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Simultaneous analysis of synthetic musks and triclosan in human breast milk by gas chromatography tandem mass spectrometry

Hao Wang[a,c], Jing Zhang[a], Fudie Gao[a,c], Yi Yang[a], Hejun Duan[a], Yongning Wu[a,b], Jean-Daniel Berset[d], Bing Shao[a,c,*]

[a] Beijing Research Center for Preventive Medicine, Beijing 100013, China
[b] Institute of Nutrition and Food Safety, China Center for Disease Control and Prevention, Beijing 100021, China
[c] School of Public Health and Family Medicine, Capital Medical University, Beijing 100089, China
[d] Water and Soil Protection Laboratory (WSPL), Environmental Organic Chemistry Group (EOCG), Office of Water and Waste (OWW), Schermenweg 11, 3014 Bern, Switzerland

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ABSTRACT

A comprehensive method was developed for the simultaneous analysis in human breast milk of 12 synthetic musks, five nitro musks, six polycyclic muks and one macrocyclic musk; as well as one musk metabolite and triclosan. The target analytes were freeze dried and extracted using the accelerated solvent extraction (ASE) procedure. The extracts were further purified by gel permeation chromatography (GPC) and florisil solid-phase extraction (SPE) and then analyzed by gas chromatography tandem mass spectrometry (GC–MS/MS). Recoveries of the analytes based on the isotopic internal standard correction ranged from 82.4% to 112%, with relative standard derivations less than 20%. The method quantification limits (MQLs) were 0.6–5.4 ng/g lipid. The analytes were detected in human breast milk samples and ranged from 11.7 to 308.6 ng/g lipid.

1. Introduction

Synthetic musks are often used as substitutes of natural odorous components and are widely used in many personal care products such as deodorants, perfumes, body lotions, soaps and laundry detergents. Combined with musks, triclosan is commonly used as an antibacterial agent for the production of deodorants, toothpastes, shaving creams, mouth washes, and cleaning supplies. It is also added to an increasing number of consumer products, such as kitchen utensils, toys, bedding, socks, and trash bags. More recently, showering or bathing with 2% triclosan has become a recommended procedure for the decolonization of patients, whose skin is carrying methicillin-resistant *Staphylococcus aureus* (MRSA) following the successful control of MRSA outbreaks in several clinical settings [1–3].

After application of the personal care product, musks and triclosan are released into the environment, and parts were adsorbed by derma and inhalation. As a result, musks have been found in almost the entire environment, including air [4,5], water [6,7], sediment [7–9] and fish [10–12]. Moreover, these compounds have been detected in human fat tissues [13,14], blood [15,16] and breast milk [13,17,18]. Furthermore, potential adverse effects of musks such as musk xylene, musk ketone have been shown by some scientists [19,20] and regulatory agencies [21,22] in recent years. Meanwhile, triclosan, a chemical used together with musks, received increasing attentions as an endocrine disruptor [23,24].

Human breast milk is a unique nutritional source for infants that cannot be replaced by any other food. Exclusive breastfeeding is recommended by world health organization (WHO) up to 6 months of age, with continued breastfeeding along with appropriate complementary food up to two years age [25]. Although pollutants, especially hydrophobic chemicals such as dioxins, polycyclic aromatic hydrocarbons (PAHs), perfluorooctanesulphonate and musks can accumulate in breast milk and infants are fragile and susceptible to these persistent contaminants, breastfeeding remains superior to infant formula from the perspective of the overall health of both mother and child. To protect infants' health, special surveillance should be applied to understand the occurring levels of these pollutants and appropriate advice to mothers should be provided. Therefore, sensitive method for the simultaneous analysis of synthetic musk and triclosan in human breast milk is necessary to assess the body burden of infants.

Various methods have been reported in the literature for the detection of synthetic musks in milk. In general, these methods include fat extraction using liquid–liquid extraction (LLE) [17,18] or Soxhlet extraction [26], purification by gel permeation-chromatography (GPC) [18] and/or solid-phase extraction (SPE)

* Corresponding author at: Beijing Research Center for Preventive Medicine, Beijing 100013, China. Tel.: +86 10 64407191; fax: +86 10 64407210.
E-mail address: shaobingch@sina.com (B. Shao).

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Table 1
Mass spectrometry conditions for the analysis of the target compounds.

