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Determination of parabens in house dust by pressurised hot water extraction followed by stir bar sorptive extraction and thermal desorption–gas chromatography–mass spectrometry

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ABSTRACT

This study describes the development of a new method for determining p-hydroxybenzoic esters (parabens) in house dust. This optimised method was based on the pressurised hot water extraction (PHWE) of house dust, followed by the acetylation of the extracted parabens, stir bar sorptive extraction (SBSE) with a polydimethylsiloxane stir bar, and finally analysis using thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS). The combination of SBSE and PHWE allows the analytes to be preconcentrated and extracted from the aqueous extract in a single step with minimal manipulation of the sample. Furthermore the in situ acetylation of parabens prior to SBSE improved their extraction efficiency and their GC–MS signal. The method showed recoveries of between 40 and 80%, good linearity, repeatability and reproducibility (<10% RSD, at 100 ng g^{-1}, $n = 5$), low limits of detection (from 1.0 ng g^{-1} for propyl paraben to 2.1 ng g^{-1} for methyl paraben) and quantification (from 3.3 ng g^{-1} for propyl paraben to 8.5 ng g^{-1} for methyl paraben). The proposed method was applied to the analysis of house dust samples. All the target parabens were found in the samples. Methyl and propyl parabens were the most abundant, with concentrations up to 2440 ng g^{-1} and 910 ng g^{-1}, respectively. The high levels of parabens found in the samples confirm the importance of determining organic contaminants in indoor environments.

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1. Introduction

Numerous studies have demonstrated that indoor air (both gas and particle phases) contains a wide spectrum of organic pollutants in high concentrations [1,2]. Furthermore, contaminants bound to indoor dust are more persistent than those bound to outdoor airborne particles because they are better protected from biotic and abiotic degradation and accumulate over time. Consequently, contaminants bound to indoor dust have a higher exposure potential [3] and this exposure is of particular importance regarding younger children, because of the ways they behave and because they tend to spend longer times in indoor environments. Indeed the main exposure route to toxic pollutants for children is the ingestion of dust: the average infant's daily ingestion of dust is estimated to be 100 mg per day, more than twice that of adults [1].

House dust is a heterogeneous complex matrix, composed of inorganic and organic materials such as skin tissues, hair fibres, mites and particulate matter emanating from carpets and furniture. Several studies have demonstrated the occurrence of a large number of toxic pollutants in house dust including metals such as lead, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalates, and other persistent pollutants [4–7]. Recently, some studies have also detected the presence of personal care products (PCPs) in house dust, such as p-hydroxybenzoic esters (parabens) [8–10] and synthetic musk fragrances [11,12]. Parabens are the most common preservatives and antimicrobial agents used in personal care, pharmaceutical and food products. These compounds are considered endocrine disrupting chemicals (EDCs), because of their endocrine activity [13,14], and have been detected in human tissues, including breast tumours [15,16]. However, there is little information about their absorption into the human body through the skin or the respiratory system. Therefore, developing reliable methods for determining parabens in house dust should be a major concern.

Because of the complexity of house dust, the selective determination of a specific group of organic pollutants usually involves a multi-step process that generally consists of an extraction procedure followed by clean-up and preconcentration steps prior to the GC analysis. Most of the extraction methods used for house dust employ organic solvents to extract the analytes either by Soxhlet extraction [8,17,18], ultrasound-assisted extraction [19,20], pressurised liquid extraction (PLE) [9,11,21,22] or by microwave

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assisted solvent extraction (MASE) [12,23]. Pressurised hot water extraction (PHWE), which is an environmentally friendly method that reduces the usage of organic solvents, might be a good alternative to more conventional extraction methods. Since the polarity of water decreases at high temperatures under pressure, PHWE can selectively extract a wide range of medium to low polarity analytes [24]. PHWE has been successfully applied to the extraction of a wide range of organic pollutants such as amines, aromatic polycyclic hydrocarbons (PAHs) and pesticides among others from different solid matrices [25–28]. However, as far as we know, this process has not yet been used for the extraction of organic pollutants from house dust.

