On-line coupling of thermal extraction with gas chromatography / tandem mass spectrometry for the analysis of semivolatile organic compounds in a few milligrams of indoor dust

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Highlights

- Simultaneous analysis of 44 SVOCs of health concern in indoor settled dust
- Simple, cost-effective and environmentally friendly method based on thermal extraction
- Precise and accurate quantification of a wide range of SVOCs from only 2 mg of sieved dust
- Suitable method for environmental monitoring programs or large-scale studies

ON-LINE COUPLING OF THERMAL EXTRACTION WITH GAS CHROMATOGRAPHY / TANDEM MASS SPECTROMETRY FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS IN A FEW MILLIGRAMS OF INDOOR DUST

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ABSTRACT

An original multiresidue method based on thermal extraction (TE) and gas chromatography/tandem mass spectrometry (GC/MS/MS) was developed to simultaneously quantify, from a very small amount of sample (a few milligrams), a wide range of concerning SVOCs, including polycyclic musks, organochlorines (OCs), organophosphates (OPs), oxadiazolones, polycyclic aromatic hydrocarbons (PAHs), polybromodiphenylethers (PBDEs), polychlorobiphenyls (PCBs), phthalates and pyrethroids, in indoor settled dust. Method limits of quantification (LOQs) ranged from 5 ng g^{-1} for PCBs, oxadiazon, 4,4'-DDE and 4,4'-DDT to 2000 ng g^{-1} for DEHP for a 2 mg sample of sieved dust. The proposed method was successfully validated in terms of accuracy and precision via replicate analysis of four different standard reference materials (SRMs 1649b (Urban Dust), 2585 (Organic Contaminants in House Dust), 2786 and 2787 (Fine Atmospheric Particulate Matter)) supplied by the National Institute of Standards and Technology (NIST) and was applied to five real indoor settled dust samples collected in French schools. In addition, its performance was compared to that of a previously published method based on pressurized liquid extraction (PLE) and GC/MS/MS. The different results obtained demonstrate the advantages of the proposed method over conventional methods and illustrate its two main features: i) its ease of use and very rapid implementation in only three steps (sieving, weighing and analysis), which make it particularly appropriate for environmental monitoring programs and large-scale studies, and ii) its ability to precisely and accurately quantify a wide range of SVOCs from trace (a few ng g^{-1}) to highly concentrated (several mg g^{-1}) compounds from only 2 mg of sieved dust.

KEYWORDS

Indoor air; indoor dust; thermal desorption; standard reference material; multiresidue method; multiclass compounds

1. Introduction

People spend a considerable amount of time in indoor environments such as homes, workplaces and schools. Due to the numerous sources of pollution in these enclosed environments, exposure to indoor contaminants is of great concern. Among these contaminants, semivolatile organic compounds (SVOCs) have attracted increasing interest over the past two decades, due to their possible reprotoxic and neurotoxic effects and the widespread exposure through different pathways, including the nondietary ingestion of dust. Floor settled dust is now increasingly used as a proxy for estimating SVOCs internal human exposure [1]. Consequently, a large number of studies dealing with the contamination of indoor settled dust by SVOCs for human exposure assessment purposes have been published in recent years [2–4], and many analytical methods have been proposed [2,5–7]. Most of these methods were dedicated to the analysis of a specific chemical family, so multiresidue methods that allow the simultaneous analysis (i.e., same analytical procedure including preparation, extraction, clean-up and determination) of many multiclass SVOCs are not well represented [8–17]. From the perspective of an assessment of cumulative exposure to mixtures of SVOCs, it seems useful, however, to develop and validate such methods rather than to perform multiple analyses of the same sample using different methods, thus wasting samples, time and money. Moreover, traditional off-line extraction techniques, such as Soxhlet extraction, microwave-assisted extraction (MAE), sonication-assisted extraction (SAE) or pressurized liquid extraction (PLE), have often been reported [2,5–7]. They require relatively large amounts of organic solvent and sample (from ten to a few hundred milligrams) despite the increased sensitivity of analytical systems, and generally involve tedious and time-consuming multistep procedures (grinding, sieving, weighing, extraction of substances of interest from the dust, clean-up and concentration of the extract, etc.) that may induce the loss

of analytes, contamination during each step of the protocol and/or high costs of analysis. It therefore seems essential to simplify the analytical methods in the context of environmental monitoring programs or large-scale studies without compromising on performance. Furthermore, it is sometimes difficult to collect enough dust to reach the limits of quantification in accordance with environmental concentrations and/or to perform multiple analyses of the same sample [18–21], especially in the context of human exposure assessment studies due to the use of sampling techniques (wipes or specifically modified vacuum cleaners) that do not allow a large quantity of dust to be collected, and in particular in some indoor environments such as nurseries, offices or schools, due to frequent floor cleaning [20]. This highlights the need to develop simple analytical methods able to simultaneously detect and quantify a wide range of substances from a few milligrams of sample.

In this context, thermal extraction seems to be a suitable on-line alternative (on-line coupling with gas chromatography) to conventional off-line extraction techniques for the analysis of SVOCs in settled dust while addressing all of the issues previously raised. The thermal extraction principle is simple, requiring only two steps. Target compounds are first thermally extracted from the matrix by heating the sample and carried by the helium flow up to a cold trap in order to cryo-focus analytes. The trapped compounds are then quickly transferred into the capillary column by heating the cold trap. This theoretically offers many advantages over off-line extraction techniques: it is organic solvent-free, is fast and simple to run (three steps: sieving, weighing and analysis), has high sample throughput, reduces analysis time and costs, is fully automated and benefits from on-line coupling with gas chromatography (GC) to significantly increase sensitivity and so decrease the amount of sample required for analysis due to the introduction of a large part of the sample into the GC system. However, this technique is not suitable for all substances. Polar, thermolabile and weakly volatile compounds cannot be analyzed by thermal extraction. To

the best of our knowledge, this technique has never been reported for the simultaneous determination of a large panel of SVOCs in indoor settled dust, but has already been used to measure polycyclic aromatic hydrocarbons (PAHs) [22–36] and many other SVOCs [37–39] in airborne particulate matter, a much less complex and heterogeneous matrix than settled dust. Indeed, a dust sample contains large particles, debris and small objects such as hair, feathers, fibers, buttons, small stones, pieces of plastic, etc., while a sample of airborne particulate matter is much more homogeneous in terms of particle size.

The present work aimed to develop a simple and efficient multiresidue method based on thermal extraction (TE) and gas chromatography/tandem mass spectrometry (GC/MS/MS) able to simultaneously quantify, from a very small amount of sample (a few milligrams), a wide range of concerning SVOCs in indoor settled dust, including polycyclic musks, organochlorines (OCs), organophosphates (OPs), oxadiazolones, PAHs, polybromodiphenylethers (PBDEs), polychlorobiphenyls (PCBs), phthalates and pyrethroids. The performance of the proposed method was assessed via replicate analysis of several standard reference materials (SRMs) and compared to that of a previously published method based on PLE and GC/MS/MS. Lastly, the proposed method was applied to real indoor settled dust samples collected in French schools.

2. Materials and methods

2.1 Selection of SVOCs

A ranking based on both toxicity through ingestion and concentrations in home settled dust from previous studies was the starting point for the selection of the SVOCs of interest [40]. The chemicals at the top of the ranked list were phthalates, pesticides, short-chain chlorinated paraffins (SCCPs), PBDEs, perfluorinated compounds (PFCs), organotin compounds, PCBs and

PAHs. The target SVOCs were then selected among these top-ranked chemicals according to their compatibility with a multiresidue TE-GC/MS/MS analysis and on the basis of preliminary results. Some compounds were dropped because they could not be analyzed simultaneously with the others (e.g., BDE 209, organotin compounds, PFCs, SCCPs) or because they were never quantified in French dust samples in previous studies [20,38] (e.g., atrazine, BDE 119, chlordane, heptachlor, PCB 126). The forty-four SVOCs ultimately considered for analysis are presented in Table 1.

2.2 Sample collection

Five indoor settled dust samples were randomly selected among those collected in a randomly selected sample of French preschools and elementary schools (n=301) during a nationwide survey (2013-2017) carried out by the French Observatory of Indoor Air Quality (OQAI) [41]. The samples were collected by vacuuming floor dust using a vacuum cleaner modified as follows. The dust was collected in a Whatman cellulose extraction thimble (28 mm I.D. x 80 mm length) (GE Healthcare Life Sciences, Little Chalfont, Buckinghamshire, UK) placed at the entrance of the tube in order to avoid any contact with the internal parts of the vacuum cleaner. After collection, the cellulose thimble was placed in a hermetically sealed 100-mL amber glass flask, previously cleaned with dichloromethane. The sample in its glass flask was transported to the investigator's premises in an ice-box at 4 °C. It was kept in a refrigerator at 4 °C until transfer to the laboratory. The samples were sent to the laboratory within 6 days after collection in an isothermal bag (4 °C). At the laboratory, it was stored in a freezer at -18 °C upon receipt [42].

