

# Determination of 48 fragrance allergens in toys using GC with ion-trap MS/MS

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**Abstract:** This paper presents a method for the simultaneous determination of 48 fragrance allergens in four types of toys (plastic toys, play clays, plush toys, and paper toys) based on GC with ion-trap MS/MS. Compared with single-stage MS, MS/MS is superior in terms of the qualification and quantification of a large range of compounds in complicated matrices. Procedures for extraction and purification were optimized for each toy type. The method proved to be linear over a wide range of concentrations for all analytes with correlation coefficients between 0.9768 and 0.9999. Validation parameters, namely, limits of detection and limits of quantification, ranged from 0.005–5.0 and from 0.02–20 mg/kg, respectively. Average recoveries of target compounds (spiked at three concentration levels) were in the range of 79.5–109.1%. Intraday and interday repeatabilities of the proposed method varied from 0.7–10.5% and from 3.1–13.4%, respectively. The proposed method was used to monitor fragrance allergens in commercial toy products. Our findings indicate that this method is an accurate and effective technique for analyzing fragrance allergens in materials composed of complex components.

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## 1 Introduction

Fragrances are a group of chemicals included in a number of products we use in our daily lives. Products like personal-care products, perfumes, cosmetics, toys, household, etc., usually contain fragrances. The primary purposes of fragrances are to impart a scent to a product, mask the odor of other chemical ingredients in the product or, in some cases, give the consumer a feeling of well being [1]. For example, scented toys are attractive to children, who are enticed to buy these products. However, some fragrances with strongly allergenic properties are called fragrance allergens [2]. Fragrance allergens are thought to trigger dermatological problems, respiratory illnesses, headaches, and mucosal symptoms [3–7] to which children are more vulnerable because they inhale more air and have thinner skin. Therefore, the determination of fragrance allergens and the health issues that they cause have gained considerable attention. For example, the revised European Toy Safety Directive 2009/48/EC prohibits or limits the use of 66 fragrance allergens [8]. According to this regulation, 55 fragrance allergens known to have strong allergenic potential are banned. However, the presence of traces of these fragrances are allowed provided that such presence is technically unavoidable under good manufacturing practice and does not exceed 100 mg/kg. Another 11 fragrance allergens with a lower allergenic potential require declaration on the packaging when their concentration exceeds 100 mg/kg.

Several analytical protocols have been developed for the determination of fragrance allergens in toys, cosmetics, water samples, and other products [9–20]. For example, Masuck

et al. [11] reported a method based on dynamic headspace GC–MS to determine the concentration of 24 fragrance allergens in saliva or sweat stimulants from toys. Lamas et al. [12] described the detection of 15 fragrance allergens in baby bathwater using solid-phase microextraction followed by GC–MS. Niederer et al. [13] proposed an approach for determining 24 fragrance allergens in cosmetics based on size-exclusion chromatography combined with GC–MS. Tsiallou et al. [14] developed a method based on dispersive liquid–liquid microextraction, integrated with chemometrics and followed by GC–MS detection to determine 21 fragrance allergens in water samples. They introduced extraction approaches for fragrance allergens, including solid-phase microextraction [15], ultrasound-assisted solvent extraction [16], headspace solid-phase microextraction [17], matrix solid-phase extraction [18], solid-phase dispersion-pressurized liquid extraction [19] and ultrasound-assisted emulsification microextraction [20]. All of the analytical techniques employed for determining of fragrances are mainly based on GC–MS. However, given the complexity of a toy matrix, the single-stage MS method may be subject to unacceptably high matrix influence. Thus, it may fail to provide the desired sensitivity and selectivity, as confirmed by our experimental results. For its capability and selectivity in a complex matrix [21–27], MS/MS is deemed an efficient candidate for identifying fragrance allergens at trace levels in toy samples.

Thus, the present paper aims to develop a general approach for the simultaneous determination of 48 fragrance allergens in multi-matrix toy samples based on GC–MS/MS. To apply this approach for different types of toys, the sample preparation procedures were optimized. Based on the optimization of the MS/MS method, we compared the

anti-interference capability of MS/MS with that of the single-stage MS method. Linearity, recovery, repeatability, LODs and LOQs were evaluated to assess the performance of the proposed method. Finally, 52 commercial toys were analyzed in order to demonstrate the applicability of the method, and to inspect the level of these fragrance allergens present in toy products.

It should be indicated that this strategy can be applied in the determination of 48 out of the 66 restricted fragrance allergens. Of the remaining 18 fragrance allergens, eight are natural extracts that are unsuitable for a chromatography-based method, and the other ten are commercially unavailable.

## 2 Materials and methods

### 2.1 Reagents and materials

Standards of the 48 fragrance allergens considered in this work were purchased from different commercial suppliers. Detailed information of these compounds, including their chemical abstract service registry numbers, suppliers, purities, and MS/MS parameters, is summarized in Table 1. Each mixture of isomers (citral, pseudoionone, and farnesol) is considered as one analyte. All organic solvents (acetone CAS: 67-64-1, methanol CAS: 67-56-1, dichloromethane CAS: 75-09-2, ethyl acetate CAS: 141-78-6, and hexane CAS: 110-54-3) were of chromatographic grade and obtained from J.T. Baker (Phillipsburg, USA).

Individual stock solutions of each compound and a mixed stock solution (500 mg/L) were prepared in acetone. Further dilutions and mixtures were prepared in acetone and then stored in amber glass vials at 4°C.