After the PHWE, the aqueous extract requires a preconcentration and further extraction step, which can be done through liquid–liquid extraction (LLE) [29], solid-phase extraction (SPE) [25], solid-phase micro extraction (SPME) [27,30,31], stir bar sorptive extraction (SBSE) [26], etc. SBSE is a powerful and sensitive solventless technique which can extract and preconcentrate the analytes from the PHWE extract in one step. However, given that parabens are quite polar compounds with a low affinity with the polydimethylsiloxane (PDMS) phase of commercial stir bars, a derivatization step such as the acetylation of the phenolic group with acetic anhydride in basic medium should be carried out prior to the extraction to enhance recoveries [32].

Therefore, the aim of this study is to develop a method for determining parabens in house dust that uses PHWE followed by the in situ acetylation of parabens with SBSE extraction and thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) analysis. To the best of our knowledge, this study represents the first time that PHWE extraction is applied to both the extraction of organic pollutants from house dust and the extraction of parabens from a solid matrix. The method described here is environmentally friendly because it uses water as the extraction solvent. This eliminates the risk of external contamination because only minimal manipulation of the sample is required. The method is also more sensitive in that it analyzes all of the extracted parabens. The method was tested to see if it could determine five parabens in several house dust samples.

2. Experimental

2.1. Chemical standards

The target parabens 4-hydroxybenzoic acid methyl ester (methyl paraben), 4-hydroxybenzoic acid ethyl ester (ethyl paraben), 4-hydroxybenzoic acid n-propyl ester (propyl paraben), and 4-hydroxybenzoic acid butyl ester (butyl paraben) were supplied by Aldrich (Steinheim, Germany) and the 4-hydroxybenzoic acid i-propyl ester (i-propyl paraben) was purchased from Alfa Aesar (Karlsruhe, Germany).

The acetylated methyl paraben (methyl 4-acetoxybenzoate, 99% purity) was supplied by Aldrich. The remaining acetylated parabens, unavailable commercially, were prepared by adding 200 μL of acetic anhydride and 5 μL pyridine to 1 mL of 500 mg L^{-1} standard solution of the parabens in ethyl acetate and mixing this in a vortex mixer for 10 min at ambient temperature [32]. The calculated efficiency of the derivatization was ca. 96%.

The individual standard solutions of parabens and the mixtures were prepared in methanol (GC grade with >99.9% purity, SDS, Peypin, France). Other solvents used in the optimisation of the method (acetone and acetonitrile) were also of GC grade from SDS. Helium gas and nitrogen gas with 99.999% purity (Carburos Metálicos, Barcelona, Spain) were used for the thermal desorption and chromatographic analysis. Ultrapure water was obtained using a Purelab ultrapurification system (Veolia water, Barcelona, Spain). Sigma–Aldrich supplied Hyflo Super Cel diatomaceous earth for filling the extraction cells of the pressurised liquid extraction equipment. The acetic anhydride for the paraben derivatization was from Scharlau Chemie (Setmenat, Spain) and the disodium hydrogen phosphate from Panreac (Barcelona, Spain).

2.2. Sample collection and preparation

House dust was collected from conventional vacuum cleaners that were in regular use in private homes. The dust was then sieved with a stainless steel sieve and a fraction under 100 μm was stored in amber glass vials and kept at 4 °C until analysis.

The method was optimised and validated with spiked samples of pooled house dust. Spiked samples were prepared by adding different volumes of the standard solution of the target parabens to acetone, always making sure that enough solution was added to cover the entire sample. The mixture was accurately homogenised and kept in a cupboard funnel at room temperature until the solvent had completely evaporated and then aged for at least one week. It was then stored in amber glass vials at 4 °C before being extracted.