2.3 Reagents and chemicals

Acetone and dichloromethane (PESTIPUR-For pesticide analysis) was purchased from CARLO ERBA Reagents S.A.S (Val de Reuil, France). Certified standards of aldrin, 4,4'-DDE, 4,4'-DDT, dieldrin, *alpha*-endosulfan, *alpha*-HCH, *gamma*-HCH (lindane), oxadiazon, permethrin, tributyl phosphate (TBP), anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, indeno(1,2,3-c,d)pyrene, phenanthrene, pyrene, PCB 105, butylbenzylphthalate (BBP), di-n-butylphthalate (DBP), di(2-ethylhexyl)phthalate (DEHP), diethylphthalate (DEP), diisobutylphthalate (DiBP), DiBP D_4 and diisononylphthalate (DiNP) were purchased from LGC Labor GmbH (Augsburg, Germany). Standard of DEP D_4 was purchased from C/D/N Isotopes Inc. (Pointe-Claire, Quebec, Canada). The purity of standards was above 97%. It should be noted that DiNP and permethrin were acquired as mixtures of isomers. Individual standard stock solutions (1 g/L) were prepared in acetone by accurately weighing 5, 10 or 25 mg (± 0.1 mg) of standards using a Sartorius Cubis MSE 225P semi-micro balance (Sartorius AG, Göttingen, Germany) into 5-, 10- or 25-mL volumetric flasks, depending on the compound, and stored at -18 °C.

Acetone solutions (100 mg/L) of 4,4'-DDT $^{13}C_{12}$ and *alpha*-endosulfan D_4; isooctane mixture (15 mg/L) of benzo(g,h,i)perylene D_{12}, chrysene D_{12}, perylene D_{12}, phenanthrene D_{10} and pyrene D_{10}; cyclohexane solutions (100 mg/L) of BBP D_4 and *alpha*-HCH D_6; and cyclohexane mixture (10 mg/L) of 8 PCBs (PCB 28, 31, 52, 101, 118, 138, 153 and 180) were purchased from LGC Labor GmbH (Augsburg, Germany). Nonane/toluene (10%) solutions (50 mg/L) of BDE 47, 85, 99, 100 and 153; nonane/toluene (3%) mixture (5 mg/L) of $^{13}C_{12}$-BDE 47, 99 and 153; and toluene solution (50 mg/L) of TBP D_{27} were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Isooctane solutions (1 g/L) of galaxolide and tonalide were purchased from Chiron AS

(Trondheim, Norway). Calibration solutions were prepared in acetone by appropriate dilution of individual standard stock solutions and commercial solutions (see Table S1 and Table S2).

The standard reference materials SRM 1649b (Urban Dust), 2585 (Organic Contaminants in House Dust), 2786 and 2787 (Fine Atmospheric Particulate Matter) were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

Pesticide grade silanized glass wool was purchased from Merck KGaA (Darmstadt, Germany). Glass tubes (straight with notch, 60 mm length x 6 mm O.D. x 5 mm I.D.) and transport adapters were purchased from Gerstel GmbH & Co. KG (Mülheim an der Ruhr, Germany). Prior to use, glass wool plugs and glass tubes were heated at 340 °C for 10 min using a Gerstel Tube Conditioner TC 2 (Gerstel GmbH & Co. KG, Mülheim an der Ruhr, Germany). Quartz microfiber filters (QFF, 25 mm) (Whatman QM-A) were purchased from GE Healthcare Life Sciences (Little Chalfont, Buckinghamshire, UK). Prior to use, QFFs were heated at 550 °C for 2 h using a Nabertherm N11 furnace (Nabertherm GmbH, Lilienthal, Germany).

2.4 Dust, SRM and calibration samples preparation

The dust was passed through a precleaned (DCM) 100 µm stainless steel sieve [16] using a Retsch AS 200 vibratory sieve shaker (Retsch GmbH, Haan, Germany) to remove coarse material (cotton and debris). The sieved dust was then weighed and stored at -18 °C in a hermetically sealed 20-mL amber glass flask until chemical analysis [42].

On the day of analysis, 1 mg of the SRMs and 2 mg of the dust samples were accurately weighed (± 1%) using a Sartorius Cubis MSA 6.6S micro balance (Sartorius AG, Göttingen, Germany) and placed on a quarter of a QFF that had been cut into four parts using scissors on a paper towel. The QFF quarter was then folded, rolled and inserted into a glass tube fitted with a glass wool plug to prevent system contamination by the particles carried by the helium flow. Each

calibration solution in acetone was spiked (1 µL) on a glass wool plug inserted into a glass tube in the presence of a QFF quarter (see Table S3). The dust sample preparation is illustrated in Figure S1.

2.5 Thermal extraction

After the addition of internal standards (ISTDs) by spiking 1 µL of the ISTD solution on the glass wool plug, each glass tube was placed on a 40-position rack that was immediately transferred to a Gerstel MPS (MultiPurpose Sampler) robotic autosampler (Gerstel GmbH & Co. KG, Mülheim an der Ruhr, Germany). Thermal extraction of the analytes was performed using a Gerstel TDU2 automatic thermal desorption device (Gerstel GmbH & Co. KG) coupled directly without transfer line to a Cooled Injection System (CIS, Gerstel GmbH & Co. KG). The thermal extraction process can be divided into two main steps: thermal extraction and transfer into the GC system. In the first step, target compounds are thermally extracted (30 to 325 °C (hold 8 min) at 60 °C/min in the TDU splitless desorption mode) and carried by the helium flow (80 mL/min) up to the cold CIS, equipped with a straight glass liner filled with silanized glass wool and cooled with liquid carbon dioxide (-40 °C), to cryo-focus and concentrate analytes prior to transfer to the capillary column. Second, the trapped compounds are quickly transferred to the capillary column for analysis by heating the CIS (-40 °C to 325 °C (hold 15 min) at 12 °C/s in the solvent vent mode). Two methods were used to cover a wide dynamic range from ultratrace to highly concentrated compounds, differing only by the amount of sample introduced into the capillary column, from 2% (split flow = purge flow to split vent = 100 mL/min; method 2) to 10% (split flow = purge flow to split vent = 18 mL/min; method 1) of the sample.

2.6 GC/MS/MS analysis

The thermal desorption device was interfaced to a 7890A GC system coupled to a 7000B GC/MS Triple Quad (Agilent Technologies, Santa Clara, California, United States) operated in electron impact ionization (EI) mode (70 eV). Helium was used as the column carrier gas at a constant flow rate of 2.0 mL/min. Chromatographic separation, largely based on previously published papers [15,38], was performed on an Rtx®-PCB capillary column (30 m length × 0.25 mm I.D., 0.25 µm film thickness) supplied by Restek Corporation (Bellefonte, Pennsylvania, United States) with the following oven temperature program: 50 °C (hold 2 min), first ramp at 30 °C/min to 140 °C (hold 0 min), second ramp at 10 °C/min to 320 °C (hold 7 min to reach an analysis time of 30 min). The MSD transfer line, ion source and quadrupole temperatures were fixed at 325, 280 and 180 °C, respectively. The mass spectrometer (triple quadrupole) was operated in multiple reaction monitoring (MRM) mode. The two most intense and specific MRM transitions of each compound (quantifier and qualifier transitions) were monitored for identification, confirmation and quantification. They were selected using the pesticides and environmental pollutants MRM database provided by Agilent Technologies for the compounds present in the database or following the usual procedure for others. For phthalates, given the very high concentrations expected for some of them, the transitions selected were not necessarily the most intense to avoid saturating the detector. Dwell times ranged between 8 and 100 ms in 17 time segments. Dwell times were thus fixed, taking into account the number of MRM transitions in each time segment and the width of the chromatographic peaks, so that each peak was represented by at least 10 data points from its beginning to the end. Analytical characteristics of measured compounds are reported in Table 1. A chromatogram of a calibration solution containing all the target

compounds is shown in Figure 1 and Figure S2. A chromatogram of a 1-mg sample of SRM 2585 is also shown in Figure 1.

< Please insert Table 1 (Analytical characteristics of measured compounds) here >

< Please insert Figure 1 (TE-GC/MS/MS complete chromatograms of a calibration solution containing all the target compounds (A) and a 1-mg sample of SRM 2585 (B) (see Table 1 to identify compounds)) here >

2.7 Validation

The limits of detection (LODs) are defined as the lowest concentration of a substance that can be distinguished from the absence of that substance. LODs were estimated from the replicate analysis of a blank sample. Limits of quantification (LOQs) were defined as the lowest concentration of a substance for which the relative standard deviation (RSD) of the raw signal (n = 5) was lower than or equal to 20%, the signal-to-noise ratio (S/N) was greater than or equal to 10, and the raw signal was greater than or equal to 5 times the signal of the blank sample.