Envi-carb SPE cartridges (500 mg, 6 mL) were provided by Supelco (Bellefonte, USA),

and 0.45  $\mu\text{m}$  PTFE membrane filters were purchased from Jinteng Company (Tianjin, China). A P300H ultrasonic bath was offered by Elma (Germany). The temperature of the bath was maintained at 30°C.

All 52 commercial toy samples from different Chinese brands and price levels were obtained from super markets, malls and convenience stores in Beijing, China. Before they were analyzed, the samples were preserved in sealed packages in order to avoid contamination.

## **2.2 Gas chromatography with Ion-trap tandem mass spectrometry (GC-IT-MS/MS)**

GC-MS/MS analysis was performed using a Varian 450-GC coupled to a Varian 240 ion trap mass spectrometer equipped with a Varian CP-8400 autosampler. The system was operated by Saturn MS workstation version 6.9.2 software.

Separations were performed on an HP-1MS capillary column (50 m  $\times$  0.2 mm i.d., 0.5  $\mu\text{m}$  film thickness) from Agilent Technologies (Palo Alto, CA, USA). Helium (purity 99.999%) was employed as the carrier gas at a constant column flow of 0.7 mL/min. The injector was operated in splitless mode at 280°C, and the inject volume was 1  $\mu\text{L}$ . The GC oven temperature was programmed from 50°C (held for 1 min) to 155°C at 5 °C/min (held for 6 min), and then to 260°C at 3 °C/min. All the compounds were separated within 63 min.

The transfer line, manifold and trap temperatures were 280, 50, and 220 °C, respectively. A filament-multiplier delay of 8 min was established in order to increase filament's service life. The analytes were ionized by electron ionization (EI), 70 eV in the positive ion mode. The EI-MS/MS process was carried out by collision-induced dissociation (CID) using a resonant waveform.

A typical chromatogram of 48 fragrance allergens under the above conditions is shown in Fig. 1.

## 2.3 Sample preparation

### 2.3.1 Extraction

Fragrance allergens are mainly used in the production of plastic toys, play clays, plush toys, and paper toys. Therefore, these samples are considered in this work.

**For plastic toys,** samples were cut into pieces smaller than  $2 \times 2 \times 2$  mm. Thereafter, 1 g of the sample was added into a 50 mL conical flask and then dissolved with 10 mL of an appropriate solvent according to the type of plastic (acetone for acrylonitrile butadiene styrene (ABS), dichloromethane for polystyrene (PS), and tetrahydrofuran for poly(vinyl chloride) (PVC)). The solution was treated in an ultrasonic bath for 15 minutes to help the dissolution of the sample, after which 10 mL of slowly dripped methanol was added. The solution was continuously shaken until the plastic substrates completely precipitated. The supernatant was then transferred into a centrifugal tube. Subsequently, 5 mL of methanol was used to wash the conical flask again. The solution was then poured into the centrifuge tube, centrifuged at 13 000 r/min at 4°C for 8 min. The supernatant solution was collected for clean-up and concentration.

**For play clays,** samples were cut into pieces smaller than  $2 \times 2 \times 2$  mm. Thereafter, 1 g of the sample was weighed and then transferred to a 50 mL conical flask, followed by ultrasonic extraction with 10 mL of acetone for 15 min. Then the solution was transferred into a centrifuge tube. The residue continued to be extracted with 10 mL of methanol and then also transferred into the centrifuge tube, after which 5 mL of methanol was used to wash the

conical flask. The combined solution in the centrifuge tube was then treated in a similar way as that of the plastic toys.

**For plush and paper toys,** samples were cut into pieces smaller than  $5 \times 5$  mm. Thereafter, 1 g of the sample was weighed and then transferred to a 50 mL conical flask, after which 20 mL of acetone was added into the flask, followed by treatment in an ultrasonic bath for 20 min. The extract was filtered through a  $0.45 \mu\text{m}$  polytetrafluoroethylene (PTFE) membrane prior to further instrumental analysis.

### **2.3.2 Clean-up and concentration process**

SPE was used to purify the analytes in the extract solution. First, an Envi-Carb cartridge was conditioned with 5 mL of methanol. The extract solution was then allowed to pass through at a flow rate of approximately 3 mL/min and then the effluent was collected rather than discarded. The cartridge was eluted with 15 mL of dichloromethane. This effluent was also collected and combined with the prior effluent. The combined solution was concentrated to approximately 5 mL through rotary evaporation at 10 kPa and  $30^\circ\text{C}$ . If the solution was more than 5 mL, a gentle stream of nitrogen was used to concentrate it to 5 mL. If it was less than 5 mL, then it was diluted to 5 mL. Finally, the solution was filtered through a  $0.45 \mu\text{m}$  PTFE membrane prior to further instrumental analysis.

For plush and paper toy samples, tests were conducted without the SPE process if the color of the solution was pure or very light after ultrasonic extraction.

## **3 Results and discussion**

### **3.1 MS/MS method optimization**

MS/MS method development was conducted in two steps. First, the individual standard

was injected in full scan mode at a scan range of 40–400 amu to select the optimal precursor ions. The most intense ion with a higher  $m/z$  relationship was selected. In certain instances, anisyl alcohol and hexyl cinnamaldehyde at 138 and 145  $m/z$ , respectively, were selected as the precursor ions rather than their respective base peaks at 109 and 129  $m/z$  to ensure better selectivity, lower noise level, and lower uncertainty in detection. Excitation energy ( $q$ ) was then set at a moderate level of 0.34. The excitation voltage was optimized for the precursor ion of each individual compound to obtain the best isolation efficiencies and ensure the maximum production or transmission of collision fragments. For all test compounds, characteristic product ions with the highest intensity were used for quantification.