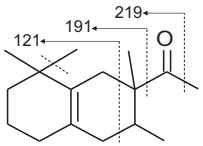
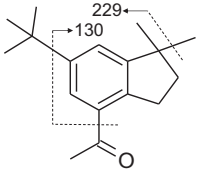
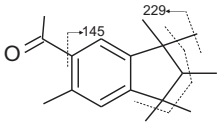
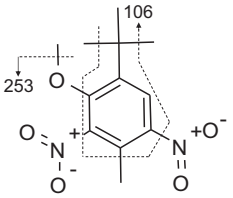
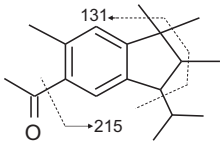
Compound	Abbreviation	Structure	Chemical name	Molecular weight	RT[a]/min	MRM transition	CE[b]/eV	Internal standard
Isocyclemone E	OTNE		[1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethylnaphthalen-2yl]ethan-1-one	234	9.06	234 → 191[c] 219 → 121	5 18	AHTN-d_3
Celestolide	ADBI		1-[6-(1, 1-dimethylethyl)-2,3-dihydro-1,1-dimethyl-1H-inden-4-yl]-ethanone	244	9.63	244 → 229[c] 229 → 130	5 20	AHTN-d_3
Phantolide	AHMI		1-[2,3-dihydro-1,1,2,3,3,6-hexamethyl-1h-inden-5-yl]-ethanone	244	10.28	244 → 229[c] 229 → 145	8 20	AHTN-d_3
Musk ambrette	MA		1-(1,1-Dimethylethyl)-2-methoxy-4-methyl-3,5-dinitrobenzene	268	11.63	268 → 253[c] 253 → 106	15 18	MX-d_{15}
Versalide	ATII		1-[2, 3-dihydro-1,1,2,6-tetramethyl-3-(1-methyl-ethyl)-1H-inden-5-yl]-ethanone	258	11.90	258 → 215[c] 215 → 131	5 20	AHTN-d_3

Table 1 (*Continued*)

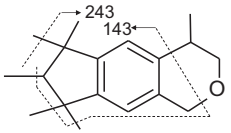
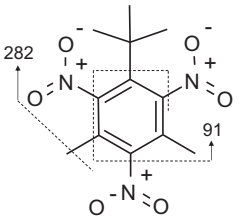
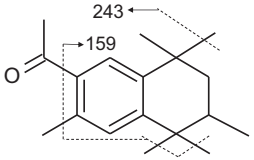
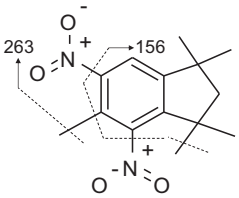
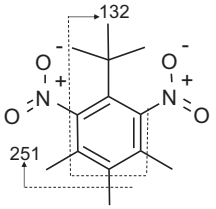
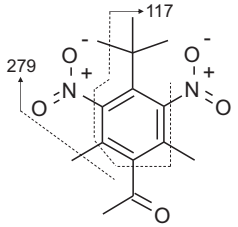
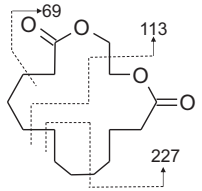
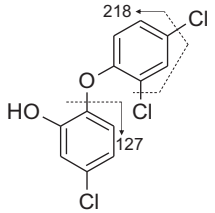
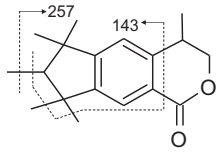
Compound	Abbreviation	Structure	Chemical name	Molecular weight	RT[a]/min	MRM transition	CE[b]/eV	Internal standard
Galaxolide	HHCB		1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyrane	258	12.01	258 → 243[c] 243 → 143	5 20	AHTN-d_3
Musk xylene	MX		1-(1,1-dimethylethyl)-3,5-dimethyl-2,4,6-trinitrobenzene	297	12.15	297 → 282[c] 282 → 91	5 25	MX-d_{15}
Tonalide	AHTN		1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)-ethanone	258	12.20	258 → 243 243 → 159[c]	5 15	AHTN-d_3
Musk moskene	MM		1,1,3,3,5-pentamethyl-4,6-dinitro-indan	278	12.57	278 → 263[c] 263 → 156	5 25	MX-d_{15}
Musk tibetene	MT		1-tert-butyl-3,4,5-trimethyl-2,6-dinitrobenzene	266	13.65	266 → 251[c] 251 → 132	5 25	MX-d_{15}