Four standard reference materials (SRMs) were used to control method accuracy and precision and identify possible interferences due to the matrix: SRM 1649b (Urban Dust), SRM 2585 (Organic Contaminants in House Dust), SRM 2786 (Fine Atmospheric Particulate Matter, Mean Particle Diameter < 4 µm) and SRM 2787 (Fine Atmospheric Particulate Matter, Mean Particle Diameter < 10 µm). Certified or reference concentrations are provided for PAHs, PCBs, chlorinated pesticides and PBDEs, depending on the standard reference material [43–45]. No certified or reference concentrations are provided for musks, OPs, phthalates or pyrethroids and to our knowledge, no other reference materials were available for these chemical classes. Indicative values were reported in the literature for synthetic musks [46], phthalates [16,20,47–

50], permethrin [16], and tributyl phosphate [16,20,47,48,51–55]. Method accuracy and precision were assessed via replicate analysis (n = 5) of the four SRMs. The arithmetic means of the measured concentrations were compared to indicative, reference or certified concentrations, and method precision was defined as the RSD of the replicates. The proposed method was then applied to five real indoor settled dust samples collected in French schools.

2.8 Quality assurance and quality control (QA/QC)

Several labeled substances were selected to best cover the physical and chemical properties of the targeted analytes. 4,4'-DDT $^{13}C_{12}$, *alpha*-endosulfan D_4, *alpha*-HCH D_6, TBP D_{27}, benzo(g,h,i)perylene D_{12}, chrysene D_{12}, perylene D_{12}, phenanthrene D_{10}, pyrene D_{10}, BBP D_4, DEP D_4, DiBP D_4 and $^{13}C_{12}$-BDE 47, 99 and 153 were added prior to the thermal extraction step and used as ISTDs. More than half of the compounds were quantified using the appropriate ISTD (Table 1) to compensate for the variability associated with the TE-GC/MS/MS analysis, from calibration curves generated for each compound by analyzing at least five different calibration samples. The remaining compounds were quantified without ISTD (external standard calibration). A quadratic fit was used to compensate for the nonlinearity of the instrument response over a wide working range.

Each batch included: i) up to 20 samples (2 mg), ii) several instrumental (glass wool plug) and procedural (QFF quarter and glass wool plug) blank samples analyzed every five samples to assess whether contamination may have occurred during analysis, iii) eight calibration samples and one calibration blank sample to generate quadratic calibration curves intended for quantification, iv) several calibration samples analyzed at the beginning and at the end of the

batch and every five samples to check for the stability of the detector response, v) one calibration sample prepared from commercial solutions provided by other suppliers to validate the preparation of the calibration solutions, and vi) one sample of SRM 2585 (1 mg) analyzed as a regular sample to check for method accuracy.

Positive values for each substance are confirmed by comparing retention times and MRM transitions ratios between calibration samples and dust samples. The data validation protocol of the proposed method included several conditions: (i) the determination coefficient of the calibration curve had to be greater than 0.995, (ii) the response of a substance (area of the chromatographic peak) in the calibration blank sample had to be lower than 50% of that in the calibration sample at the LOQ level, (iii) the concentration of a substance measured in the procedural blank samples analyzed every five samples had to be lower than 25% of that measured in the associated samples, (iv) the concentration of a substance measured in the calibration samples analyzed at the beginning and at the end of the batch and every five samples had to be within ±25% of its nominal concentration value, (v) the concentration of a substance measured in the calibration sample at the LOQ level had to be within ±50% of its nominal concentration value, (vi) the concentration of a substance measured in the calibration sample prepared from commercial solutions provided by other suppliers had to be within ±25% of its nominal concentration value, and (vii) the concentration of a substance measured in the sample of SRM 2585 had to be within the limits set by the laboratory for the current year (±30 to 50% of the mean concentration obtained via replicate analysis of the SRM 2585 on 20 different days (n = 20), depending on whether the measured concentration was close to the limit of quantification or not). If all these conditions were not met, samples were reanalyzed.

To minimize procedural blank contamination, many precautions were taken throughout the protocol. Plastic materials were obviously avoided, and glass materials such as tubes, flasks and

syringes were rigorously rinsed with acetone prior to use. Transport adapters without septa were preferred to those with septa because septa release some compounds such as fluorene and DEP. Furthermore, prior to use, glass wool plugs and glass tubes were heated at 340 °C for 10 min and QFFs at 550 °C for 2 h to remove trace organic compounds and thus minimize background peaks. Despite these precautions and the fact that the LOQs were estimated by accounting for concentrations observed in blank samples during the optimization experiments, some compounds such as phthalates were detected in the procedural blank samples. If concentrations measured in a procedural blank sample exceeded 25% of those measured in a dust sample from the same batch, this sample was reanalyzed. Otherwise, concentrations reported here were not adjusted for procedural blank concentrations.

3. Results and discussion

3.1 Optimization experiments

The main tests carried out during the development of the proposed method focused on the mass of dust sample to be considered for analysis and the percentage of sample to be introduced into the capillary column. These two points were closely linked, because the goal was in both cases to reach the lowest quantification limits, while preserving the robustness of the method. Indeed, thermal extraction of the analytes (30 to 325 °C (hold 8 min) at 60 °C/min) is directly performed from 2 mg of the raw sample, which means that particles and any substances in the sample that can be volatilized are carried by the helium flow up to the injection system to be cryo-focused and concentrated prior to transfer to the capillary column. In these conditions, the system became dirty very quickly, particularly the thermal desorption device, injection system, glass liner and first centimeters of the capillary column, impacting the shape of the chromatographic peaks and

the performances of the method for certain compounds such as PAHs or 4,4'-DDT. It is possible to limit this phenomenon by reducing the amount of sample introduced into the system, which automatically leads to an increase in the limits of quantification. The objective of these tests was therefore to find the best compromise between robustness and sensitivity. It was decided to define the optimal amount of sample to be introduced into the system as the maximum amount that allowed the analysis of 20 samples in the same batch without having to replace the glass liner, clean the thermal desorption device and injection system and/or remove the first centimeters of the capillary column. To do this, two parameters were tested: i) the mass of dust sample to be analyzed (1, 2, 3 or 5 mg) and ii) the split flow (= purge flow to split vent) from which the percentage of sample introduced into the capillary column can be estimated (percentage of sample introduced into the capillary column = helium flow rate x 100 / (helium flow rate + split flow)). The best compromise between robustness and sensitivity was obtained with a mass of 2 mg and a split flow of 18 mL/min, corresponding to the introduction of 10% of the sample into the capillary column. The LOQs thus achieved were satisfactory, but the liners had to be replaced, the thermal desorption device and the injection system required cleaning, and the first centimeters of the capillary column were cut away after each batch of 20 samples (less than 1 h of system shutdown). In addition, the first 30 centimeters of the capillary column had to be removed approximately once for every 4 batches of 20 samples.

3.2 Instrumental performance indicators

Two thermal extraction methods were developed to cover a wide dynamic range, differing only by the amount of sample introduced into the capillary column. The main method (method 1) allowed the introduction of 10% of the sample. In these conditions, LOQs ranged from 5 ng g^{-1} for PCBs, oxadiazon, 4,4'-DDE and 4,4'-DDT to 2000 ng g^{-1} for DEHP for a 2 mg sample of

sieved dust. The second method (method 2), in which only 1% of the sample is introduced, was only implemented for some highly concentrated compounds such as PAHs and phthalates. In these conditions, LOQs were 1875 ng g^{-1} for PAHs and 50,000 ng g^{-1} for phthalates for a 2 mg sample of sieved dust. The combination of the two methods covered several orders of magnitude (3 for PAHs and 4 for phthalates). Quadratic calibration curves were established for each compound by analyzing at least five different calibration samples from the LOD. The determination coefficients were higher than 0.999 for all compounds. This demonstrates that the proposed method (combination of the two methods) is very sensitive while covering a wide dynamic range from ultratrace to highly concentrated compounds. Calibration curve setup is summarized in Table 2.

< Please insert Table 2 (Calibration curve setup of the TE-GC/MS/MS method) here >

3.3 Analysis of SRMs

Target SVOCs were then determined according to the proposed method in five samples (1 mg) of four different standard reference materials (SRM) supplied by the NIST: SRM 1649b (Urban Dust), 2585 (Organic Contaminants in House Dust), 2786 and 2787 (Fine Atmospheric Particulate Matter). Only three compounds were never detected in any of the four SRMs (aldrin, *alpha*-HCH and *gamma*-HCH), and several compounds were quantified for the first time to our knowledge in one or more of these materials (*alpha*-endosulfan in SRM 1649b, oxadiazon in SRM 2585, PCB 28 in SRM 2787, 4,4'-DDE, 4,4'-DDT, tributyl phosphate, PCB 101, 138, 153 and 180, and permethrin in SRMs 2786 and 2787, and BBP, DBP, DEHP, DEP and DiNP in SRMs 1649b, 2786 and 2787). The results are reported in Table 3.