2.3. Pressurised hot water extraction and stir bar sorptive extraction

PHWE was performed using an ASE 200 Accelerated Solvent Extraction system (Dionex, Sunnyvale, CA, USA) in 11 mL stainless steel extraction cells. Under the optimised conditions, 100 mg of sieved house dust was dispersed in a mortar with 1 g of diatomaceous earth. Next, the extraction cells were filled with two cellulose filters placed at the bottom of the cell, followed by 1 g of diatomaceous earth, the dispersed sample, and then more diatomaceous earth until the cell was full. Extraction began with a preheating step of 5 min, followed by a 5 min static period at 80 °C and a pressure of 1500 psi. The extraction process was performed in 4 cycles with a flush volume of 100% and a purge time of 120 s. Diatomaceous earth was previously conditioned at 400 °C in a muffle for 6 h and then kept in a desiccator.

Prior to the SBSE process, the aqueous extracts from the PHWE (ca. 25–35 mL) were filtered under vacuum using 45 μm nylon filters (Whatman, Maidstone, UK), increased to 100 mL with ultrapure water and placed into vials. Next, 0.5 g of Na_2HPO_4 and 1000 μL of acetic anhydride were added for the in situ acetylation of the parabens. A clean stir bar was then placed in the vial containing the sample and the vial was immediately capped and stirred at 900 rpm for 4 h at room temperature. After extraction, the stir bars were magnetically removed, rinsed with ultrapure water, dried with a lint-free tissue and placed inside a thermally cleaned stainless-steel tube for thermal desorption.

SBSE extraction of the target parabens was carried out with PDMS coated stir bars (20 mm length × 0.5 mm film thickness with ca. 48 μL of PDMS phase, from Gerstel (Mülheim an der Ruhr, Germany)). Before each use, the stir bars were thermally cleaned at 300 °C for 3 h in pure helium flow of 100 mL min^{-1} and stored in clean 2 mL vials until use.

PHWE and SBSE processes were optimised using house dust samples spiked at a final concentration of 1000 ng g^{-1} of each paraben. In order to assess possible contamination, procedural blanks were also made by filling the cells only with diatomaceous earth. No signal of the target parabens was found in these blanks.

2.4. TD–GC–MS analysis

Thermal desorption of the stir bars was performed in a Unity Thermal Desorption system combined with an Ultra A autosampler (both from Markes International Limited, Llantrisant, UK). Stir bars were placed in empty stainless-steel tubes for thermal des-

Table 1
Target parabens and the retention times (t_R), quantifier and qualifier ions (with their percent abundances in brackets) of the acetylated derivatives.

Compound	t_R (min)	Quantifier ion	Qualifier ions
Methyl paraben (MeP)	5.76	121	91 (90), 152 (80)
Ethyl paraben (EtP)	6.57	121	166 (70), 138 (40)
i-Propyl paraben (i-PrP)	6.74	121	138 (80), 180 (50)
Propyl paraben (PrP)	7.93	138	121 (80), 180 (25)
Butyl paraben (BuP)	9.48	138	121 (50), 194 (15)

orption (9 cm length × 6.35 mm o.d. × 5 mm i.d., also from Markes). Prior to the analysis, the empty tubes were thermally cleaned at 300 °C for 15 min and then stored in a hermetic glass jar under nitrogen atmosphere. The optimised stir bar thermal desorption conditions were: pre-purge for 1 min at room temperature, stir bar desorption at 300 °C for 15 min using helium carrier gas at 100 mL min^{-1} in splitless mode, trapping at 0 °C in a Tenax TA trap and finally trap desorption at 320 °C for 10 min with a split of 5 mL min^{-1}.

Separation and detection were performed in a 6890N gas chromatograph and 5973 *inert* mass spectrometer (Agilent Technologies. Palo Alto, CA, USA) using a Zebron ZB-50 capillary column (30 m × 0.25 mm × 0.25 μm) provided by Phenomenex (Le Pecq Cedex, France). For the GC–MS analysis, the helium carrier gas flow was set at 2 mL min^{-1}. The oven temperature program began at 100 °C, was then increased to 150 °C at 30 °C min^{-1}, then to 190 °C at 5 °C min^{-1} and finally to 290 °C at 15 °C min^{-1}. The GC–MS interface was set at 290 °C. The MS-detector acquired in the selective ion monitoring mode (SIM) operated at an electron impact energy of 70 eV. Table 1 shows the retention times and the quantifier and qualifier ions used for the SIM detection of the acetylated derivatives of the parabens.