In the second step, a standard mixture of 48 compounds was injected in full scan mode. Almost all compounds were sufficiently separated through the careful optimization of chromatography conditions. Based on the retention time and the precursor ion of each compound, the chromatogram was divided into 13 segments. The MS/MS method was then applied, and the isolation window (precursor ion width) was maintained at 3–5  $m/z$  based on the conditions. To ensure the highest S/N, the product ion scan range was kept as narrow as possible. The MS/MS parameters are presented in Table 1.

### **3.2 Comparison of the single-stage MS and MS/MS methods**

Determining fragrance allergens is made difficult by the complicated composition of some toys. For example, plastic toys may contain polymers, dyes, solvents, plasticizers, and other additives. Play clays may contain polymers, organic acids, colorants, plasticizers, flavors, etc. Furthermore, given the wide range of polarity in the 48 fragrance allergens, thorough elimination of matrix interferences using SPE or other purification techniques becomes more

difficult. Consequently, the application of single-stage MS may facilitate the emergence of a “false positive” or a “difficult to quantify” conditions as well as unacceptably high matrix interferences. Fig. 2A shows the chromatogram of a play clay sample containing *trans*-2-heptenal with single-stage MS (SIS mode in IT-MS). Evidently, the peak of *trans*-2-heptenal was almost “buried” in the background, thereby hindering accurate quantification. A similar phenomenon was also observed in a play clay sample containing D-limonene (Fig. 2C). To address this problem, the MS/MS method was adopted. As shown in Figs. 2B and 2D, the peaks were extremely sharp in the MS/MS mode, such that qualification and quantification could be significantly improved.

### **3.3 Optimization of sample preparation**

#### **3.3.1 Extraction**

Several methods have been developed for the extraction of fragrances in cosmetics, water, or other products, but few in toys. Masuck et al. introduced extraction approaches of fragrances in toys, including dynamic headspace [11] and headspace solid-phase microextraction [17]. In this study, different extraction methods were selected for different toy materials.

For plastic toys, we selected toys made of three common materials ABS, PS and PVC from the market. Samples were extracted by the dissolution–precipitation approach [28]. At first, plastic samples were dissolved completely in the selected solvents (acetone for ABS, dichloromethane for PS, and tetrahydrofuran for PVC), and then methanol was added slowly until the plastic substrates were completely precipitated. In this way, the complete extraction

of fragrances could be obtained from plastic samples. To calculate the extraction efficiency of fragrances from the toys, home-made reference samples were prepared. For all compounds, the obtained recoveries of the extraction step exceeded 90%.

For plush toys and paper toys, an ultrasound-assisted extraction method, which is easily operated and widely reported has been used. Optimal extraction conditions, including the extract solvent and the extract time, were obtained through studying the recoveries of all 48 compounds in the extracts of home-made reference samples. Taking as an example the extraction of six representative fragrances (4-methoxyphenol, cinnamal, anisyl alcohol, eugenol, 4-phenyl-3-buten-2-one, coumarin) from plush toy, the steps of method optimization were as follows. First, 1g of the sample was ultrasonically extracted for 30 min in 20 mL of five different extracting solvents (hexane, dichloromethane, ethyl acetate, acetone, and methanol). As shown in Fig. 3A, the best result was achieved by using acetone. Then, 1g of the sample was extracted in 20 mL of acetone for different extraction times ranged from 10 to 40 min (six points). As shown in Fig. 3B, 20 min was selected as the appropriate extraction time since satisfactory recoveries could be obtained in a short time.

For play clays, samples were also extracted by ultrasound. 1g of the sample was extracted for 20 min in 20 mL of five different extracting solvents (hexane, dichloromethane, ethyl acetate, acetone, and methanol). It can be seen from Fig.4A that recoveries of six representative fragrances were unsatisfactory (<85%). The major reason could be the more complex composition of play clays. Therefore, a two-step extraction method was attempted to extract the samples. First, 1 g of sample was ultrasonically extracted in 10 mL of acetone for 15 min. Then the solution was transferred into a conical flask. The residue was extracted in

10 mL of five of the above solvents for 15 min. The solution was combined in the conical flask and then analyzed. As shown in Fig.4B, recoveries of fragrances increase obviously according to two-step method. In addition, the use of the combination of 10 mL acetone and 10 mL methanol achieved the optimal result (>90%).