Table 1 (*Continued*)

Compound	Abbreviation	Structure	Chemical name	Molecular weight	RT[a]/min	MRM transition	CE[b]/eV	Internal standard
Musk ketone	MK		1-[4-(1,1-dimethylethyl)-2,6-dimethyl-3,5-dinitrophenyl]-ethanone	294	14.67	279 → 117[c] 294 → 279	5 23	MX-d_{15}
Astratone	Musk T		1,4-dioxacycloheptadecane-5,17-dione	270	15.80	227 → 113[c] 113 → 69	6 25	AHTN-d_3
–	Triclosan		5-Chloro-2-(2,4-dichlorophenoxy)phenol	289	18.86	288 → 218[c] 218 → 127	10 25	AHTN-d_3
Galaxolidone	HHCB-lactone		1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyran-1-one	272	20.28	272 → 257[c] 257 → 143	8 20	AHTN-d_3
Phenanthrene-d_{10}	–		–	289	11.19	188 → 160[c] 160 → 132	18 18	–
Musk xylene-d_{15}	MX-d_{15}		–	312	11.86	312 → 294[c] 294 → 138	8 18	–
Tonalide-d_3	AHTN-d_3		–	261	12.10	261 → 246[c] 246 → 160	13 20	–

[a] Retention time.
[b] Collision energy.
[c] Quantification ion.

Table 2
Relative recoveries (%, mean, R.S.D.) of 14 target compounds from cow milk samples ($n = 6$).

Compound	Linear range (μg/L)	Spiking level (ng/g lipid)						MQL (ng/g lipid)
		S_0		$2.5S_0$		$5S_0$		
		Recovery	R.S.D.	Recovery	R.S.D.	Recovery	R.S.D.	
OTNE	2.0–1000.0	97.9	14	105	5.7	98.5	8.3	1.5
ADBI	1.0–1000.0	111	8.3	104	8.9	101	7.2	0.6
AHMI	1.0–1000.0	96.9	5.5	90.3	6.0	106	6.9	0.8
MA	5.0–1000.0	98.3	4.9	82.4	8.6	109	9.6	5.2
ATII	5.0–1000.0	96.1	12	100	15	101	10	2.6
HHCB	1.0–1000.0	101	8.3	105	4.5	107	8.6	1.1
MX	5.0–1000.0	96.7	11	99.4	4.4	102	7.5	3.5
AHTN	1.0–1000.0	98.1	6.6	111	11	112	7.4	0.6
MM	5.0–1000.0	98.8	3.6	103	11	105	5.7	5.4
MT	5.0–1000.0	85.8	7.7	106	6.4	102	7.4	3.6
MK	2.0–1000.0	109	8.3	102	13	91.7	10	1.4
Musk T	5.0–1000.0	105	9.7	108	16	105	5.1	3.7
Triclosan	5.0–1000.0	108	9.2	101	13	102	6.7	3.5
HHCB-lactone	2.0–1000.0	107	16	104	12	111	2.6	0.7

S_0: 2.0 ng/g lipid for OTNE, ADBI, AHMI, HHCB, AHTN, MK, HHCB-lactone; 10.0 ng/g lipid for MA, ATII, MM, MX, Musk T, MT, triclosan.