3. Results and discussion

3.1. Method optimisation

3.1.1. TD–GC–MS

Acetylated parabens are less polar than the non-acetylated parabens. As a result, the derivatives present much more symmetrical chromatographic peaks because the acetylation of the phenolic groups prevents the hydroxyl group from interacting with the GC capillary column. The acetylated parabens also showed higher retention times than the non-derivatizated parabens, and their mass spectra were similar to the parabens and their mass spectra were similar to the mass spectra of those non-derivatized parabens with increased molecular ion [33]. For the GC separation, a midpolarity phase capillary column was used (50% diphenyl/50% dimethyl polysiloxane) that separated the acetylated parabens in less than 10 min.

Regarding the TD process, the acetylated derivatives of parabens are semivolatile compounds with relatively high boiling points (between 249 and 300 °C). Therefore, high desorption temperatures and flow should be applied to the PDMS stir bars for the quantitative desorption of the analytes. This study tested different desorption temperatures (from 250 to 300 °C), times (from 5 to 20 min) and flows (from 50 to 100 mL min^{-1}). Higher temperatures can degrade the PDMS phase and higher flows can prevent the analytes from being retained in the cryogenic trap. Carry-over of the acetylated parabens was under 1% when the maximal temperature (300 °C) and flow (100 mL min^{-1}) were applied for 15 min. Longer times did not improve the extraction efficiencies. The acetylated parabens were then trapped in a Tenax TA cryogenic trap set at 0 °C during stir bar desorption and then desorbed at 320 °C for 10 min with a split flow of 5 mL min^{-1}.

3.1.2. PHWE and SBSE

Parabens are quite polar compounds with relatively low octanol–water partition coefficients ($\log K_{ow}$ between 2.0 for methyl paraben and 3.5 for butyl paraben). Theoretical recoveries range from 4.5% to 58% for these compounds when calculated for PDMS stir bars with 48 μL of phase and 100 mL of sample volume. Consequently, it was decided to test to see if the acetylation of parabens with acetic anhydride in the presence of a basic salt prior to the SBSE extraction would improve their recoveries in the PDMS phase. When optimising the PHWE process, the initial acetylation and SBSE conditions were set as follows: 0.5 g of Na_2HPO_4 and 100 μL of acetic anhydride extracted with a PDMS stir bar (20 mm × 0.5 mm) stirred at 900 rpm and at room temperature for 3 h. Because of their high viscosity and turbidity, the extracts were filtered under vacuum with 45 μm nylon filters and diluted to 100 mL with ultrapure water prior to the SBSE process in order to prevent interferences during the extraction. Spiked house dust samples at a concentration of 1000 ng g^{-1} were used for the optimisation phase.

Initial PHWE experiments were carried out in order to determine the optimal amount of house dust and the extraction solvent. The first experiments were conducted with 1 g of house dust extracted with ultrapure water in mild conditions (1 cycle, 80 °C, 1500 psi for 5 min). However, the extracts obtained were dark brown with high viscosity and a thick foam on the surface and were very difficult to filter. One explanation for this may be that, as mentioned in the introduction, skin tissues are a common component of house dust. PHWE could, therefore, extract the fatty acids bound to these tissues, which have very low solubility in cold water, thus increasing the viscosity of the extracts. Extractions were then performed using a smaller quantity of sample: 800 mg, 500 mg, 200 mg and 100 mg. Finally, an amount of 100 mg was chosen for the study because the viscosity and turbidity of the extracts decreased at smaller quantities. Smaller quantities of house dust would compromise the sensitivity of the method.

