3.0	10–100	0.999 3	91.4 (4.5)	92.3 (6.3)	97.2 (6.2)	0.9	2.0
DPP	0.1	0.3	1–100	0.997 3	106.6 (8.3)	104.1 (7.6)	96.5 (7.8)	1.0	2.5
trans-Nonachlor	0.1	0.3	1–100	0.998 2	94.1 (8.3)	95.3 (6.5)	80.2 (9.1)	4.9	8.0
4,4'-DDE	0.1	0.3	1–100	0.998 3	108.6 (5.7)	102.2 (5.1)	95.4 (5.2)	1.9	4.9
Dieldrin	0.3	1.0	3–100	0.999 1	80.2 (11.1)	103.1 (7.3)	96.4 (5.5)	2.5	3.0
2,4'-DDD	0.3	1.0	3–100	0.996 1	83.4 (9.1)	81.4 (9.3)	106.3 (9.1)	0.7	4.0
Endrin	0.3	1.0	3–100	0.999 2	82.8 (8.6)	105.4 (9.1)	96.2 (8.3)	0.6	3.8
α-Endosulfan	0.3	1.0	3–100	0.998 4	84.1 (7.2)	94.3 (4.4)	107.5 (6.6)	0.8	2.6
PCB 118	0.3	1.0	3–100	0.999 1	93.7 (9.2)	118.1 (8.4)	117.2 (7.1)	3.1	7.5
4,4'-DDD	0.5	1.5	5–100	0.999 0	111.6 (7.7)	103.8 (8.9)	92.1 (9.2)	0.7	2.6
2,4'-DDT	0.5	1.5	5–100	0.995 1	97.2 (9.1)	94.2 (9.3)	107.4 (8.5)	1.2	3.1
cis-Nonachlor	0.5	1.5	5–100	0.995 2	101.3 (5.3)	84.4 (9.5)	106.6 (7.7)	1.4	1.6
PCB 138	0.5	1.5	5–100	0.996 1	85.5 (4.6)	90.7 (8.8)	96.9 (7.2)	6.4	11.2
DHXP	0.5	1.5	5–100	0.999 8	97.5 (9.2)	103.4 (8.5)	98.6 (7.7)	0.9	1.2
BBP	0.1	0.3	1–100	0.999 3	81.6 (9.5)	92.3 (6.1)	94.5 (5.2)	1.3	2.2
4,4'-DDT	0.1	0.3	1–100	0.999 6	90.4 (4.3)	97.2 (5.3)	100.2 (6.3)	2.3	2.2
PCB 153	0.1	0.3	1–100	0.999 1	94.5 (6.6)	83.7 (8.8)	107.9 (8.1)	0.9	4.5
BaA	0.3	1.0	3–100	0.999 5	84.5 (8.4)	95.3 (8.2)	104.5 (7.1)	0.9	3.8
DBEP	0.3	1.0	3–100	0.997 7	87.5 (4.6)	104.7 (5.8)	96.9 (8.0)	0.7	3.8
Chr	0.1	0.3	1–100	0.999 5	83.5 (4.2)	103.3 (7.3)	93.1 (7.3)	1.2	3.0
PCB 180	0.1	0.3	1–100	0.998 0	102.3 (9.6)	94.4 (7.2)	103.1 (4.2)	2.2	2.5
DCHP	0.1	0.3	1–100	0.999 5	96.4 (7.1)	92.5 (8.3)	105.5 (7.2)	0.8	4.4
DEHP	0.1	0.3	1–100	0.999 3	98.2 (7.3)	95.8 (6.6)	113.4 (7.2)	2.2	4.5
DPhP	0.1	0.3	1–100	0.997 3	80.5 (7.2)	104.1 (4.4)	97.3 (9.1)	1.1	3.6
Mirex	0.1	0.3	1–100	0.998 2	97.5 (9.2)	92.5 (8.4)	101.3 (4.4)	2.0	4.4
5-Mchr	0.5	1.5	5–100	0.9983	82.4 (8.1)	103.3 (8.5)	88.2 (4.5)	2.3	4.0
DNOP	0.3	1.0	3–100	0.999 1	104.2 (7.3)	96.3 (7.1)	94.2 (8.2)	1.3	3.7
BbFlu	0.3	1.0	3–100	0.996 1	114.1 (6.4)	113.5 (9.1)	80.2 (7.4)	0.2	2.3
BkFlu	0.3	1.0	3–100	0.999 2	92.9 (9.2)	113.1 (8.2)	99.3 (6.4)	3.9	4.5
BeP	0.3	1.0	3–100	0.998 4	102.3 (4.2)	119.3 (9.2)	92.1 (9.1)	2.0	4.9
BaP	0.3	1.0	3–100	0.999 1	87.8 (4.4)	97.9 (6.3)	88.6 (8.2)	1.1	2.9
PCB 209	0.5	1.5	5–100	0.999 0	95.4 (6.7)	108.5 (9.6)	102.4 (8.2)	1.8	4.4
DNP	0.5	1.5	5–100	0.995 1	89.6 (7.5)	111.4 (6.3)	100.5 (5.2)	1.0	7.8
BghiP	0.5	1.5	5–100	0.995 2	95.4 (6.2)	110.3 (4.6)	80.4 (9.8)	1.3	1.8
IP	0.5	1.5	5–100	0.996 1	92.7 (7.8)	113.1 (6.3)	99.3 (9.1)	1.1	5.0
DBahA	1.0	3.0	10–100	0.999 0	81.6 (6.7)	82.5 (8.2)	84.5 (6.4)	3.9	3.8
DBaeP	1.0	3.0	10–100	0.995 1	75.1 (2.9)	78.5 (8.2)	76.4 (7.5)	1.6	6.1
DBaiP	1.0	3.0	10–100	0.995 2	78.3 (8.1)	75.4 (5.2)	77.3 (6.2)	0.5	3.5
DBahP	1.0	3.0	10–100	0.996 1	78.4 (7.1)	79.6 (6.6)	75.3 (9.1)	6.7	7.8