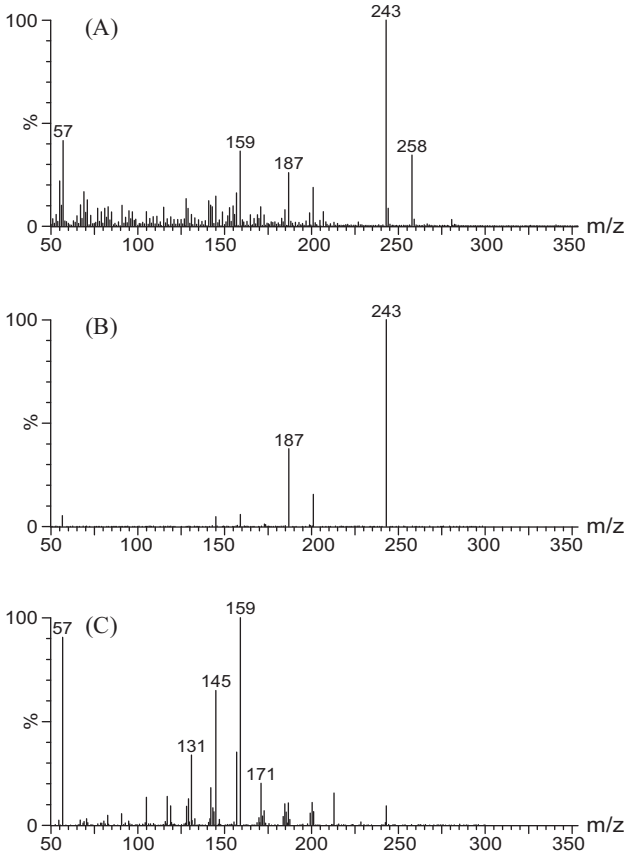


Fig. 1. Mass spectrum of AHTN. (A) Full scan of AHTN; (B) product ion scan of m/z 258; (C) product ion scan of m/z 243.

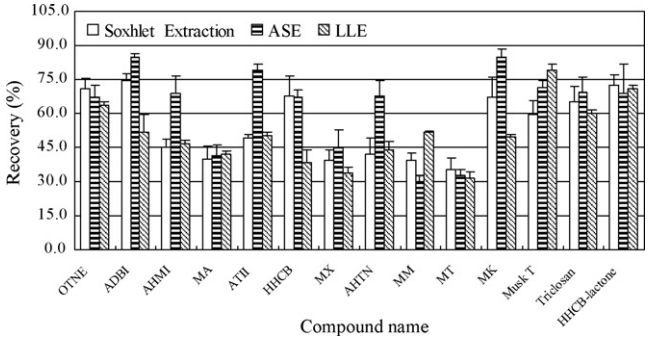


Fig. 2. Absolute recoveries (%, mean ± S.D.) of 14 target compounds spiked at 100 μg/L using different extraction methods ($n = 3$).

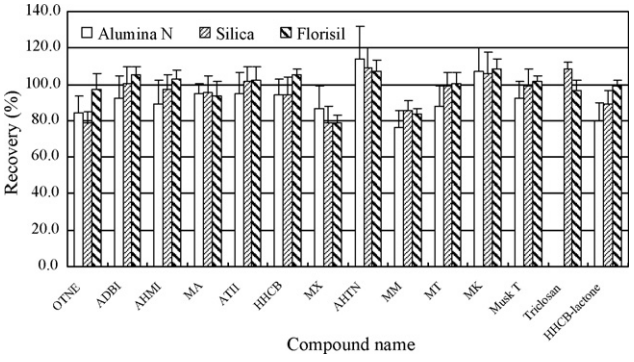


Fig. 3. Absolute recoveries (%, mean ± S.D.) of 14 target compounds spiked at 100 μg/L using different SPE cartridges ($n = 5$).

procedure [17]. Finally, the resulting extracts are detected by gas chromatography coupled with mass spectrometry (GC–MS) [13,17,18] with method detection limits of 5 ng/g lipid for tonalide (AHTN), galaxolide (HHCB) and 2 ng/g lipid for musk ketone (MK), musk xylene (MX). However, these methods were mainly focused on nitro musks and polycyclic musks. Macrocyclic musks, although they are increasingly used in recent years, were not involved in these papers. Regarding triclosan in milk, several articles reported the occurrence of this compound using LLE for further cleanup, and finally analysis by GC–MS. There are, however, no reports about the simultaneous analysis of synthetic musks and triclosan in human breast milk although they are often used in combination.

In this paper, a comprehensive method was developed for the simultaneous detection of triclosan and synthetic musks, including five nitro musks, six polycyclic musks, one macrocyclic musk and a metabolite of polycyclic musk in human breast milk. The method involved ASE and SPE clean-up and final GC–MS/MS analysis. After thorough validation, the method was applied to real human breast milk samples.