### 3.3.2 Clean-up and concentration

In our approach, SPE was conducted to eliminate matrix co-extractants in the extract solution, such as dyes or pigments, because at large amounts, these materials pollute the flow-path of GC-MS as well as the ion source. For this purpose, Envi-Carb cartridges (functional graphitized carbon used as sorbent) were used. Fig. 5 indicates the capability of SPE to remove dyes and/or pigments. As graphitized carbon could also adsorb a portion of fragrances, the next task was to identify a suitable eluting solvent to achieve acceptable recovery. Acetone, methanol, hexane, ethyl acetate, and dichloromethane were tested as eluting solvents. Sample extracts spiked with a standard solution of 48 fragrances (the final concentration and volume were 4 mg/L and 20 mL, respectively) were prepared and then subjected to the SPE process described in Section 2.3.2. Experimental results indicate that acceptable recoveries (>80%) could be achieved with all five kinds of solvents for most fragrance allergens. However, for some substances, such as *trans*-2-hexenal diethyl acetal, anisyl alcohol, 4-(*p*-methoxyphenyl)-3-butene-2-one, eugenol, benzyl salicylate, and 7-ethoxy-4-methylcoumarin, the recoveries significantly varied among different solvents. As shown in Fig. 6, the best results were obtained by using dichloromethane as the eluting solvent. Thus, dichloromethane was selected for further studies.

After SPE treatment, recoveries were extremely low (<60%) for ethyl acrylate, methyl

*trans*-2-butenate, D-limonene, and *trans*-2-hexenal diethyl acetal when the solution was concentrated by rotary evaporation. This finding might be attributed to the high saturated vapor pressure of these compounds. To mitigate this problem, the solution was directly diluted to 50 mL, and then filtered after the SPE process prior to further instrumental analysis.

### **3.4 Method validation**

For target compounds spiked into blank toy samples, LODs and LOQs were estimated based on the values obtained in the range of three and ten times the S/N, respectively, but applying a more conservative criteria. The LODs and LOQs ranged from 0.005–5.0 and from 0.02–20 mg/kg, respectively, depending on the fragrances (see Tables 2–5). All obtained LOQs were several orders of magnitude lower than the established limits in 2009/48/EC (100 mg/kg). If necessary, these limits can be further improved by concentrating the solution.

Recovery studies were conducted by applying the optimized method to four types of blank toy samples spiked at three different levels. Tables 2 and 3 present the results of 48 fragrance allergens in plush toys and paper toys, respectively. Tables 4 and 5 show the obtained results of 48 fragrance allergens in plastic toys and play clays, respectively. The obtained recoveries ranged from 79.5–109.1%. Meanwhile, in all cases, the relative standard deviation values for intraday repeatability were lower than 10.5%, with an average of 3.7%, whereas those for interday repeatability varied between 3.1 and 13.4%.

### **3.5 Analysis of commercial toys**

The approach was applied to the analysis of 52 commercially available toys (13 each of

plastic toys, play clays, plush toys, and paper toys). Among these toys, 17 samples were found to contain at least one fragrance allergen (Table 6), and three samples were found to contain fragrance allergens with concentrations higher than 100 mg/kg (S8, S11, and S15). According to the substance category, 11 banned fragrances were detected in several analyzed samples, but their levels were lower than 100 mg/kg which means that these toys still meet the requirements of the Toy Safety Directive 2009/48/EC. Five allowed fragrances were detected. The contents of benzyl benzoate exceeded 100 mg/kg in two toys (245.0 mg/kg in a paper toy and 433.5 mg/kg in a plastic toy), and D-limonene in one toy (183.2 mg/kg in a play clay) and thus would have actually required appropriate declaration on the package (which was missing).

As shown in Fig. 7, several fragrance allergens including benzyl alcohol (**6**), coumarin (**27**), and benzyl benzoate (**44**), appeared in at least seven samples. Thus, we supposed that these fragrances were commonly used in scented toys. Fig. 8 illustrates the chromatograms of several toys containing fragrance allergens. The complete chromatogram is the total ion chromatography (TIC) chromatogram corresponding to the abundance of precursor ion of a compound. The small ones, at the bottom of each complete chromatogram, are the MS/MS chromatogram of each compound corresponding to the abundance of daughter ion produced by the precursor ion.

## 4 Conclusions

In this study, we report a GC-IT-MS/MS method for determining 48 fragrance allergens in multi-matrix toy samples. Our results indicate that applying MS/MS instead of single-stage MS is significant for the simultaneous detection of fragrance allergens. No method has been

previously reported to determine more than 26 fragrance allergens in toys or other related products simultaneously. To apply this approach to different types of toys, the sample preparation procedures were optimized. The proposed approach was validated by analyzing target compounds in commercial toys. This investigation demonstrated that the application of GC–IT-MS/MS is an accurate and effective technique for analyzing fragrance allergens in materials composed of complex components.

## Acknowledgement

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Fig. 1 Total ion chromatogram of a standard mixture of 48 fragrance allergens at a concentration of 40 mg/L in acetone (identification numbers are consistent with those in Table 1).