RSDs were systematically less than 25% and most often less than 10%, indicating an excellent precision of the method even at concentrations close to the limits of detection, along with a high degree of homogeneity of the 4 SRMs, while the recommended minimum sample size is 150 mg for the SRM 1649b and 30 mg for the SRMs 2786 and 2787 (no minimum recommended sample size for the SRM 2585). The concentrations measured in the 4 SRMs were overall in good agreement with indicative, reference or certified concentrations. Measured concentrations ranged from 56% (benzo[a]pyrene) to 151% (DEP) of the indicative, reference or certified concentrations (most often between 70 and 120%), except for anthracene (396%) and 4,4'-DDT (45%) in the SRM 2585. Regarding the higher value for anthracene in SRM 2585, a similar result was already reported in previous studies [16,20,37,38], and the authors' hypothesis was that an interfering compound was probably present in the standard reference material; however, no evidence of coelution (splitting or deformation of the chromatographic peak) was observed to validate this hypothesis. A similar result was also reported on an old SRM, the SRM 1649a [29]. The authors initially suspected the possible formation of anthracene during the desorption steps by pyrolysis, but this hypothesis was experimentally discarded. Another hypothesis can be made if we look more closely at the reference concentrations proposed by the NIST for some PAHs, including anthracene, in the other 3 SRMs. Several reference concentrations were indeed proposed depending on the extraction conditions and, in particular, the extraction temperature. The reference concentrations sometimes increase very significantly with the increase in the extraction temperature. For example, the reference concentration for anthracene in the SRM 1649b is 410 ng g^{-1} with an extraction temperature of 100 °C, 601 ng g^{-1} with an extraction temperature of 150 °C, and 978 ng g^{-1} with an extraction temperature of 200 °C, more than twice that at an extraction temperature of 100 °C. Measured concentrations for the PAHs targeted in the present study (i.e., anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[g,h,i]perylene,

fluoranthene and phenanthrene) were compared to the highest provided reference concentrations. In these conditions, measured concentrations for anthracene in the SRMs 1649b, 2786 and 2787 ranged from 112 to 131% of the reference concentrations. The extraction temperature is not specified in the certificate of analysis of the SRM 2585, which was developed a few years earlier than the other three (2005 for SRM 2585, 2009 for SRM 1649b and 2011 for SRMs 2786 and 2787), and only one value (a certified concentration) is available for anthracene. We suspect that the increase of the concentration of some PAHs, including anthracene, with the increase in the extraction temperature would probably also be observed on SRM 2585, and therefore, the result obtained in this study possibly provides a better estimate of the real concentration of anthracene in SRM 2585. As to the lower value for 4,4'-DDT in SRM 2585, a partial degradation of the substance may be considered, but the labeled analogue should have behaved in the same way.

< Please insert Table 3 (SVOC concentrations (ng g^{-1}) in SRMs 1649b, 2585, 2786 and 2787 (1 mg, n = 5)) here >

3.4 Comparison of TE- and ASE-GC/MS/MS methods

The proposed method was compared to a previously published multiresidue method based on pressurized liquid extraction (PLE) and gas chromatography / tandem mass spectrometry (GC/MS/MS) for the simultaneous analysis of almost the same SVOCs in indoor settled dust. A detailed description of this method is available elsewhere [16,56]. Briefly, SVOC extractions were performed on 200 mg of sieved dust with DCM using an Accelerated Solvent Extractor ASE 350 (Dionex Corporation). Organic extracts were concentrated to 1 mL and quantitatively transferred onto Chromabond® NH_2 glass columns prewashed with 6 mL of DCM. Elution was performed with 5 mL of DCM. Organic extracts were then concentrated to 0.5 mL, transferred

into an amber glass vial and stored at -18 °C prior to analysis by GC/MS/MS using a gas chromatograph Trace GC Ultra coupled to a mass spectrometer TSQ Quantum XLS (Thermo Scientific) operated in electron impact ionization (EI) mode (70 eV).

Both methods were compared in terms of LOD and LOQ, and in terms of accuracy and precision on the basis of the results obtained on the SRM 2585. All of these data are shown in Table 4. While the amount of sample required for analysis is 100 times lower (2 mg vs 200 mg) with the proposed method, LODs and LOQs were equivalent to or better than those of the previously published method (except for galaxolide, *alpha*-endosulfan, benzo[a]pyrene, BDE 85 and DEHP), which were low enough to detect thirty-two compounds in more than half of the 145 dust samples collected in French dwellings [56]. The precision of both methods, defined as the RSD of the replicates (5 for the proposed method and 18 for the published one), was systematically lower than 21%. For the accuracy, measured concentrations with the proposed method ranged from 72% (PCB 153) to 151% (DEP) of the certified, reference or indicative concentrations, except for anthracene (396%), and from 68% (PCB 153) to 145% (tributyl phosphate) with the published method, except again for anthracene (193%). These results show that the performances of both methods are relatively close, highlighting the capabilities of the proposed method to detect and quantify a large panel of SVOCs from a very small amount of sample without impact on the performance in terms of accuracy and precision.

Finally, both methods were compared in terms of operator time required to prepare a batch of twenty samples (excluding the sieving step). With the proposed method, the sample preparation procedure is limited to i) the cutting of the QFFs into four parts, ii) the weighing of the sieved dust directly on a quarter of a QFF, iii) the folding and rolling of the QFF quarters before their introduction into the glass tubes, and iv) the addition of the ISTDs. Approximately 2 h are required to complete these different steps. With the previously published method, the sample

preparation procedure is much longer since it includes i) the weighing and mixing of the sieved dust and diatomaceous earth, ii) the preparation and filling of the extraction cells, iii) the addition of the ISTDs, iv) the handling of the extraction system, v) the postextraction purification of the organic extracts preceded and followed by a concentration step and vi) the transfer of the extracts to 1.5-mL vials. The operator time to complete the sample preparation procedure is estimated at 8 h, 4 times that of the proposed method, which shows that our method allows for significantly reduced operator time compared to a conventional method and thus a lower cost of analysis.

< Please insert Table 4 (Comparison of TE- and ASE-GC/MS/MS methods) here >

3.5 Application to five real dust samples

The proposed method was applied to five randomly selected real indoor settled dust samples (noted as sample 1, sample 2, sample 3, sample 4 and sample 5) collected in French schools during the nationwide survey (2013-2017) carried out by the French Observatory of Indoor Air Quality (OQAI). Each sample was analyzed five times for the calculation of mean concentrations and RSDs. The results are presented in Table S5. All compounds were detected above LOD at least once, except for BDE 85, and 33 of the 44 target compounds were detected in all five samples. Concentrations were widely varied, ranging from several ng g^{-1} for PBDEs, PCBs and organochlorines to several mg g^{-1} for some phthalates (BBP, DEHP, DiBP and DiNP). These results demonstrate the presence of a large panel of SVOCs in French schools and confirm, once again, the capabilities of the proposed method to detect and quantify SVOCs from a very small amount of sample.

Moreover, RSDs were mostly less than 20% (nearly 83% of results above the LOD), confirming the excellent precision of the method already demonstrated on SRMs, even at concentrations close to the limits of detection. However, some compounds presented higher RSDs, up to 90%,

on one or two samples. This was the case for some PBDEs in samples 2 and 3 and some PCBs in samples 4 and 5 because, each time, one of the five results was much higher than the others. The homogeneity of the dust sample and the way the SVOCs contaminate the floor dust may explain these results. Indeed, a dust sample is very heterogeneous [57] because it contains large particles, debris and small objects such as hair, feathers, fibers, buttons, small stones, pieces of plastic, etc. To obtain a homogeneous sample, all dust samples were passed through a 100-µm sieve. However, even after this sieving step, some dust samples remain visually heterogeneous, because hair and fibers can pass through the sieve and possibly affect the analytical results, especially when the analysis is performed from a very small part of the sample. It should be noted that the SRM 2585 was prepared from approximately 70% of material passed through a 100-µm sieve and 30% of material mixed, tumbled and separated from unwanted debris and finally passed through a 90-µm sieve. The SRM 1649b was prepared from atmospheric particulate material passed through a 63-µm sieve and then mixed. For the SRMs 2786 and 2787, they consist of particles with a mean diameter of less than 4 and 10 µm, respectively. The protocols used for the preparation of these SRMs allow a more homogeneous sample to be obtained than the present protocol, which may explain why this phenomenon has not been observed on SRMs, while the amount of SRMs required for analysis was even smaller (1 mg for SRMs vs 2 mg for samples). Furthermore, the contamination of dust by SVOCs may occur via volatilization and recondensation of the SVOCs on dust particles, direct transfer from horizontal surfaces to dust, or weathering or abrasion of polymers [58]. SVOCs can therefore be sorbed onto the surface of dust particles or be a constituent of these particles, which may explain why some compounds presented higher RSDs than others for the same sample. To test this hypothesis, three samples (2, 3 and 4) were reanalyzed after a grinding step. Approximately 30 mg of sieved dust sample was accurately weighed (± 0.1 mg) on a piece of paper and transferred to a 5-mL stainless steel

grinding jar with one 10 mm ball per jar. Grinding was performed in the mixer mill MM400 (Retsch GmbH, Haan, Germany) for 10 min at 25 Hz. The dust powder, after recovery on a piece of paper, was transferred into an amber glass vial that was then sealed and stored at -18 °C until analysis. The results for compounds with the highest RSDs are presented in Table S5 and illustrated in Figure 2. In these conditions, RSDs have been significantly reduced, indicating that a grinding step can be used in the case of samples that remain heterogeneous after the sieving step and for which there is consequently a risk of under- or overquantification.

