



Rapid screening and identification of multi-class substances of very high concern in textiles using liquid chromatography-hybrid linear ion trap orbitrap mass spectrometry



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ABSTRACT

A new analytical method was established and validated for the analysis of 19 substances of very high concern (SVHCs) in textiles, including phthalic acid esters (PAEs), organotins (OTs), perfluorochemicals (PFCs) and flame retardants (FRs). After ultrasonic extraction in methanol, the textile samples were analyzed by high performance liquid chromatography-hybrid linear ion trap Orbitrap high resolution mass spectrometry (HPLC-LTQ/Orbitrap). The values of LOQ were in the range of 2–200 mg/kg. Recoveries at two levels (at the LOQ and at half the limit of regulation) ranged from 68% to 120%, and the repeatability was lower than 13%. This method was successfully applied to the screening of SVHCs in commercial textile samples and is useful for the fast screening of various SVHCs.

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1. Introduction

Substances having potential serious and irreversible effects on human health and the environment are identified as substances of very high concern (SVHCs) [1]. SVHCs are one group of chemicals listed in the REACH, which is a European Union regulation adopted to protect humans and the environment from the risks posed by chemicals used in different areas while enhancing the competitiveness of the EU chemical industry [2]. SVHCs such as phthalic acid esters (PAEs), organotins (OTs), perfluorochemicals (PFCs) and flame retardants (FRs) are widely used in the manufacturing of textiles as plasticizers, stabilizers, stain-resistant materials and flame retardant additives, and their health effects have gained public attention. The European Chemicals Agency (ECHA) requires that the weight of an SVHC used at more than one thousand kilograms a year cannot exceed 0.1% of the total weight of the products; otherwise, the producer must abide by the notification obligation of REACH regulations. Additionally, other regulations such as OEKO-TEX® Standard 100 [3] and the Restricted Substances List (RSL) [4] define criteria for the use and limitations of SVHCs.

At present, methods used for the determination of PAEs, OTs, PFCs and FRs are mainly GC coupled with flame photometric detectors or mass spectrometric detectors [5–7] or LC-MS and LC-MS/MS [8–11]. However, GC has some limitations for the analysis of SVHCs. As for OTs, GC inevitably includes a derivatization step that affects the accuracy and precision, especially for the analysis of complex biological or environmental matrices [12]. For most brominated flame retardants, the high temperature of GC may lead to their degradation [13]. LC can avoid these drawbacks. In particular, LC-MS/MS has high sensitivity and a wide linear range when operated in the selected reaction monitoring (SRM) mode. However, LC-MS/MS also has some limitations: the number of analytes is limited when operating in SRM mode. In full-scan mode, LC-MS/MS shows a low sensitivity, which limits the capabilities for screening applications. Moreover, because of “unit resolution” MS, these methods cannot be used for the analysis of untargeted compounds [14]. The Orbitrap with high resolution and high mass accuracy shows high sensitivity and selectivity, which can allow for the analysis of compounds in complex matrices with minimum or even no sample clean-up. The full-scan mode in the Orbitrap can provide data for all the compounds in a sample, which is useful for screening analysis.

To date, the Orbitrap has been used extensively in proteomics and food safety research [14–16], but few studies have been reported on the detection of SVHCs in textiles [17,18]. Due to the

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difficulties in establishing a simultaneous method of analysis for multi-class compounds with different physicochemical properties, previous reports have mainly involved a single class of SVHCs. Therefore, the aim of this study is to develop a rapid and reliable screening and confirmation method for the detection of 19 SVHCs, including PAEs, OTs, PFCs and FRs, in textiles using the HPLC-LTQ/Orbitrap.

2. Experimental

2.1. Materials and chemicals

Methanol, acetonitrile and dichloromethane (HPLC-grade) were purchased from Merck (Darmstadt, Germany). Formic acid (HPLC-grade) and ammonium acetate (HPLC-grade) were purchased from Sigma–Aldrich (Steinheim, Germany). Ultra-pure Milli-Q water with $18.2 \text{ M}\Omega \text{ cm}^{-1}$ was obtained using a Milli-Q® Advantage A10® system (Millipore, Milford, MA, USA). SVHC analytical standards, including dipentyl phthalate (DPP) (99.2%), diisopentyl phthalate (DIPP) (99.5%), *n*-pentyl-isopentyl phthalate (DniPP) (49.0%), bis(2-methoxyethyl) phthalate (DMEP) (98.0%), diisobutyl phthalate (DIBP) (99.0%), dibutyl phthalate (DBP) (99.0%), bis(2-ethylhexyl) phthalate (DEHP) (98.5%), benzyl butyl phthalate (BBP) (98.4%), 1,2-benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C₇-rich (DIHP) (99.0%), dihexyl phthalate (DHP) (98.0%), bis(tributyltin)oxide (TBTO) (96.5%), hexabromocyclododecane (HBCD) (95.1%) and tris(2-chloroethyl)phosphate (TCEP) (98.5%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Ammonium pentadecafluorooctanoate (APFO) ($\geq 98.0\%$), pentadecafluorooctanoic acid (PFOA) (96.0%), hencosafluoroundecanoic acid (PFUdA) (95.0%), tricosfluorododecanoic acid (PFDoA) (95.0%), pentacosfluorotridecanoic acid (PFTra) (97.0%), heptacosfluorotetradecanoic acid (PFTeA) (97.0%), alpha-hexabromocyclododecane (α -HBCD) (100%), beta-hexabromocyclododecane (β -HBCD) (100%) and gamma-hexabromocyclododecane (γ -HBCD) (100%) were purchased from Sigma–Aldrich (Steinheim, Germany).