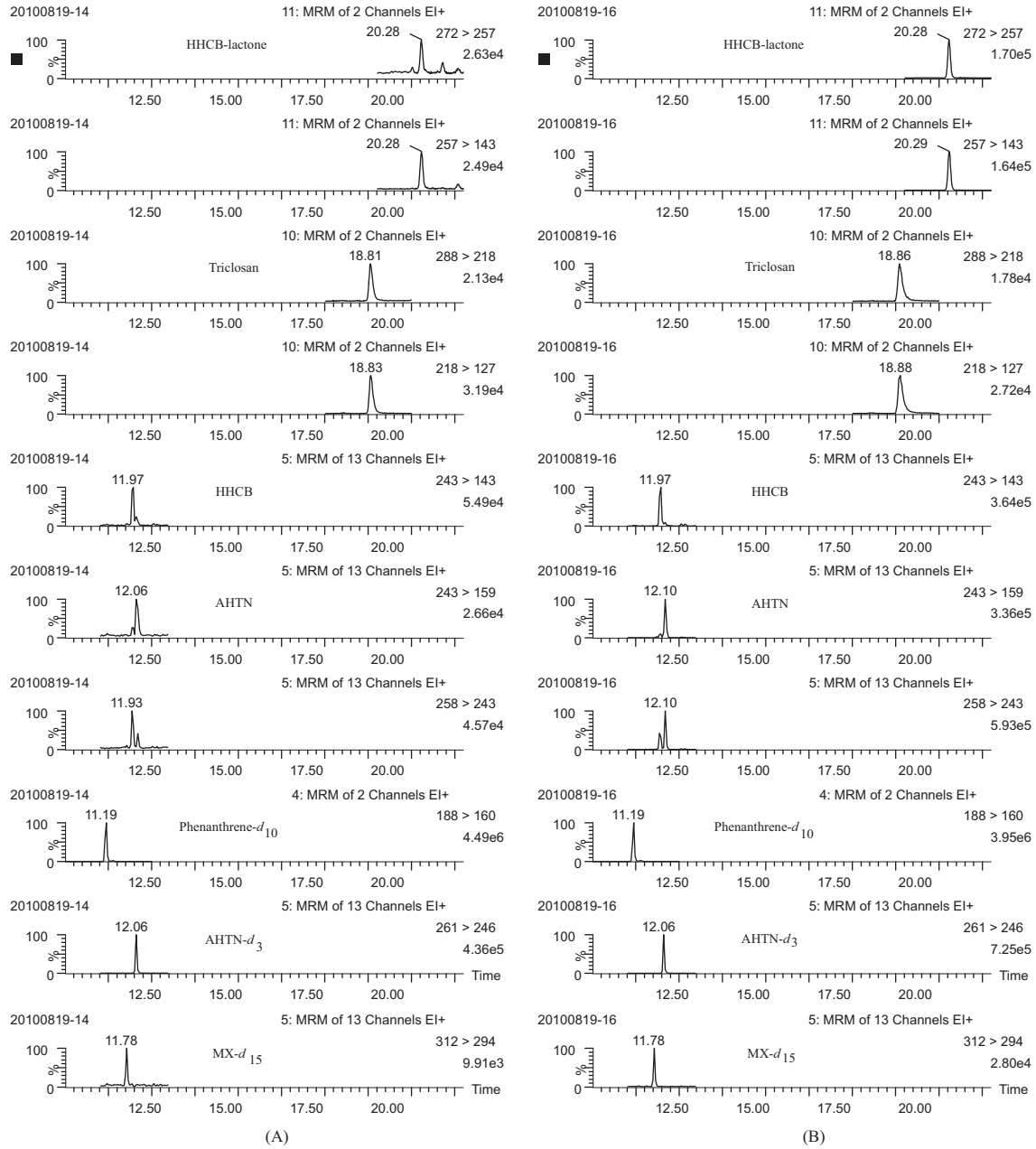


Fig. 4. MRM chromatograms of a standard solution (A, 50 μg/L) and a breast milk sample (B).