< Please insert Figure 2 (Box plots showing minimum, maximum, 25th and 75th percentiles, arithmetic mean (+) and median (n = 5) of PBDE concentrations (ng g^{-1}) in the sieved samples 2 and 3 (A) and PCB concentrations (ng g^{-1}) in the sieved sample 4 (B) with (w/) and without (w/o) grinding) here >

4. Conclusions

To the best of our knowledge, this is the first study to propose an analytical method based on thermal extraction for the determination of such a large panel of SVOCs in settled dust samples. Provided that the system is thoroughly cleaned between each batch of twenty samples, this method is simple, sensitive, accurate and precise, while offering a cost-effective and environmentally friendly sample preparation procedure. It provides many advantages over conventional methods, but two features are particularly interesting: i) its ability to precisely and accurately quantify a wide range of SVOCs from trace (a few ng g^{-1}) to highly concentrated (several mg g^{-1}) compounds from only 2 mg of sieved sample and ii) its ease of use and very rapid implementation in only three steps (sieving, weighing and analysis), therefore making it

particularly appropriate for environmental monitoring programs and large-scale studies and usable by the largest number of laboratories. This method was then applied to the floor dust samples collected during the school nationwide survey (2013-2017) carried out by the French Observatory of Indoor Air Quality (OQAI) in 588 classrooms from 301 schools randomly drawn across France [41]. It should also be noted that for this method, the laboratory obtained Cofrac (French Committee for Accreditation) accreditation in accordance with the ISO/CEI 17025 standard.

CRediT author statement

- Fabien Mercier: conceptualization, methodology, validation, formal analysis, writing - Original Draft, visualization, supervision, funding acquisition
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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1

Analytical characteristics of measured compounds.

	Compound[a]	CAS number	Chemical family	ISTD	Time segment	t_R (min)	Quantifier MRM transition Precursor > Product (CE (eV))	Qualifier MRM transition Precursor > Product (CE (eV))
	Target compounds							
1	DEP	84-66-2	Phthalates	DEP D_4	1	10.6	177.0 > 65.0 (35)	176.0 > 149.0 (5)
2	TBP	126-73-8	OPs	TBP D_{27}	1	10.8	99.0 > 81.0 (20)	99.0 > 63.0 (35)
3	*alpha*-HCH	319-84-6	OCs	*alpha*-HCH D_6	2	12.3	216.9 > 181.0 (5)	218.9 > 183.0 (5)
4	*gamma*-HCH	58-89-9	OCs	*alpha*-HCH D_6	3	13.1	181.1 > 145.0 (15)	216.9 > 181.0 (5)
5	Galaxolide	1222-05-5	Musks	DiBP D_4	3	13.1	243.0 > 213.0 (11)	258.0 > 243.0 (7)
6	Tonalide	21145-77-7	Musks	None	3	13.2	258.0 > 243.0 (5)	243.0 > 187.0 (5)
7	DiBP	84-69-5	Phthalates	DiBP D_4	3	13.3	167.0 > 149.0 (5)	104.0 > 50.0 (30)
8	Phenanthrene	85-01-8	PAHs	Phenanthrene D_{10}	3	13.4	178.1 > 152.1 (25)	176.1 > 150.1 (25)
9	Anthracene	120-12-7	PAHs	Phenanthrene D_{10}	3	13.6	178.1 > 152.1 (25)	178.1 > 151.1 (30)
10	PCB 31	16606-02-3	PCBs	None	4	14.1	256.0 > 186.0 (25)	258.0 > 186.0 (25)
11	PCB 28	7012-37-5	PCBs	None	4	14.2	256.0 > 186.0 (25)	258.0 > 186.0 (25)
12	DBP	84-74-2	Phthalates	DiBP D_4	4	14.4	223.0 > 149.0 (5)	205.0 > 149.0 (5)
13	PCB 52	35693-99-3	PCBs	None	5	14.7	255.0 > 220.0 (10)	289.9 > 219.9 (25)
14	Aldrin	309-00-2	OCs	None	5	14.8	262.9 > 192.9 (35)	254.9 > 220.0 (20)
15	PCB 101	37680-73-2	PCBs	None	6	16.4	253.9 > 184.0 (35)	325.9 > 255.9 (30)
16	Fluoranthene	206-44-0	PAHs	Pyrene D_{10}	6	16.5	201.1 > 200.1 (15)	202.1 > 152.1 (30)
17	Oxadiazon	19666-30-9	Oxadiazolones	None	6	16.6	174.9 > 112.0 (15)	174.9 > 76.0 (35)
18	*alpha*-Endosulfan	959-98-8	OCs	*alpha*-Endosulfan D_4	6	16.7	194.9 > 159.0 (5)	194.9 > 160.0 (5)
19	4,4'-DDE	72-55-9	OCs	None	7	17.0	246.1 > 176.2 (30)	315.8 > 246.0 (15)
20	Pyrene	129-00-0	PAHs	Pyrene D_{10}	7	17.1	201.1 > 200.0 (15)	200.1 > 174.0 (25)
21	Dieldrin	60-57-1	OCs	None	7	17.2	262.9 > 193.0 (35)	277.0 > 241.0 (5)
22	PCB 118	31508-00-6	PCBs	None	8	17.9	325.9 > 255.9 (30)	325.9 > 253.9 (30)
23	PCB 153	35065-27-1	PCBs	None	8	18.1	359.9 > 289.9 (25)	287.9 > 217.9 (40)
24	BBP	85-68-7	Phthalates	BBP D_4	8	18.3	123.0 > 79.0 (10)	123.0 > 77.0 (25)
25	PCB 105	32598-14-4	PCBs	None	8	18.4	325.9 > 255.9 (30)	325.9 > 253.9 (30)
26	PCB 138	35065-28-2	PCBs	None	9	18.7	359.9 > 289.9 (30)	287.9 > 217.9 (40)
27	4,4'-DDT	50-29-3	OCs	4,4'-DDT $^{13}C_{12}$	9	18.7	235.0 > 165.2 (20)	237.0 > 165.2 (20)
28	DEHP	117-81-7	Phthalates	None	10	19.4	167.0 > 65.0 (35)	113.0 > 71.1 (0)
29	PCB 180	35065-29-3	PCBs	None	10	19.9	393.8 > 323.8 (30)	393.8 > 358.8 (15)
30	Benzo(a)anthracene	56-55-3	PAHs	Chrysene D_{12}	11	20.2	228.1 > 226.1 (30)	114.0 > 101.1 (10)
31	BDE 47	5436-43-1	PBDEs	BDE 47 $^{13}C_{12}$	11	20.3	325.8 > 218.8 (30)	325.8 > 216.8 (30)
32	Chrysene	218-01-9	PAHs	Chrysene D_{12}	11	20.4	228.1 > 226.1 (30)	113.1 > 112.1 (10)
33	DiNP	68515-48-0	Phthalates	None	11	20.5-22.3	293.0 > 149.0 (7)	167.0 > 65.0 (35)
34	Permethrin	52645-53-1	Pyrethroids	BDE 99 $^{13}C_{12}$	11	21.1-21.3	183.1 > 165.1 (10)	183.1 > 168.1 (10)
35	BDE 100	189084-64-8	PBDEs	BDE 99 $^{13}C_{12}$	11	21.8	563.6 > 403.7 (20)	403.7 > 296.7 (35)
36	BDE 99	60348-60-9	PBDEs	BDE 99 $^{13}C_{12}$	11	22.3	563.6 > 403.7 (20)	565.6 > 405.6 (20)
37	Benzo(b)fluoranthene	205-99-2	PAHs	Chrysene D_{12}	12	22.9	252.1 > 250.1 (35)	126.0 > 113.1 (10)
38	Benzo(k)fluoranthene	207-08-9	PAHs	Perylene D_{12}	12	22.9	252.1 > 250.1 (30)	126.1 > 113.1 (10)
39	BDE 85	182346-21-0	PBDEs	BDE 153 $^{13}C_{12}$	13	23.4	564.0 > 404.0 (23)	406.0 > 297.0 (35)
40	Benzo(a)pyrene	50-32-8	PAHs	Perylene D_{12}	14	23.7	252.1 > 250.1 (35)	125.0 > 124.1 (10)
41	BDE 153	68631-49-2	PBDEs	BDE 153 $^{13}C_{12}$	15	24.3	643.6 > 483.6 (20)	483.7 > 323.6 (40)
42	Dibenzo(a,h)anthracene	53-70-3	PAHs	Benzo(g,h,i)perylene D_{12}	16	27.1	278.1 > 276.1 (35)	125.0 > 124.1 (10)