Individual stock standard solutions of each SVHC, except for HBCD, were prepared at a concentration of 1000 mg/L in methanol, while HBCD was prepared at a concentration of 100 mg/L due to its low solubility in methanol. All the standard solutions were stored in the refrigerator at -18°C . Standards can be used by diluting the stock standard solutions to the concentration needed with methanol/water (3/1, v/v).

2.2. Sample preparation

A total of 0.5 g of textile samples (5 mm \times 5 mm) were weighed into 40 mL glass tubes. Then, 30 mL methanol was added, and the tubes were capped and extracted by an ultrasonic generator (40 KHz, KQ-500DE, Kun Shan, China) at a temperature of 50°C for 20 min. After standing for 3 min, 50 μL supernatant was diluted with 950 μL methanol/water (3/1, v/v) to a volume of 1 mL, then filtered by a 0.22 μm nylon membrane.

2.3. Preparation of spiked samples

Approximately 0.5 g of three different kinds of blank textile swatches (including pure cotton, polyester and polyester/wool blend, 5 mm \times 5 mm) were weighed into 40 mL glass tubes. A certain amount of standard stock solutions of 4 representatives (DHP, TBTO, PFOA and HBCD) were added to submerge the blank textile samples. After an equilibration time of 24 h (overnight), the solvent was eliminated using a gentle stream of nitrogen [8]. Then, these

samples (containing about 500 mg/kg four representatives listed above) were used for the optimization of extraction methods.

2.4. LC conditions

The chromatographic separation of the 19 SVHCs was carried out using an ACQUITY LC (Waters, Milford, MA, U.S.A.) equipped with an Accucore C₁₈ column (100 mm \times 2.1 mm, 2.6 μm , Thermo Fisher, MA, U.S.A.). The mobile phase was 5 mmol/L ammonium acetate (containing 0.5% formic acid) (A)–methanol (B) in positive ionization mode, and 5 mmol/L ammonium acetate (A)–acetonitrile (B) in negative ionization mode. The LC gradient elution program in positive ionization mode was as follows: 0–14 min, 60–95% B, 14–17 min, 95% B, 17.1 min, 60% B, 17.1–24 min, 60% B. The LC elution gradient program in negative ionization mode was as follows: 0–7 min, 50–95% B, 7–10 min, 95% B, 10.1 min, 50% B, 10.10–17 min, 50% B. The total flow rate was 0.2 mL/min.

2.5. MS conditions

The LTQ/Orbitrap XL (Thermo Fisher, MA, U.S.A.), equipped with an electrospray ionization (ESI) source, was chosen for the screening and identification of 19 SVHCs. The parameters in positive ionization mode were as follows: Ispray voltage, 3 kV, capillary voltage, 30 V, tube lens, 60 V. The parameters in negative ionization mode were as follows: Ispray voltage, -2.5 kV, capillary voltage, -4 V, tube lens, -70 V. The parameters common to both of the two ionization modes were as follows: vaporizer temperature, 50°C , capillary temperature, 350°C , sheath gas flow rate, 30 arbitrary units, auxiliary gas flow rate, 10 arbitrary units. Rapid screening data acquisition occurred under the full-scan mode with a resolution of 30,000 and a scan range of m/z 100–1000. The MS² confirmation was performed with a resolution of 7500. For compounds measured in positive ionization mode, collision-induced dissociation (CID) (at a normalized collision energy of 35%) was performed. For compounds measured in negative ionization mode, higher energy collision-induced dissociation (HCD) (at an optimized collision energy of each SVHC) was performed.

The related software Trace Finder (Version 2.1, Thermo Fisher Scientific) was used for the rapid screening of compounds, and Mass Frontier (Version 5.0, Thermo Fisher Scientific) was used for predicting the generation of fragments in MS².

The width of the ion-extraction window of Xcalibur 2.2 software was 5×10^{-6} (5 ppm). The retention times and targeted MS parameters of the HPLC-LTQ/Orbitrap for the analysis of the 19 SVHCs are shown in Table 1.

3. Results and discussion

In this work, 19 SVHCs were studied, including PAEs, OTs, PFCs and FRs. To obtain the best analytical conditions, the optimization of chromatographic separation and MS confirmation was necessary, especially for the detection of multi-class compounds that have a wide range of physicochemical properties.

3.1. Extraction procedure

Various methods aiming to extract a certain type of SVHCs from textiles, such as microwave-assisted extraction (MAE) [19], ultrasonic-assisted extraction (UAE) [20,21] and accelerated solvent extraction (ASE) [22] were reported previously, among which UAE was a common method for the extraction of PAEs, OTs, PFCs and FRs [10,21,23,24]. The extraction solvents also vary with the different types of SVHCs. Generally, dichloromethane and toluene, etc. are used for extraction of PAEs and FRs, which have a relatively

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