Adding certain organic modifiers to the water may improve the extraction efficiencies of analytes [24]. Therefore, the addition of organic solvents was tested to see if it had any influence. This was done by adding volumes of 10, 25 and 50% methanol, acetone and acetonitrile. The total volume of these solvents in the SBSE samples (once the extracts were diluted to 100 mL with ultrapure water) ranged between 1.5 and 10% (taking into account that ca. 15–20 mL of extract was obtained in 1 cycle of PHWE). In general, responses decreased as more organic solvent was added, except for i-propyl paraben whose responses increased as more acetonitrile was added. Decreases in the paraben responses after the addition of larger amounts of organic modifiers can be explained by the negative effect of these solvents on the SBSE step (either because the efficiency of the in situ acetylation of the parabens decreases or because the affinity of the compounds with the PDMS phase decreases). The i-propyl paraben may behave differently because the organic modifier added during the PHWE step had a positive effect on it which was higher than the negative effect that the organic modifier had on the i-propyl paraben during the subsequent SBSE step.

By way of an example, Fig. 1 shows how the type and amount of organic solvent influence the responses of acetylated i-propyl paraben (Fig. 1A) and acetylated butyl paraben (Fig. 1B). In the light of these results, ultrapure water without any organic modifier was selected as the extraction solvent.

The influence of extraction temperature, time and number of cycles was evaluated using a multifactorial design 3^2 2^1 composed of 18 experiments. Table 2 summarizes the factors and levels selected for the design. The factor levels were selected on the basis of previous PLE papers that investigated organic solvents that determined parabens from dust [9] and from sewage sludge [34].

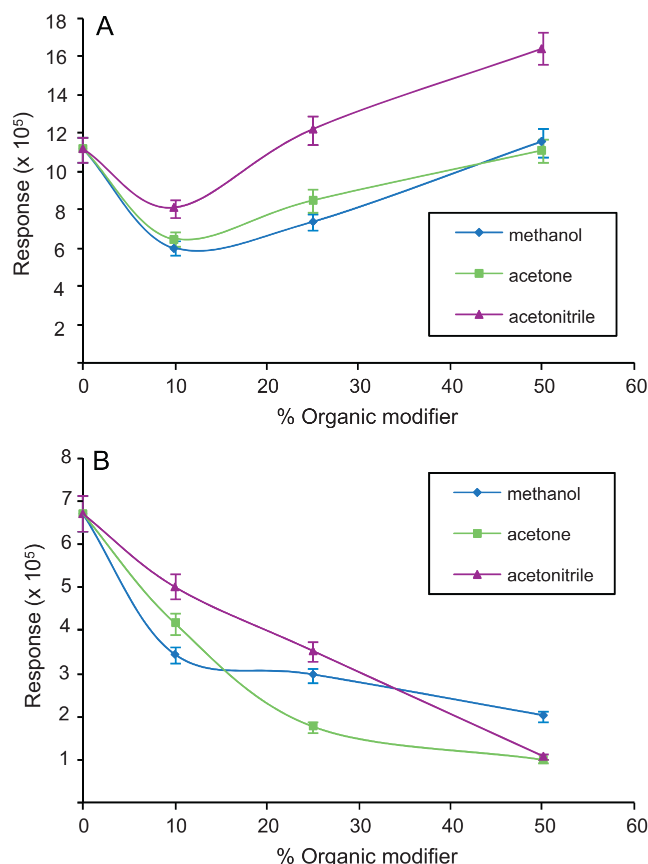

Fig. 1. Influence of the type and amount of organic modifier in the PHWE responses for the acetylated i-propyl paraben (A) and the acetylated butyl paraben (B) (PHWE conditions: 80 °C, 1500 psi, 5 min, 1 cycle, 100% flush volume and 120 s purge).

Table 2
Factors and levels selected for the 3^2 2^1 design.