	Compound[a]	CAS number	Chemical family	ISTD	Time segment	t_R (min)	Quantifier MRM transition Precursor > Product (CE (eV))	Qualifier MRM transition Precursor > Product (CE (eV))
43	Indeno(1,2,3-cd)pyrene	193-39-5	PAHs	Benzo(g,h,i)perylene D_{12}	16	27.1	138.1 > 137.1 (10)	137.0 > 136.0 (15)
44	Benzo(g,h,i)perylene	191-24-2	PAHs	Benzo(g,h,i)perylene D_{12}	17	28.2	138.0 > 137.0 (15)	137.0 > 136.0 (15)
	Labeled ISTDs							
a	DEP D_4	93952-12-6	Phthalates		1	10.6	181.0 > 153.0 (7)	152.7 > 69.0 (23)
b	TBP D_{27}	61196-26-7	OPs		1	10.6	103.0 > 83.0 (21)	103.0 > 62.9 (41)
c	*alpha*-HCH D_6	86194-41-4	OCs		2	12.2	223.9 > 186.9 (5)	221.9 > 184.9 (7)
d	DiBP D_4	358730-88-8	Phthalates		3	13.3	152.7 > 69.0 (19)	152.7 > 97.0 (19)
e	Phenanthrene D_{10}	1517-22-2	PAHs		3	13.4	188.1 > 184.1 (35)	94.0 > 80.0 (9)
f	*alpha*-Endosulfan D_4	203645-57-2	OCs		6	16.7	198.8 > 164.0 (7)	198.8 > 129.0 (25)
g	Pyrene D_{10}	1718-52-1	PAHs		7	17.1	212.2 > 208.1 (45)	106.0 > 92.0 (11)
h	BBP D_4	93951-88-3	Phthalates		8	18.3	153.2 > 69.0 (25)	153.2 > 97.0 (17)
i	4,4'-DDT $^{13}C_{12}$	104215-84-1	OCs		9	18.7	223.9 > 188.1 (33)	223.9 > 161.0 (39)
j	BDE 47 $^{13}C_{12}$	n/a	PBDEs		11	20.3	337.8 > 149.0 (56)	497.7 > 337.9 (23)
k	Chrysene D_{12}	1719-03-5	PAHs		11	20.3	240.1 > 236.2 (39)	120.1 > 106.1 (9)
l	BDE 99 $^{13}C_{12}$	n/a	PBDEs		11	22.3	415.8 > 148.0 (60)	575.7 > 415.9 (23)
m	Perylene D_{12}	1520-96-3	PAHs		14	23.9	264.0 > 260.2 (45)	132.0 > 118.1 (13)
n	BDE 153 $^{13}C_{12}$	n/a	PBDEs		15	24.3	495.7 > 335.9 (45)	655.7 > 495.9 (23)
o	Benzo(g,h,i)perylene D_{12}	93951-66-7	PAHs		17	28.1	144.1 > 142.1 (19)	288.2 > 284.2 (45)

[a] Compounds listed in order of retention times

Table 2

Calibration curve setup of the TE-GC/MS/MS method.

Compound	Concentration (ng g^{-1})[a]								Curve fit (CF)	CF origin	CF weight	R^2
	Level 1 (LOD)	Level 2 (LOQ)	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8				
Method 1												
PCBs and oxadiazon, 4,4'-DDE and 4,4'-DDT	2.5	5	12.5	25	62.5	125	312.5	625				
Aldrin, dieldrin, *alpha*-HCH, *gamma*-HCH and BDE 47, 99 and 100	5	10	25	50	125	250	625	1250				
PAHs and BDE 85 and 153	10	20	50	100	250	500	1250	2500				
Tonalide	12.5	25	62.5	125	312.5	625	1562.5	3125				
Permethrin and *alpha*-endosulfan	25	50	125	250	625	1250	3125	6250	Quadratic	Ignore	None	0.999
Galaxolide and tributyl phosphate	50	100	250	500	1250	2500	6250	12,500				
DEP, DiBP and BBP	200	400	1000	2000	5000	10,000	25,000	50,000				
DBP and DiNP	500	1000	2500	5000	12,500	25,000	62,500	125,000				
DEHP	1000	2000	5000	10,000	25,000	50,000	125,000	250,000				
Method 2												
PAHs	1875	4687.5	9375	18,750	37,500	75,0000	-	-	Quadratic	Ignore	None	0.999
Phthalates	50,000	125,000	250,000	500,000	1,000,000	2,000,000	6,250,000	12,500,000				

[a] for a 2 mg sample of sieved dust

Table 3

SVOC concentrations (ng g^{-1}) in SRMs 1649b, 2585, 2786 and 2787 (1 mg, n = 5).

Compound	SRM 1649b			SRM 2585			SRM 2786			SRM 2787		
	Measured (RSD %)	Reported	Measured/ reported (%)	Measured (RSD %)	Reported	Measured/ reported (%)	Measured (RSD %)	Reported	Measured/ reported (%)	Measured (RSD %)	Reported	Measured/ reported (%)
Musks												
Galaxolide	< 200	n.r.	-	1600 (10)	1460[c]	110	<200	n.r.	-	< 200	n.r.	-
Tonalide	< 50	n.r.	-	1700 (5)	1650[c]	103	< 50	n.r.	-	< 50	n.r.	-
OCs												
4,4'-DDE	62 (3)	50.7[a]	122	300 (2)	261[a]	115	25 (7)	n.r.	-	35 (2)	n.r.	-
4,4'-DDT	350 (4)	235[b]	149	50 (19)	111[a]	45	85 (7)	n.r.	-	83 (6)	n.r.	-
Aldrin	< 20	n.r.	-	< 20	n.r.	-	< 20	n.r.	-	< 20	n.r.	-
Alpha-endosulfan	120 (24)	n.r.	-	< 100	n.r.	-	< 100	n.r.	-	< 100	n.r.	-
Alpha-HCH	< 20	13.7[b]	-	< 20	n.r.	-	< 20	n.r.	-	< 20	n.r.	-
Dieldrin	< 20	n.r.	-	100 (8)	88.0[b]	114	< 20	n.r.	-	< 20	n.r.	-
Gamma-HCH	< 20	3.1[b]	-	< 20	4.06[b]	-	< 20	n.r.	-	< 20	n.r.	-
OPs												
Tributyl phosphate	< 200	n.r.	-	290 (21)	240[d]	121	711 (24)	n.r.	-	1500 (21)	n.r.	-
Oxadiazolones												
Oxadiazon	< 10	n.r.	-	15 (12)	n.r.	-	< 10	n.r.	-	< 10	n.r.	-
PAHs												
Anthracene	1100 (7)	978[b]	112	380 (5)	96.0[a]	396	750 (12)	607[b]	124	520 (6)	398[b]	131
Benzo[a]anthracene	1900 (9)	2350[b]	81	1200 (4)	1160[a]	103	3900 (5)	4820[a]	81	3600 (2)	5790[b]	62
Benzo[a]pyrene	1700 (14)	3040[b]	56	860 (7)	1140[a]	75	2600 (10)	3700[a]	70	1900 (4)	3228[a]	59
Benzo[b]fluoranthene	6700 (4)	6180[a]	108	3900 (6)	2700[a]	144	9800 (3)	7510[a]	130	8200 (5)	6560[a]	125
Benzo[g,h,i]perylene	3000 (4)	4310[b]	70	1900 (7)	2280[a]	83	4200 (7)	5600[a]	75	3400 (2)	4990[a]	68
Benzo[k]fluoranthene	1200 (9)	1702[a]	71	830 (5)	1330[a]	62	2300 (9)	3480[a]	66	2000 (4)	2940[a]	68
Chrysene	2600 (8)	3045[a]	85	1900 (5)	2260[a]	84	6900 (5)	6820[a]	101	6500 (2)	7740[a]	84
Dibenzo[a,h]anthracene	340 (7)	294[b]	116	340 (6)	301[a]	113	610 (7)	717[a]	85	520 (3)	530[b]	98
Fluoranthene	5600 (9)	6600[b]	85	4000 (5)	4380[a]	91	8400 (4)	10,280[a]	82	8900 (2)	12,280[a]	72
Indeno[1,2,3-cd]pyrene	2300 (5)	2890[a]	80	1900 (6)	2080[a]	91	3900 (8)	4870[a]	80	3300 (2)	4180[a]	79
Phenanthrene	4500 (9)	4400[b]	102	2200 (5)	1920[a]	115	3800 (8)	4140[b]	92	3900 (5)	4550[b]	86
Pyrene	4800 (11)	4980[a]	96	3100 (6)	3290[a]	94	7500 (4)	8010[a]	94	8200 (3)	9600[a]	85
PBDEs												
BDE 47	< 20	n.r.	-	500 (3)	497[a]	101	< 20	n.r.	-	< 20	9.5[b]	-
BDE 85	< 40	n.r.	-	42 (4)	43.8[a]	96	< 40	n.r.	-	< 40	n.r.	-
BDE 99	< 20	n.r.	-	820 (5)	892[a]	92	< 20	7.60[a]	-	< 20	5.83[a]	-
BDE 100	< 20	n.r.	-	140 (2)	145[a]	97	< 20	2.34[b]	-	< 20	2.19[b]	-
BDE 153	< 40	n.r.	-	110 (5)	119[a]	92	< 40	1.71[b]	-	< 40	1.52[b]	-