2. Experimental

2.1. Reagents and chemicals

All solvents including cyclohexane, ethyl acetate (EA), chloroform, dichloromethane (DCM), and hexane were supplied by Dikma (Lake Forest, USA). MX, [CAS No: 81–15–2], MK, [81–14–1], musk ambrette (MA, [83–66–9]), musk tibetene (MT, [145–39–1]), musk moskene (MM, [116–66–5]), HHCB, [1222–05–5], AHTN, [1506–02–1], celestolide (ADBI, [13171–00–1]), phantolide (AHMI, [15323–35–0]), traseolide (ATII, [68140–48–7]), galaxolidone, the metabolite of galaxolide (HHCB-lactone) and triclosan ([3380–34–5]) were kindly donated by Dr. Berset (Water and Soil Protection Laboratory, Switzerland). Musk T ([105–95–3], 10 mg/L in cyclohexane) and internal standard (AHTN-d_3 and MX-d_{15}, 100 mg/L in isooctane) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). OTNE ([54464–57–2], 98%) were purchased from Toronto Research Chemicals Inc. (North York, Ontario, Canada). Chemical names and molecular structures of these target compounds were shown in Table 1. Phenanthrene-d_{10}, 4003 mg/L) in DCM, was obtained from Accustandard Inc. (New Haven, CT).

Individual stock solutions (100 mg/L) were prepared by dissolving an appropriate amount of each substance in isooctane (ACROS Organic, New Jersey, USA). Mixtures of working standards were prepared by diluting the stock solution in isooctane. Diluted internal standard solutions (1 mg/L) were prepared in isooctane. All standard solutions were stored at −18 °C. Sep-Pak silica, neutral alumina and Florisil cartridges (500 mg, 6 mL) were all purchased from Waters Co. (Milford, MA, USA).

2.2. Sample preparation

About 15 g of frozen milk samples were freeze-dried and 100 μL of internal standard solution (1 mg/L) were added. After 30 min, 5 g

Table 3
The concentration of target compounds in human breast milk (ng/g lipid).

	HHCB	AHTN	MK	Triclosan	Musk T	HHCB-lactone
Sample 1	37.9	54.3	<MQL	<MQL	n.d.	44.3
Sample 2	46.2	113.8	n.d.	n.d.	n.d.	58.5
Sample 3	46.3	83.8	<MQL	n.d.	n.d.	66.3
Sample 4	22.1	23.1	<MQL	n.d.	n.d.	20.0
Sample 5	63.6	117.9	<MQL	n.d.	n.d.	68.6
Sample 6	58.1	52.4	n.d.	308.6	n.d.	51.4
Sample 7	32.5	22.9	n.d.	n.d.	<MQL	20.4
Sample 8	67.6	92.9	<MQL	n.d.	<MQL	70.6
Sample 9	11.7	33.0	n.d.	n.d.	n.d.	n.d.
Sample 10	31.0	63.3	<MQL	27.6	n.d.	n.d.
U.S. [12]	5–917	5–144	2–212	–	–	10–88
Germany [13]	16–108	11–58	5–15	–	–	–
Danmark [17]	38–422	5.6–37.9	n.d.–26.9	–	–	–
Japan [26]	<50–440	<50–190	–	–	–	–

n.d.: not detected.

of Celite was added and fully mixed. The mixtures were packed into 22 mL stainless steel ASE cells and the extraction was performed on an ASE 200 apparatus (Dionex, Sunnyvale, CA, USA) using hexane/DCM (1:1, v/v) as extraction solvent. First the extraction cell was heated to 120 °C and filled with the solvent until the pressure reached 1500 psi (10.34 MPa). After an oven heat-up time of 6 min, two static extractions at constant pressure and temperature of 8 min were performed. After the static period, fresh solvent was introduced to flush the lines and cell, and the extract was collected in a 60-mL glass vial. The residue solvent in the cell was purged into the collection vial with pressurized nitrogen. The crude extracts of about 30 mL were concentrated to near dryness with a rotary evaporator in a temperature controlled bath (38 °C) and the lipids were weighed and redissolved with 5 mL EA/cyclohexane (1:1, v/v) for GPC using a J2 Scientific packed glass column (225 mm × 2.0 mm i.d, J2 Scientific). The mobile phase was a mixture of EA/cyclohexane (1:1, v/v) at a flow rate of 5 mL/min. After discarding the first 42.5 mL elution, the following 50 mL were collected and concentrated with a rotary evaporator to near dryness and redissolved with 5 mL of cyclohexane for further purification by a Sep-Pak Florisil cartridge (500 mg, 6 mL) preconditioned with 6 mL 10% EA in pentane. The target analytes were eluted using 15 mL 10% EA in pentane. The extract was concentrated to near dryness after adding 0.5 mL isooctane as keeper. To the final sample 200 μg/L phenanthrene-d_{10} were added and brought to 0.5 mL for GC–MS/MS analysis.