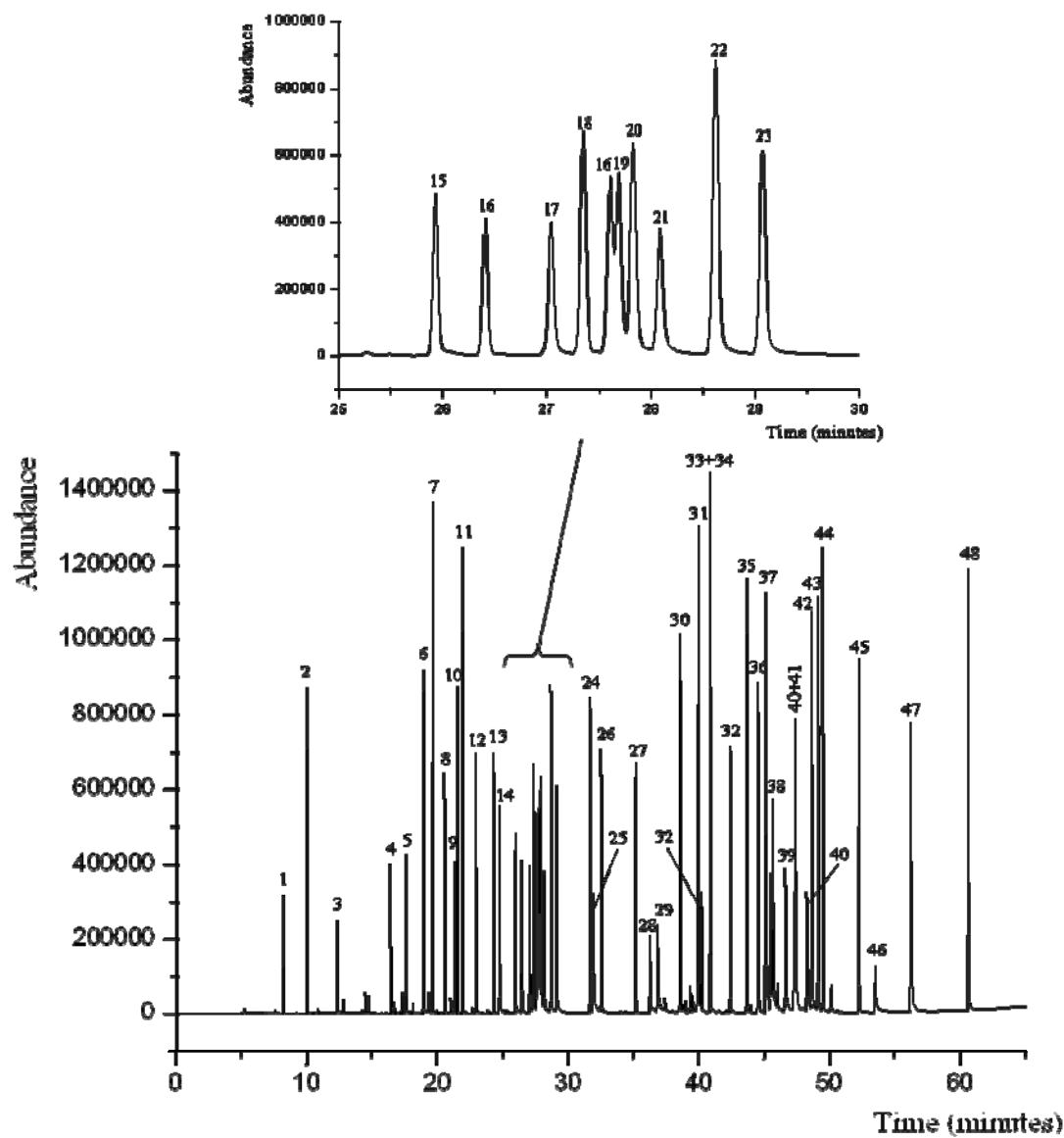


Fig. 2 Comparison of the determination of certain fragrance allergens in toy samples by using SIS mode and MS/MS mode of IT-MS (fragrance concentrations in toy samples: *trans*-2-heptenal, 2.6 mg/kg and D-limonene, 18.2 mg/kg).