Compound	SRM 1649b			SRM 2585			SRM 2786			SRM 2787		
	Measured (RSD %)	Reported	Measured/ reported (%)	Measured (RSD %)	Reported	Measured/ reported (%)	Measured (RSD %)	Reported	Measured/ reported (%)	Measured (RSD %)	Reported	Measured/ reported (%)
PCBs												
PCB 28	17 (9)	17.8[b]	96	13 (8)	13.4[a]	97	< 10	n.r.	-	10 (5)	n.r.	-
PCB 31	14 (20)	14.6[b]	96	20 (13)	14.0[a]	143	< 10	n.r.	-	< 10	n.r.	-
PCB 52	17 (11)	24.3[a]	70	21 (8)	21.8[a]	96	< 10	n.r.	-	< 10	n.r.	-
PCB 101	39 (16)	56.4[a]	69	30 (3)	29.8[a]	101	12 (10)	n.r.	-	16 (6)	n.r.	-
PCB 105	8.9 (6)	10.0[a]	89	15 (10)	13.2[a]	114	< 10	n.r.	-	< 10	n.r.	-
PCB 118	18 (8)	24[b]	75	29 (9)	26.3[a]	110	< 10	n.r.	-	< 10	n.r.	-
PCB 138	50* (9)	61[b]	82	36 (12)	27.6[a]	130	43 (6)	n.r.	-	54 (3)	n.r.	-
PCB 153	58* (10)	76.6[a]	76	29 (8)	40.2[a]	72	41 (7)	n.r.	-	54 (3)	n.r.	-
PCB 180	70* (13)	74.2[b]	94	19 (11)	18.4[a]	103	56 (5)	n.r.	-	66 (8)	n.r.	-
Phthalates												
BBP	3300 (3)	n.r.	-	71,000 (7)	91,000[e]	78	1700 (7)	n.r.	-	900 (7)	n.r.	-
DBP	2900 (4)	n.r.	-	29,000 (9)	30,000[e]	97	12,000 (6)	n.r.	-	11,000 (4)	n.r.	-
DEHP	32,000 (1)	n.r.	-	450,000 (1)	490,000[e]	92	95,000 (5)	n.r.	-	61,000 (4)	n.r.	-
DEP	1000 (11)	n.r.	-	11,000* (10)	7300[e]	151	< 800	n.r.	-	< 800	n.r.	-
DiBP	< 800	n.r.	-	6200 (9)	6100[e]	102	2200 (8)	n.r.	-	2200 (4)	n.r.	-
DiNP	7100 (2)	n.r.	-	170,000 (4)	170,000[f]	100	58,000 (5)	n.r.	-	57,000 (3)	n.r.	-
Pyrethroids												
Permethrin	< 100	n.r.	-	4800 (3)	4970[g]	97	161 (9)	n.r.	-	160 (6)	n.r.	-

n.r., not reported; [a] Certified concentration from the certificate of analysis of the Standard Reference Material (SRM); [b] Reference concentration from the certificate of analysis of the Standard Reference Material (SRM); [c] Indicative concentration from Peck et al. [46]; [d] Arithmetic mean of indicative concentrations from Mercier et al. [16], Raffy et al. [20], Bergh et al. [47], Luongo et al. [48], Van den Eede et al. [51], Ali et al. [52], Brandsma et al. [53], Brandsma et al. [54] and Van den Eede et al. [55] (Table S4); [e] Arithmetic mean of indicative concentrations from Mercier et al. [16], Raffy et al. [20], Bergh et al. [47], Luongo et al. [48], Larsson et al. [49] and Christia et al. [50] (Table S4); [f] Arithmetic mean of indicative concentrations from Mercier et al. [16], Raffy et al. [20], Luongo et al. [48], Larsson et al. [49] and Christia et al. [50] (Table S4); [g] Indicative concentration from Mercier et al. [16]; * n = 4

Table 4

Comparison of TE- and ASE-GC/MS/MS methods.

Compound	TE-GC/MS/MS method from 2 mg of sieved dust (this method)					ASE-GC/MS/MS method from 200 mg of sieved dust (Mandin et al. [56])				
	LOD (ng g^{-1})	LOQ (ng g^{-1})	SVOC concentrations (ng g^{-1}) in SRM 2585 (1 mg, n = 5)			LOD (ng g^{-1})	LOQ (ng g^{-1})	SVOC concentrations (ng g^{-1}) in SRM 2585 (200 mg, n = 18)		
			Measured (RSD %)	Reported	Measured/ reported (%)			Measured (RSD %)	Reported	Measured/ reported (%)
Musks										
Galaxolide	50	100	1600 (10)	1460[c]	110	26.3	65.8	1430 (16)	1460[c]	98
Tonalide	12.5	25	1700 (5)	1650[c]	103	26.3	65.8	1700 (16)	1650[c]	103
OCs										
4,4'-DDE	2.5	5.0	300 (2)	261[a]	115	2.1	5.3	201 (16)	261[a]	77
Aldrin	5.0	10	< 20	n.r.	-	5.3	13.2	< 13.2	n.r.	-
Alpha-endosulfan	25	50	< 100	n.r.	-	5.3	13.2	< 13.2	n.r.	-
Dieldrin	5.0	10	100 (8)	88.0[b]	114	5.3	13.2	88.2 (18)	88.0[b]	100
Gamma-HCH	5.0	10	< 20	4.06[b]	-	5.3	13.2	< 13.2	4.06[b]	-
OPs										
Tributyl phosphate	50	100	290 (21)	240[d]	121	65.8	197	347 (14)	240[d]	145
Oxadiazolones										
Oxadiazon	2.5	5.0	15 (12)	n.r.	-	5.3	13.2	< 13.2	n.r.	-
PAHs										
Anthracene	10	20	380 (5)	96.0[a]	396	13.2	26.3	186 (14)	96.0[a]	193
Benzo[a]pyrene	10	20	860 (7)	1140[a]	75	5.3	13.2	996 (10)	1140[a]	87
Phenanthrene	10	20	2200 (5)	1920[a]	115	13.2	26.3	1860 (16)	1920[a]	97
PBDEs										
BDE 47	5.0	10	500 (3)	497[a]	101	5.3	13.2	512 (15)	497[a]	103
BDE 85	10	20	42 (4)	43.8[a]	96	5.3	13.2	40.8 (16)	43.8[a]	93
BDE 99	5.0	10	820 (5)	892[a]	92	5.3	13.2	827 (14)	892[a]	93
BDE 100	5.0	10	140 (2)	145[a]	97	5.3	13.2	140 (21)	145[a]	96
BDE 153	10	20	110 (5)	119[a]	92	21.1	52.6	105 (20)	119[a]	88
PCBs										
PCB 28	2.5	5.0	13 (8)	13.4[a]	97	2.1	5.3	16.1 (20)	13.4[a]	120
PCB 31	2.5	5.0	20 (13)	14.0[a]	143	2.1	5.3	12.5 (15)	14.0[a]	89
PCB 52	2.5	5.0	21 (8)	21.8[a]	96	2.1	5.3	18.0 (16)	21.8[a]	82
PCB 101	2.5	5.0	30 (3)	29.8[a]	101	2.1	5.3	31.1 (20)	29.8[a]	104
PCB 105	2.5	5.0	15 (10)	13.2[a]	114	2.1	5.3	11.2 (16)	13.2[a]	85
PCB 118	2.5	5.0	29 (9)	26.3[a]	110	2.1	5.3	25.7 (17)	26.3[a]	98
PCB 138	2.5	5.0	36 (12)	27.6[a]	130	2.1	5.3	28.5 (18)	27.6[a]	103
PCB 153	2.5	5.0	29 (8)	40.2[a]	72	2.1	5.3	27.1 (18)	40.2[a]	68