2.3. GC–MS/MS

Analysis was performed on a Waters Micromass Quattro micro GC tandem mass spectrometer (Waters, USA) and an Agilent 6890 GC equipped with a 30m × 0.25 mm × 0.25 μm DB-5MS capillary column (Agilent Technologies, Foster City, CA, USA). Helium was used as carrier at a constant flow rate of 1.0 mL/min. 1 μL sample was injected splitlessly at 280 °C. After a holding time of 0.5 min, the GC oven temperature program was from 70 °C to 180 °C at a rate of 20 °C/min and then increased to 220 °C at 2 °C/min followed by 30 °C/min to 280 °C, with a final hold time of 2 min.

The MS/MS analysis was carried out in electron ionization (EI) mode using the multiple reaction monitoring (MRM) mode. The ion source was operated at 200 °C with electron energy of 70 eV and a filament current of 200 μA. Two specific MRM transitions/compound were chosen. The temperature of the interface and source were set at 200 °C and 250 °C, respectively. Ultra pure argon was used as collision gas and the pressure of the chamber maintained 3.5×10^{-3} mbar. The electron multiplier was set at 650 V. The collision energies of each compound were optimized and are listed in Table 1.

2.4. Quality control

For assessment of accuracies and precisions, musks standard mixtures were spiked into cow milk at three levels (Table 2). Isotopic standard AHTN-d_3 and MX-d_{15} were added to correct the loss in sample-extraction and clean-up procedures. Based on their chemical structures, AHTN-d_3 and MX-d_{15} were used as internal standard of polycyclic musks and nitro musks, respectively, while triclosan was also calibrated by AHTN-d_3. The stability of GC–MS/MS was monitored by addition of phenanthrene-d_{10} into the reconstituted solutions. MQL was defined as the minimum detectable amount of analytes from cow milk lipid in MRM mode with a signal-to-noise ratio (S/N) of 10:1.

Because of their ubiquitous occurrence in perfumes, hand lotions and other personal care products, strict measures were taken to prevent possible contamination during sample collection, storage, preparation and analyzing procedure. A new breast pump was provided to each breast-feeding mother for milk collection. The collection tubes were used only once and prewashed with hexane. All the glass vessels were baked out at 400 °C for 4 h before use. The mothers were asked not to use perfumes and hand lotions before sample collection. The analysts also avoided to use any perfumes and hand lotions during experimental work. In addition, procedural blanks were submitted to the whole analytical procedure with pure cow milk to monitor potential contamination after every six samples.

3. Results and discussion

3.1. Optimization of GC–MS/MS

In previous papers [18,27], GC–MS in the single ion monitoring (SIM) mode was often used for the detection of synthetic musks. In order to improve the selectivity and sensitivity of the analytical method without loss of identification capability, GC–MS/MS was used in this study to reduce background noise of the complex matrix [28]. For the optimization of MS/MS parameters, all the analytes were acquired in full scan mode (m/z 50–350). The high abundance ions were selected as precursor ions for further fragmentation, and then different collision energies were applied to obtain appropriate ion transitions. For AHTN as an example, the high abundance ion m/z 243 and 258 were selected as precursor ions (Fig. 1), and a product ion scan was applied. Consequently, the two most sensitive transitions 258 → 243 and 243 → 159 was selected for quantification and qualitation, respectively. Bond cleavages and optimized parameters for the 14 target chemicals are given in Table 1. The GC–MS/MS chromatograms of a standard sample are shown in Supplementary material.

3.2. Sample extraction

LLE and Soxhlet extraction are frequently used to extract fat and synthetic musks from milk and tissues [13]. However, these extraction procedures are both solvent and time-consuming, and emulsification might occur during LLE. ASE is a fully automated technique using common solvents to rapidly extract solid and semisolid samples at elevated temperature and pressure, which was widely used trace in contaminants analysis of foodstuffs. These three extraction procedures were compared at a spiking level of 100 μg/kg (wet weight). LLE and Soxhlet extraction procedures were performed according to the methods of Duedahl-Olesen et al. [17] and Ueno et al. [26], respectively, while ASE was carried out as written in Section 2.3. The results (Fig. 2) indicate that for most of target analytes the absolute recoveries using ASE are higher than those of LLE and Soxhlet extraction.