3.7 Analysis of actual samples

This study involved the analysis of 100 samples from 3 categories of infant cereal-based supplementary foods collected from the Chinese market, including rice flour (40 samples), biscuits (35 samples), and noodles (25 samples). Orbitrap GC-MS was employed for the simultaneous multi-objective analysis of 70 organic pollutants in these foods. The results revealed that PAEs and PAHs were detected in 9.0% of the samples, while OCPs and PCBs were not found in any of the samples, confirming the feasibility of the proposed analytical method. In particular, five biscuit samples contained BaP and BaA at concentrations ranging 2.5–4.9 and 15.2–45.7 μg/kg, respectively, significantly exceeding the European Commission's maximum limit of 1.0 μg/kg for PAHs in infant cereal-based supplementary foods[33]. Notably, these positive samples included vegetable oils such as rice bran oil, sunflower oil, coconut oil, and butter, which are known dietary sources of PAHs. Separate detections of DBP ((4.7 ± 1.2) μg/kg), DEHP ((36.5 ± 0.6) μg/kg), DMP ((1.5 ± 0.3) μg/kg), and DIBP ((21.7 ± 0.3) μg/kg) were observed in 4 different infant cereal-based supplementary products. Additionally, DEHP and DBP were concurrently detected in another sample at concentrations of (35.2 ± 0.2) and (12.8 ± 0.4) μg/kg, respectively. The co-presence of BaP ((4.2 ± 0.1) μg/kg) and DBP ((1.8 ± 0.3) μg/kg) was identified in the same sample of infant cereal-based supplementary food. Fig. 7 displays the total ion chromatogram of the biscuit samples testing positive, while Fig. 8 presents the ion overlays and mass spectra of DBP and BaP in the standards (Figs. 8a and c) and the biscuit samples testing positive (Figs. 8b and d). The established method in this experiment is capable of screening trace organic pollutants with rapid analysis speeds and precise qualitative and quantitative accuracy, fully meeting the requirements for actual sample screening.