Factors	Lower	Intermediate	Upper
Temperature (°C)	80	100	120
Time (min)	5	10	15
Cycles	2	–	3

Statistical analysis was carried out with Statgraphics-Plus 5.1 (Magnugistic, Rockville, MD, USA). In all experiments, pressure was set at 1500 psi (enough to maintain water in a liquid state in this range of temperatures), flush volume at 100% and purge time at 120 s (until the extraction cell content was completely dry).

Fig. 2 shows the calculated standardised effects of the three-factor and the two-factor interactions for the acetylated methyl paraben. The standardised effect is obtained by dividing the estimated effect by its standard error. The vertical line indicates the statistically significant bound at the 95% confidence level. Fig. 3 compares the response surface of the extraction temperature with the extraction time for 2 extraction cycles for the same paraben.

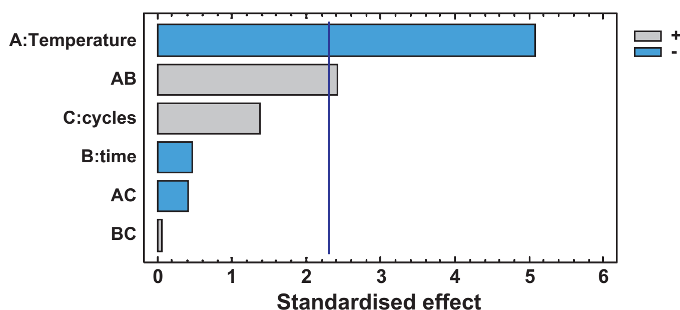

Fig. 2. Standardised Pareto chart of the mean effects and two-factor interactions for the factorial design of acetylated methyl paraben.

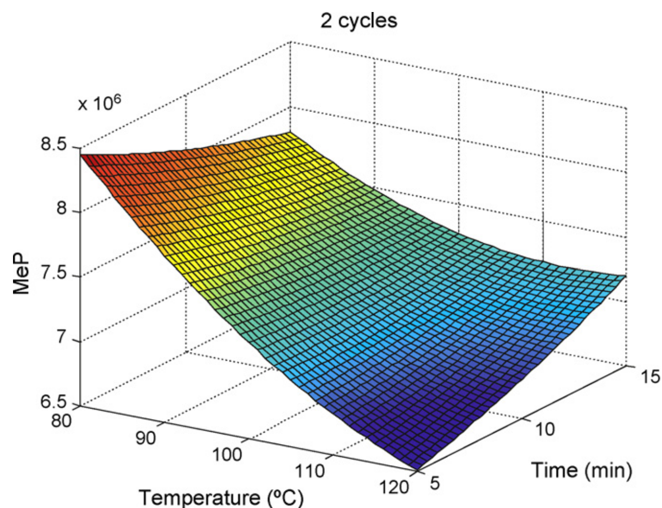

Fig. 3. Acetylated methyl paraben response surface for the extraction temperature against the extraction time (2 cycles).

Extraction temperature had the largest effect on the extraction efficiency, with lower temperatures being more favourable than higher temperatures. One possible explanation may be that extract viscosity increased with higher temperatures. High viscosity may decrease the efficiency of the derivatization reaction and the affinity of the acetylated parabens for the PDMS phase. The extraction time depended on the temperature. The increase in time from 5 to 15 min decreased the response at low temperatures, whilst at high temperatures the effect was the opposite. This temperature–time interaction (AB) was responsible for the nonstatistical significance of the effect of time (Fig. 2). The number of cycles had the lowest effect on the response.

Results were similar for all acetylated parabens, except for the acetylated butyl paraben (the least polar of the target compounds) for which higher responses were obtained at the highest temperature (120 °C) and highest extraction time (15 min). Consequently, an extraction temperature of 80 °C and an extraction time of 5 min were set as a compromise between the results. In order to enhance the responses, different numbers of cycles (from 2 to 5) were tested in these conditions. For the acetylated i-propyl paraben and butyl paraben the best responses were obtained at 4 cycles of extraction. For the acetylated derivatives of methyl, ethyl and propyl paraben, the responses were less affected by the number of cycles and only a slight increase was detected between 3 and 4 cycles. Therefore, 4 cycles were selected as the optimum number.