It was reported that triclosan could be metabolized and excreted either as glucuronide and/or sulphate conjugates in humans. Ye et al. [30] found that the free triclosan prevailed in human milk, rather than the conjugates. Here, we detected total triclosan in real sample by sulphuric acid hydrolysis followed LLE [29]. According to Allmyr et al. [29], target analytes involved in this study were tested, only triclosan was found with 40.8% absolute recovery and the other 13 species were all lost. Three real samples were prepared according to the previous sample-preparation procedure [29] and this study. The results (corrected by recoveries) indicate that there are almost no difference between the total amount of triclosan and the free, which is consistent with the literature [30]. Thus, hydrolysis procedure is not necessary for the analysis of triclosan in milk samples and the method used in this study can be applied to the simultaneous extraction of synthetic musks and triclosan.

3.3. Sample cleanup

The sample extracts are subjected to GPC to remove the lipids, and then were concentrated and further purified using SPE. As for the SPE procedure, Florisil cartridge was initially used according to a previous report [17] by loading a standard solution (100 μg/L) in isooctane. Based on the polarity of the target compounds, pentane was chosen as elution solvent for the target analytes and a small amount of EA was added to adjust the polarity. The amount of EA in pentane was tested from 0% to 20%. The result showed that 10% EA in pentane could elute the targets efficiently. Additionally, different volumes of elution solvent were compared. Each 3 mL of the eluate was collected orderly for analysis after sample loading, the target analytes were not found in 6th fraction. Therefore, 15 mL 10% EA in pentane was used. For the comparison, neutral alumina and Florisil SPE cartridges were used for further purification following the procedure above. About 75–114% of absolute recoveries were obtained using neutral alumina except for triclosan. The low recovery of the latter compound can be ascribed to its acidity which leads to strong adsorption to neutral alumina. As to Florisil cartridge, the absolute recoveries (Fig. 3) are more quantitative compared to those of silica cartridge for most analytes. Therefore, Florisil SPE was selected for further purification.

3.4. Method validation

To assess accuracy and precision, three levels of mixture standard solutions were spiked into pure cow milk and prepared for analysis according to the procedure described above. Each level was performed in six replicates. The average recoveries corrected with internal standards were above 82.4% (Table 2), which was satisfactory. The relative standard derivations were lower than 20.0%. The calibration standards (Table 2) were prepared ranging from 1 μg/L to 1000 μg/L with 200 μg/L of internal standard, resulting in acceptable linearities for all compounds (correlation coefficients of $r > 0.99$). The MQLs were 0.6–5.4 ng/g lipid, which was lower or comparable with previous studies [13,17].

3.5. Investigation of target compounds in Chinese breast milk

The developed method was applied to the analysis of target analytes in 10 breast milk samples collected in 2009 from 10 anonymous donors in Chengdu, China. MRM chromatograms of the analytes in a real sample, along with them in a standard solution, were shown in Fig. 4. As listed in Table 3, HHCB and AHTN were found in all samples with concentration ranging of 11.7–67.6 ng/g lipid and 22.9–117.9 ng/g lipid, respectively. These results were similar with those reported in Germany [13], United States [18], Denmark [17] and Japan [26]. HHCB-lactone, a metabolite of HHCB, occurred in eight out of ten samples with concentrations ranging from 20.0 to 70.6 ng/g lipid. MK and Musk T were found in 6 of 10 and 2 of 10 samples below the MQL. Finally, triclosan was found in 3 of 10 samples, at concentrations ranging from <MQL to 308.6 ng/g lipid.

4. Conclusions

A novel, reliable method for simultaneous determination of nitro musks, polycyclic musks, macrocyclic musk and triclosan in human breast milk was developed. The method includes extraction using ASE, GPC combined with Florisil SPE purification and GC–MS/MS analysis. The use of tandem mass spectrometry improved the sensitivities of polycyclic musks and triclosan and matrix interferences were eliminated. Using this method, a limited amount of Chinese breast milk samples were investigated. HHCB, HHCB-lactone, AHTN, MK, Musk T and triclosan were mainly found and ranged from 11.7 to 308.6 ng/g lipid.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jchromb.2011.04.036.

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