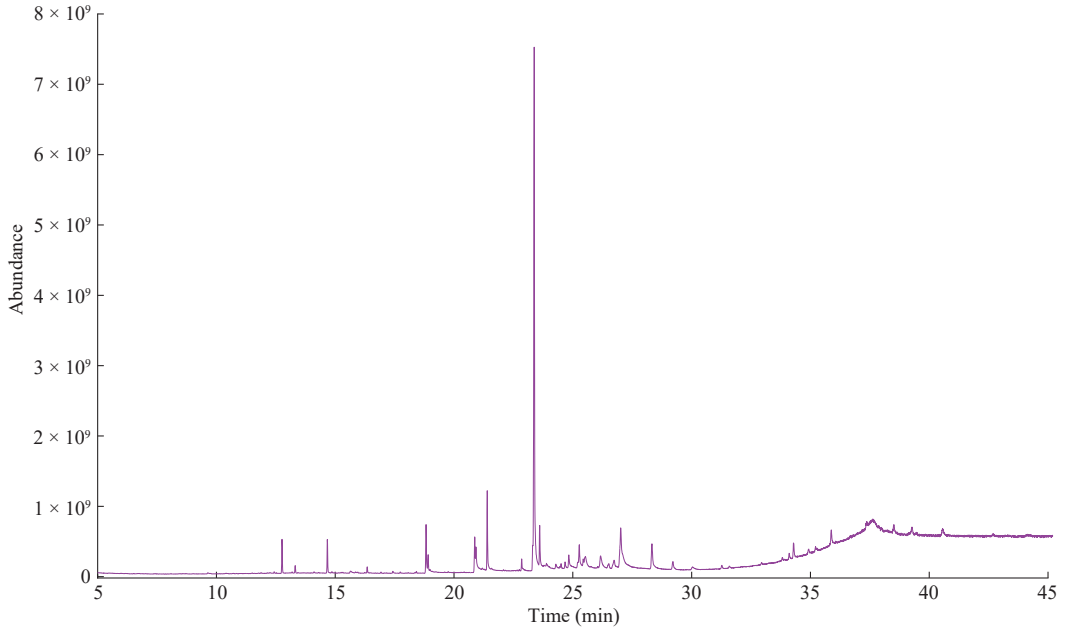

Fig. 7 Total ion chromatogram of infant and toddler biscuit samples detecting both DEHP and DBP simultaneously.

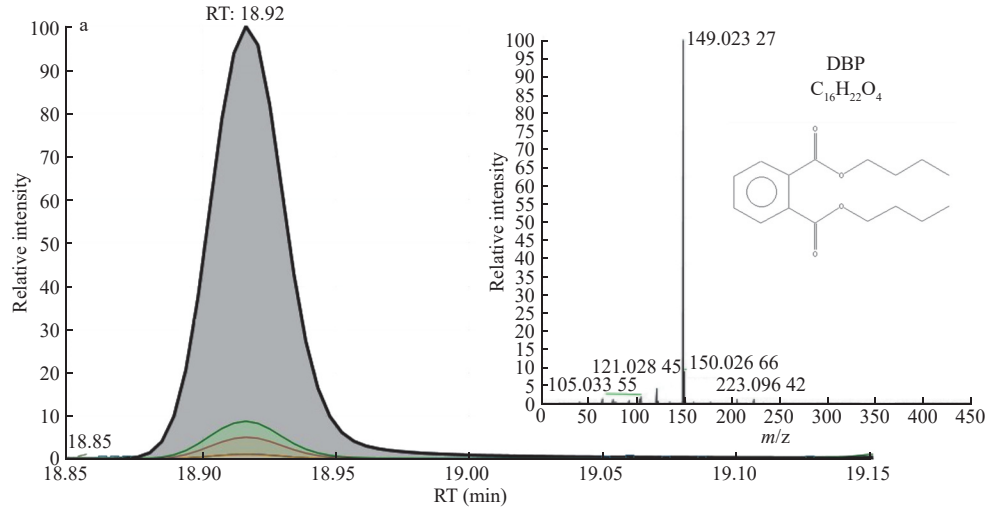

Fig. 8 Ion overlay and mass spectrum of DBP and BaP in the standard samples (a) and (c), as well as in the positive infant and toddler biscuit samples (b) and (d).