Once the PHWE parameters were established, the amount of the derivatizing agents for the in situ acetylation of parabens prior to the SBSE was optimised. The amount of basic salt was fixed at 0.5 g because higher amounts gave rise to a precipitate in the extracts. The amount of acetic anhydride was optimised by adding different amounts of this reactive (from 100 μL to 5 mL) to the extracts. The highest responses for all parabens were obtained with 1 mL of acetic anhydride (results not shown). Larger volumes of this reactive provided an acidic medium that was unfavourable for the equilibrium of the acetylation reaction. A similar tendency has been observed in other studies [32,35]. Therefore, a volume of 1 mL of acetic anhydride was used. Under these acetylation conditions no signal of the non-acetylated parabens was detected in the chromatograms, therefore it was assumed that the derivatization of the parabens was complete.

Table 3
Optimised conditions for the PHWE and the in situ acetylation-SBSE of parabens in house dust.

Pressurised hot water extraction	
Amount of sample	100 mg
Solvent	Water
Cell volume	11 mL
No. of cycles	4
Static time	5 min
Temperature	80 °C
Pressure	1500 psi
Flush volume	100%
Purge time	120 s
Stir bar sorptive extraction	
Sample volume	100 mL
Stirring speed	900 rpm
Temperature	Room temp.
Time	4 h
Acetic anhydride	1000 μL
Na_2HPO_4	0.5 g

Finally, different SBSE times were studied. Results showed that the equilibrium was reached between 3 and 5 h. Consequently, a 4 h extraction time was selected as a compromise between sample preparation time and extraction efficiency. Table 3 shows the optimised parameters for the PHWE and SBSE processes.

3.2. Method validation

Table 4 shows the main method parameters of the acetylated parabens for the optimised PHWE followed by in situ derivatization and SBSE–TD–GC–MS. Calibration was performed by spiking 100 mg of house dust sample with different amounts of the standards, these amounts ranging from the LOD of each paraben (see Table 4) to 1500 ng g^{-1}. Linearity was good with the coefficient of determination (r^2) values above 0.996 for all the target parabens.

To calculate recoveries of the whole method, the peak areas obtained at two calibration levels (100 and 1000 ng g^{-1}) were compared with a calibration curve obtained by spiking the same amount of the standards of the acetylated parabens (see Section 2.1) in a tube filled with thermally cleaned deactivated glass wool. As Table 4 shows, recoveries were similar for both levels and ranged from 40% for the acetylated methyl paraben to 80% for the acetylated propyl paraben. The low recovery for the acetylated methyl paraben can be explained by its low affinity with the PDMS phase of the stir bar [32].

Repeatability and reproducibility between days were also checked at two calibration levels (100 and 1000 ng g^{-1}). Repeatability values, expressed as %RSD, ranged between 1.9% for the acetylated methyl and propyl paraben and 8.1% for the i-propyl paraben. Reproducibility between days ranged from 2.3% for the acetylated propyl paraben to 9.5% for the acetylated i-propyl paraben.

The limits of detection (LODs) were determined as three times the standard deviation of the target ion's signal in the non-spiked house dust samples (n = 5). The LODs ranged from 1 ng g^{-1} for propyl paraben to 2.1 ng g^{-1} for methyl paraben (see Table 4). The limit of quantification (LOQ), which was fixed as the lowest calibration level of each compound, ranged from 3.3 ng g^{-1} for propyl paraben to 8.5 ng g^{-1} for methyl paraben. It is worth mentioning that these limits are comparable with the limits obtained in previous methods which used organic solvents instead of water for the pressurised extraction of parabens in indoor dust [9,10].