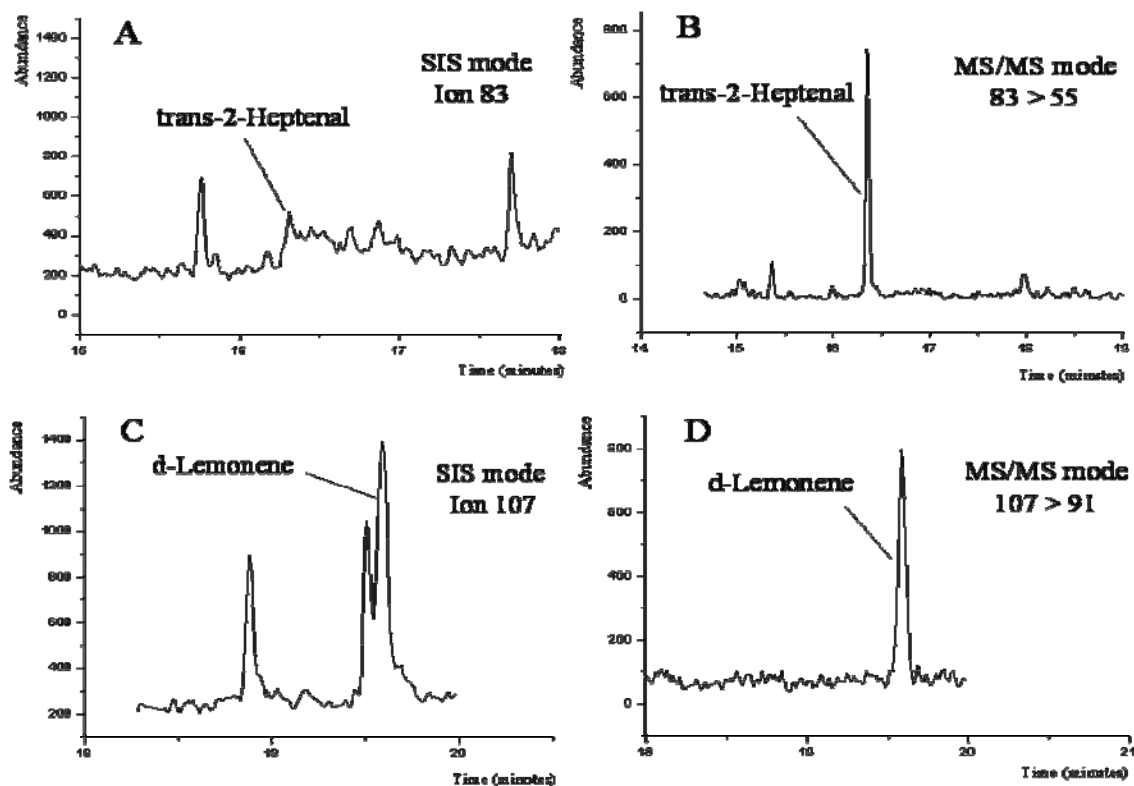


Fig. 3 Recoveries of six representative fragrances in plush toys with different extracting solvents (A) and different extraction times (B) ( $n=3$ ).

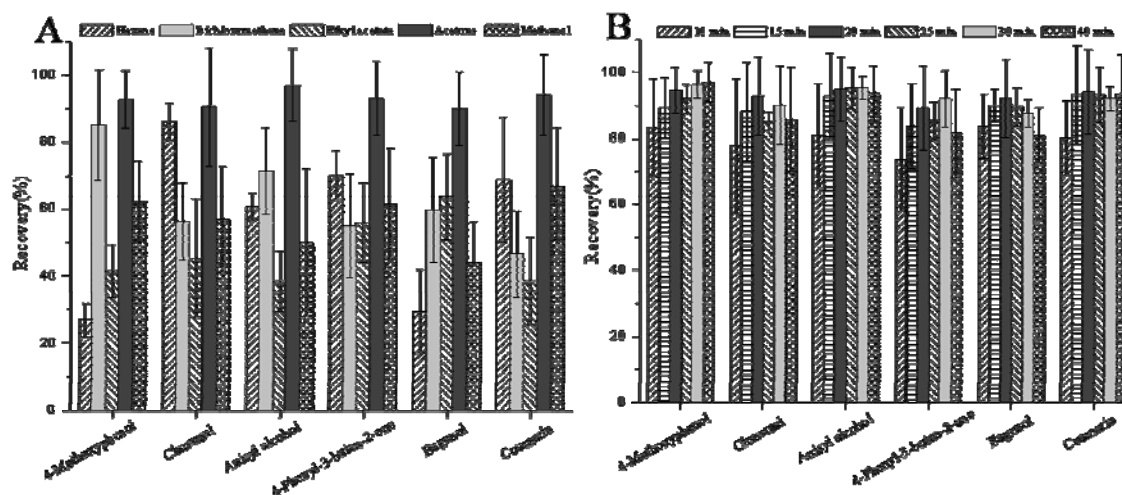


Fig. 4 Recoveries of six representative fragrances in play clays with a one-step extraction method (A) and a two-step extraction method (B) ( $n=3$ ).

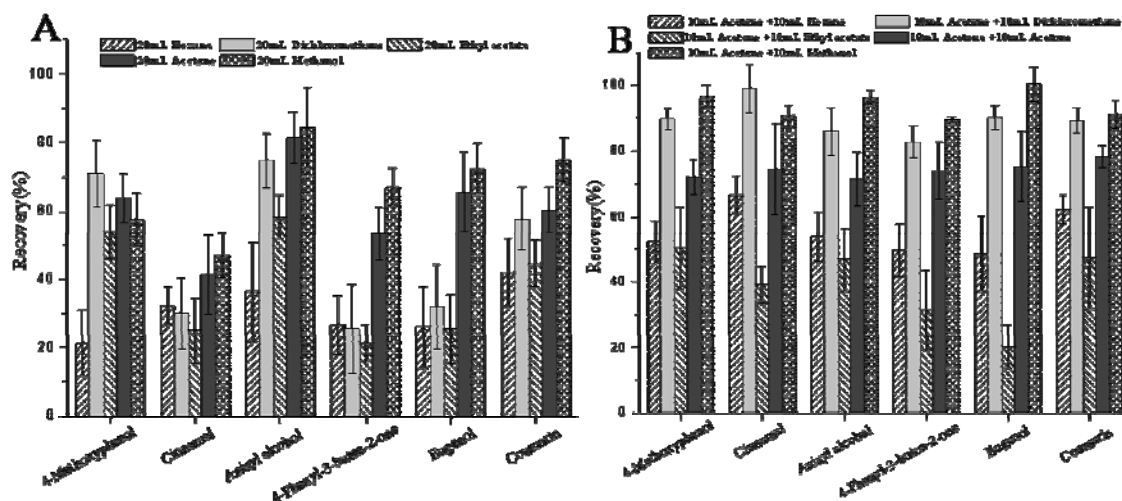


Fig. 5 (A) Play clay samples before preparation; (B) solutions of the play clay samples after ultrasonic extraction, and (C) solutions of the play clay samples after SPE clean-up.