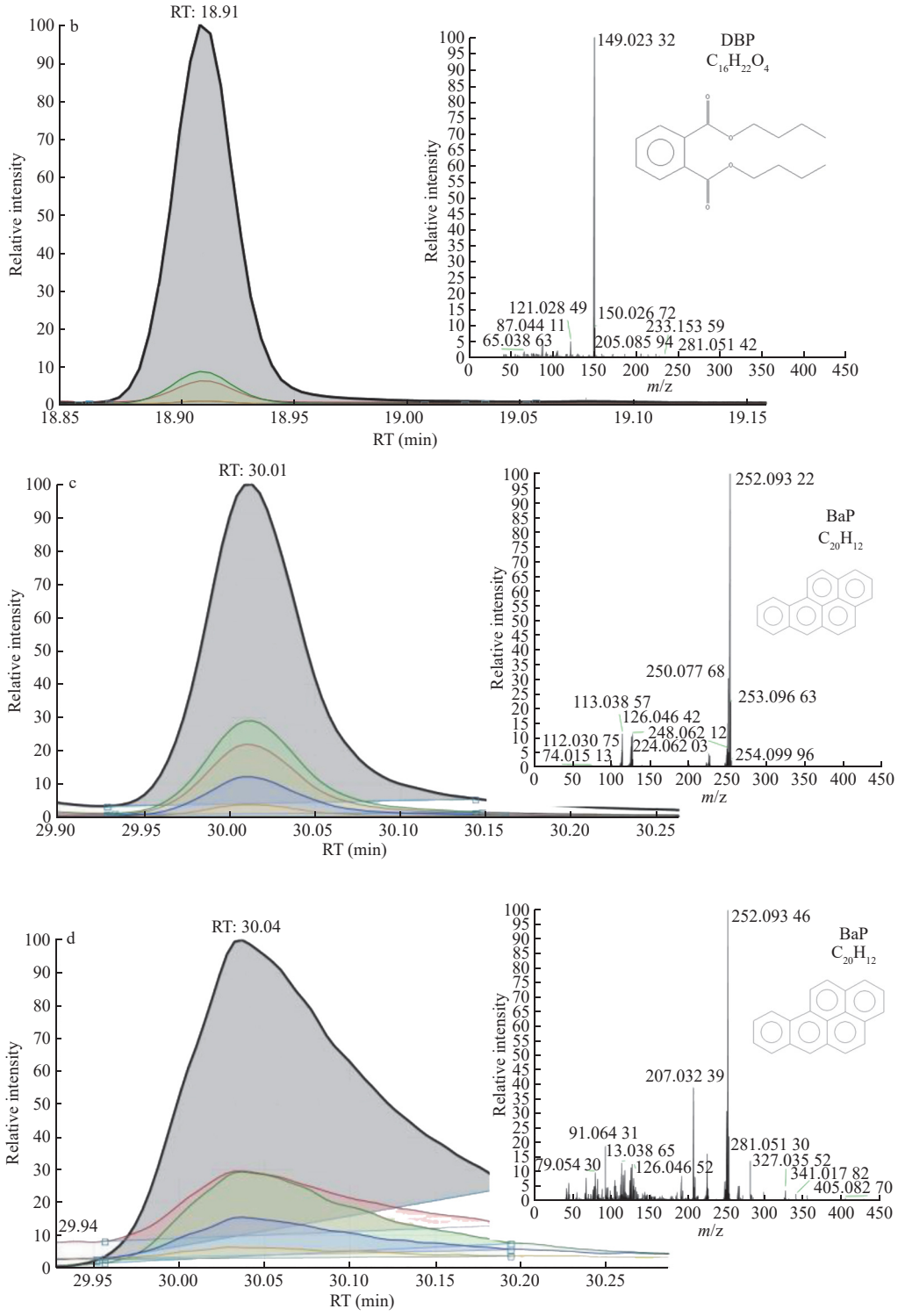

Fig. 8 (*Continued*)

4. Conclusion

The experiment utilized a combination of cryogenic centrifugation and LPAS purification, alongside Orbitrap GC-MS, to establish a method for the screening and quantification of 70 types of organic pollutants across 3 categories of infant cereal-based supplementary foods (rice flour, biscuits, and noodles). This method eliminates the need for SPE and GPC, rendering it simple, fast, economical, and environmentally friendly. It capitalizes on the high sensitivity, resolution, and strong anti-interference capabilities of Orbitrap GC-MS for detection. The target compounds are accurately identified using retention times and an accurate mass database and quantified using external standard calibration curves. This enables the effective screening, confirmation, and quantification of 70 organic pollutants in

infant cereal-based supplementary foods, yielding satisfactory results. The method demonstrates low matrix effects and effective purification, reducing the potential for false positives/negatives, and providing high precision and accuracy. It is suitable for the rapid detection of 70 types of organic pollutants in infant cereal-based supplementary foods and offers a significant technical approach for determining trace organic pollutants in these products.

The study analyzed 70 types of organic pollutants in 3 categories of infant cereal-based supplementary foods from the Chinese market by this method. The concurrent detection of PAEs and PAHs in commercial infant cereal-based supplementary foods underscores the necessity of establishing new analytical methods for monitoring multiple organic pollutants in infant foods to ensure their safety and quality. This study highlights the importance of assessing the dietary exposure of vulnerable consumer groups to various pollutants. Furthermore, it suggests that China should implement stricter legislation to guarantee the safety of food and infant cereal-based supplementary products.

Conflict of interest

Yan Zhang is an associate editor for *Food Science and Human Wellness* and was not involved in the editorial review or the decision to publish this article. The authors declare no conflict of interest.

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Data availability statement

Data will be made available on request.

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