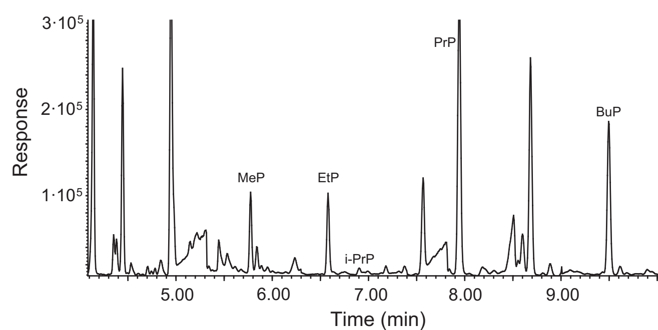

Fig. 4. Chromatogram of a house dust sample, indicating peaks of the acetylated parabens.

Table 5
Average, maximal and minimal concentrations of the target parabens found in the house dust samples, expressed in ng g^{-1} (6 different samples, n = 3).

Paraben	MeP	EtP	i-PrP	PrP	BuP
Average	912	276	33	425	212
Max.	2440	977	45	910	285
Min.	178	56	<LOQ	112	95

<LOQ, value under the limit of quantification.

3.3. Analysis of house dust samples

The PHWE–SBSE–TD–GC–MS method described above with in situ acetylation of parabens was used to determine the presence of the target parabens in different house dust samples. Each sample was analysed in triplicate. Fig. 4 shows the SIM chromatogram of a non-spiked house dust sample with the peaks corresponding to the acetylated parabens indicated.

Table 5 shows the concentration of the target parabens found in the house dust samples. The most abundant parabens were methyl paraben (178–2440 ng g^{-1}) and propyl paraben (112–910 ng g^{-1}), which is consistent with the fact that they are the most commonly used parabens due to the antimicrobial synergic effect produced when using the two parabens together [36]. Ethyl paraben values ranged from 56 to 977 ng g^{-1}, butyl paraben from 95 to 285 ng g^{-1} and i-propyl paraben, which was the least abundant, from values below the limit of quantification to 45 ng g^{-1}. The values of parabens found in this study are similar to those found previously in other private houses [9,10]. This fact can demonstrate the accumulation of parabens in dust particles and, therefore, the importance of determining these compounds in house dust.

Table 4
Main method parameters for the acetylated parabens at a midpoint (100 ng g^{-1}) and a high (1000 ng g^{-1}) calibration level: recovery, repeatability and reproducibility between days, and the detection and quantification of the method.

Acetylated paraben	Recovery (%)		Repeatability (%RSD, n = 5)		Reproducibility (%RSD, n = 5)		LOD (ng g^{-1})	LOQ (ng g^{-1})
	100 ng g^{-1}	1000 ng g^{-1}	100 ng g^{-1}	1000 ng g^{-1}	100 ng g^{-1}	1000 ng g^{-1}		
MeP	43	40	2.3	1.9	2.6	2.4	2.1	8.5
EtP	59	57	3.1	2.8	3.3	3.4	1.9	6.0
i-PrP	54	52	7.9	8.1	8.5	9.4	1.3	3.8
PrP	78	80	1.9	1.8	2.6	2.3	1.0	3.3
BuP	60	61	4.9	4.8	5.4	5.2	1.5	4.2

4. Conclusions

This study successfully developed a method for determining parabens in house dust The optimised method was based on the PHWE of house dust, followed by the acetylation of the extracted parabens, SBSE with a PDMS stir bar, and analysis by means of TD–GC–MS. The method avoids the risk of background contamination because it requires minimal manipulation of the sample. Furthermore, the acetylation of the parabens prior to SBSE increased the affinity of these compounds with the PDMS and improved their chromatographic signal. The method showed good linearity, repeatability, reproducibility and limits of detection and quantification at low ng g^{-1} levels.

The proposed method was used to analyze house dust samples. All the target parabens were found in the samples, with methyl and propyl parabens being the most abundant. The high values of these PCPs found in the samples confirm the importance of determining organic contaminants in indoor environments.

Acknowledgments

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