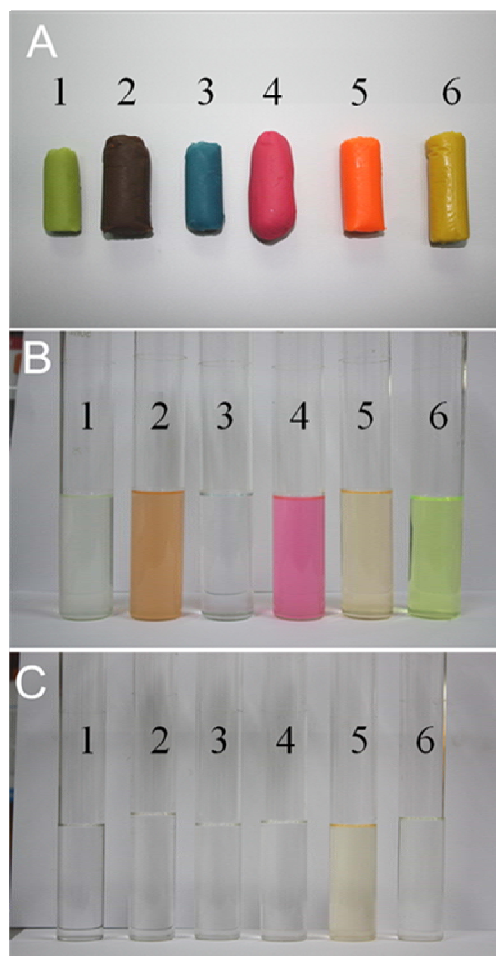


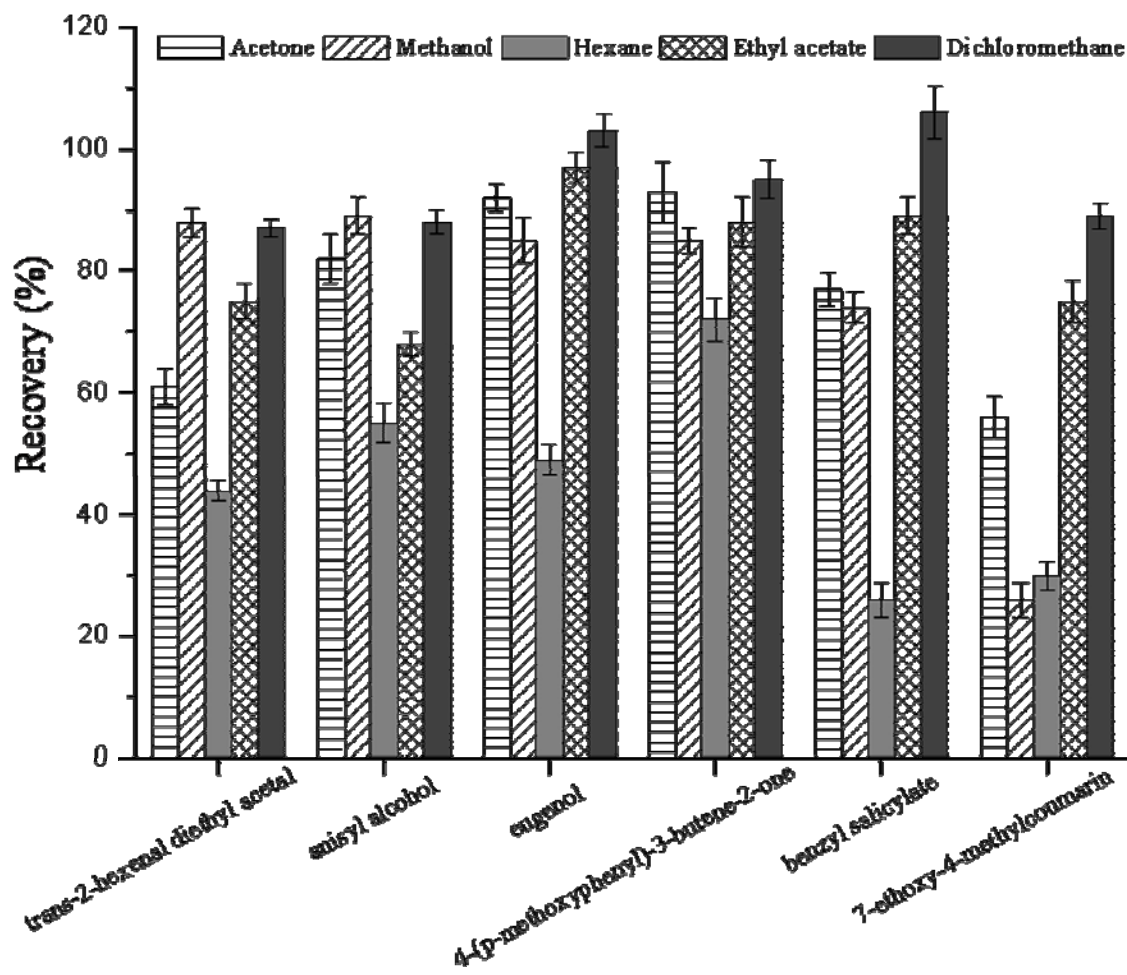
Fig. 6 Recoveries of representative fragrance allergens with different eluting solvents ( $n=4$ ).

Fig. 7 Monitoring of fragrance allergens in commercial toys.