Compound	TE-GC/MS/MS method from 2 mg of sieved dust (this method)					ASE-GC/MS/MS method from 200 mg of sieved dust (Mandin et al. [56])				
	LOD (ng g^{-1})	LOQ (ng g^{-1})	SVOC concentrations (ng g^{-1}) in SRM 2585 (1 mg, n = 5)			LOD (ng g^{-1})	LOQ (ng g^{-1})	SVOC concentrations (ng g^{-1}) in SRM 2585 (200 mg, n = 18)		
			Measured (RSD %)	Reported	Measured/ reported (%)			Measured (RSD %)	Reported	Measured/ reported (%)
Phthalates										
BBP	200	400	71,000 (7)	91,000[e]	78	526	1053	98,000 (14)	91,000[e]	108
DBP	500	1000	29,000 (9)	30,000[e]	97	526	1053	29,000 (9)	30,000[e]	97
DEHP	1000	2000	450,000 (1)	490,000[e]	92	421	1053	540,000 (14)	490,000[e]	110
DEP	200	400	11,000* (10)	7300[e]	151	1053	2632	8610 (15)	7300[e]	118
DiBP	200	400	6200 (9)	6100[e]	102	526	1053	6310 (20)	6100[e]	103
DiNP	500	1000	170,000 (4)	170,000[f]	100	421	1053	178,000 (12)	170,000[f]	105
Pyrethroids										
Permethrin	25	50	4800 (3)	4970[g]	97	26.3	65.8	5070 (8)	4970[g]	102

n.r., not reported; [a] Certified concentration from the certificate of analysis of the Standard Reference Material (SRM); [b] Reference concentration from the certificate of analysis of the Standard Reference Material (SRM); [c] Indicative concentration from Peck et al. [46]; [d] Arithmetic mean of indicative concentrations from Mercier et al. [16], Raffy et al. [20], Bergh et al. [47], Luongo et al. [48], Van den Eede et al. [51], Ali et al. [52], Brandsma et al. [53], Brandsma et al. [54] and Van den Eede et al. [55] (Table S4); [e] Arithmetic mean of indicative concentrations from Mercier et al. [16], Raffy et al. [20], Bergh et al. [47], Luongo et al. [48], Larsson et al. [49] and Christia et al. [50] (Table S4); [f] Arithmetic mean of indicative concentrations from Mercier et al. [16], Raffy et al. [20], Luongo et al. [48], Larsson et al. [49] and Christia et al. [50] (Table S4); [g] Indicative concentration from Mercier et al. [16]; * n = 4

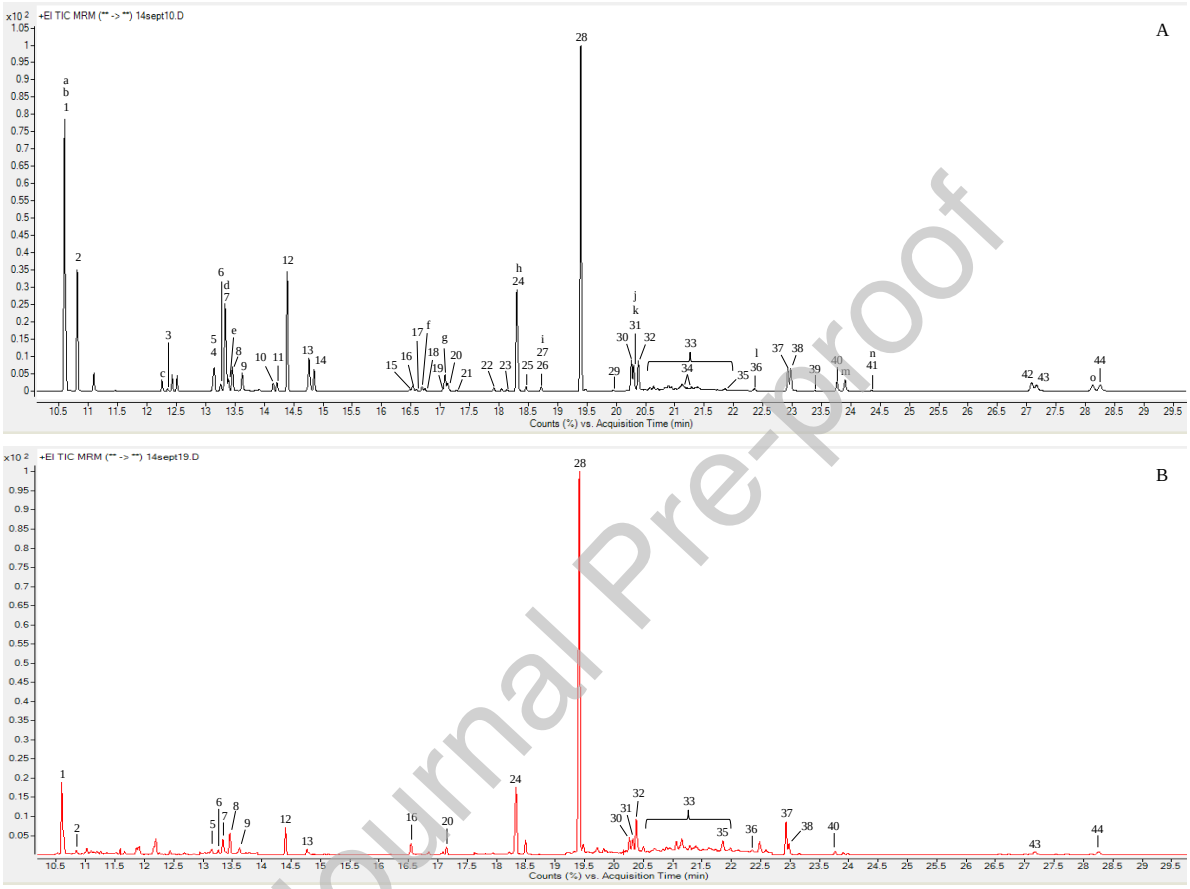

Figure 1

TE-GC/MS/MS complete chromatograms of a calibration solution containing all the target compounds (A) and a 1-mg sample of SRM 2585 (B) (see Table 1 to identify compounds).

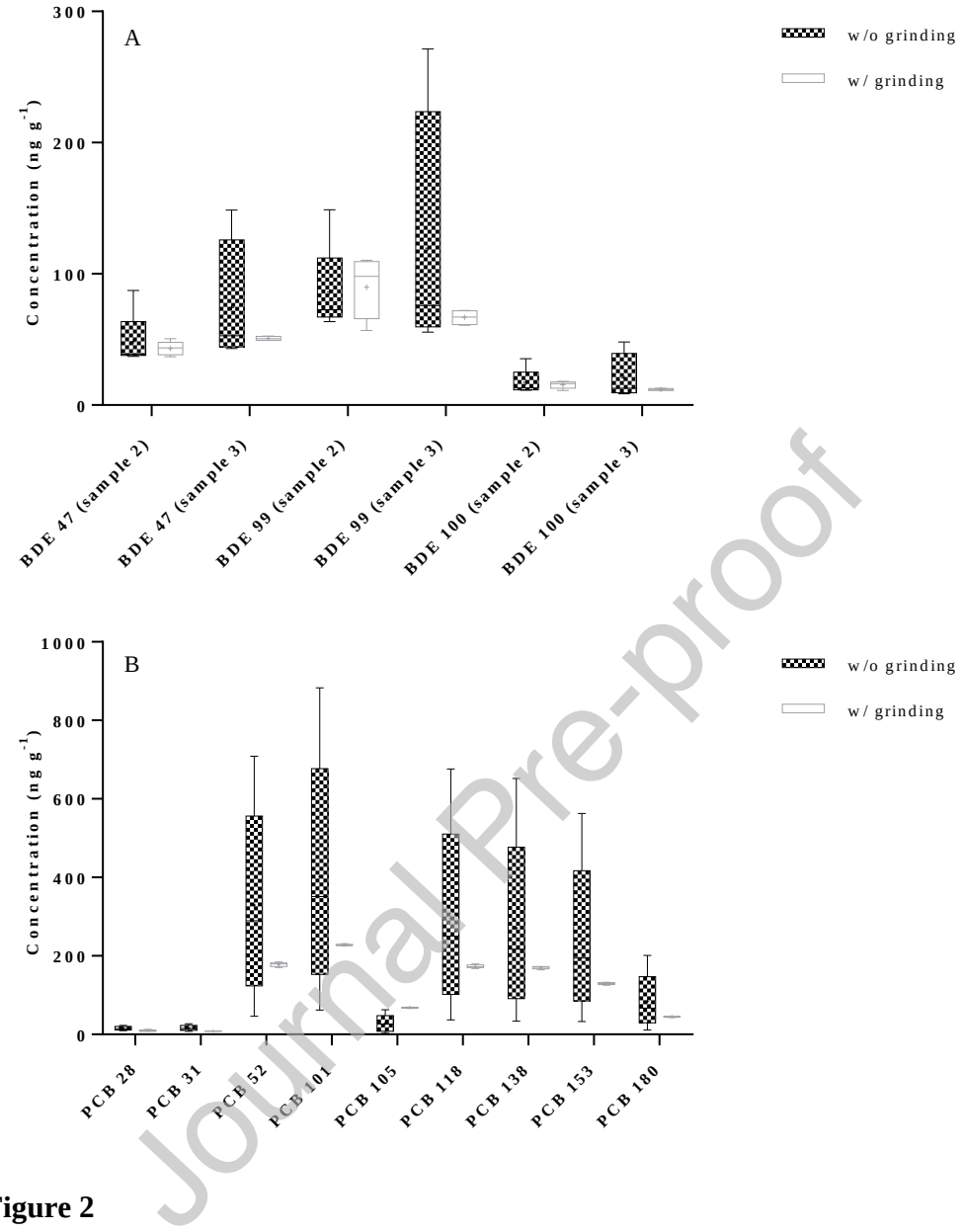

Figure 2

Box plots showing minimum, maximum, 25th and 75th percentiles, arithmetic mean (+) and median (n = 5) of PBDE concentrations (ng g^{-1}) in the sieved samples 2 and 3 (A) and PCB concentrations (ng g^{-1}) in the sieved sample 4 (B) with (w/) and without (w/o) grinding.