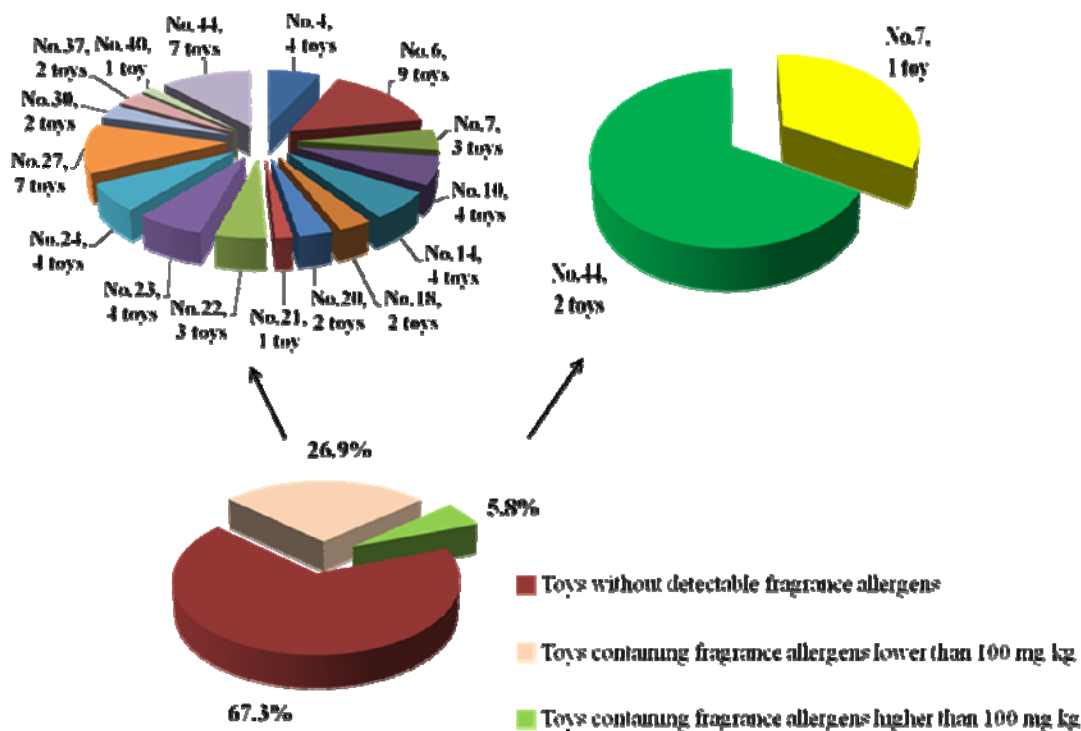
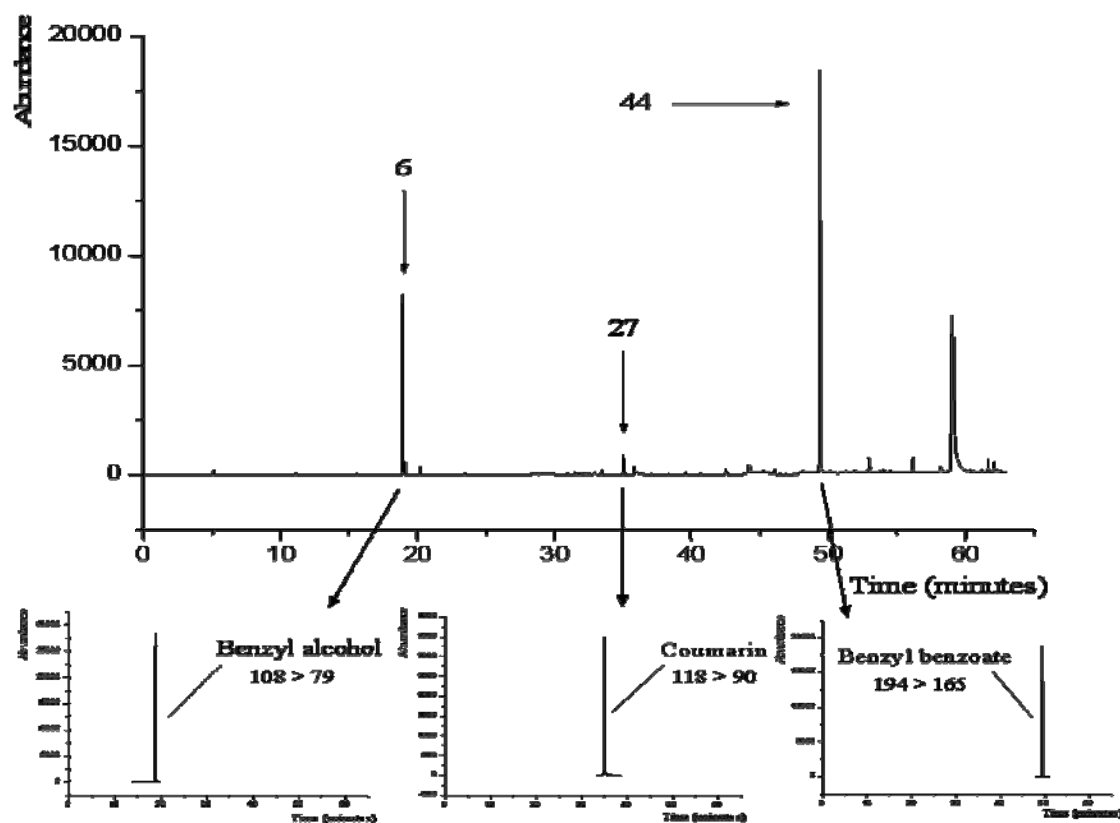


Fig. 8 Total ion chromatogram and MS/MS chromatograms corresponding to three real samples (A, S2; B, S11; and C, S15).



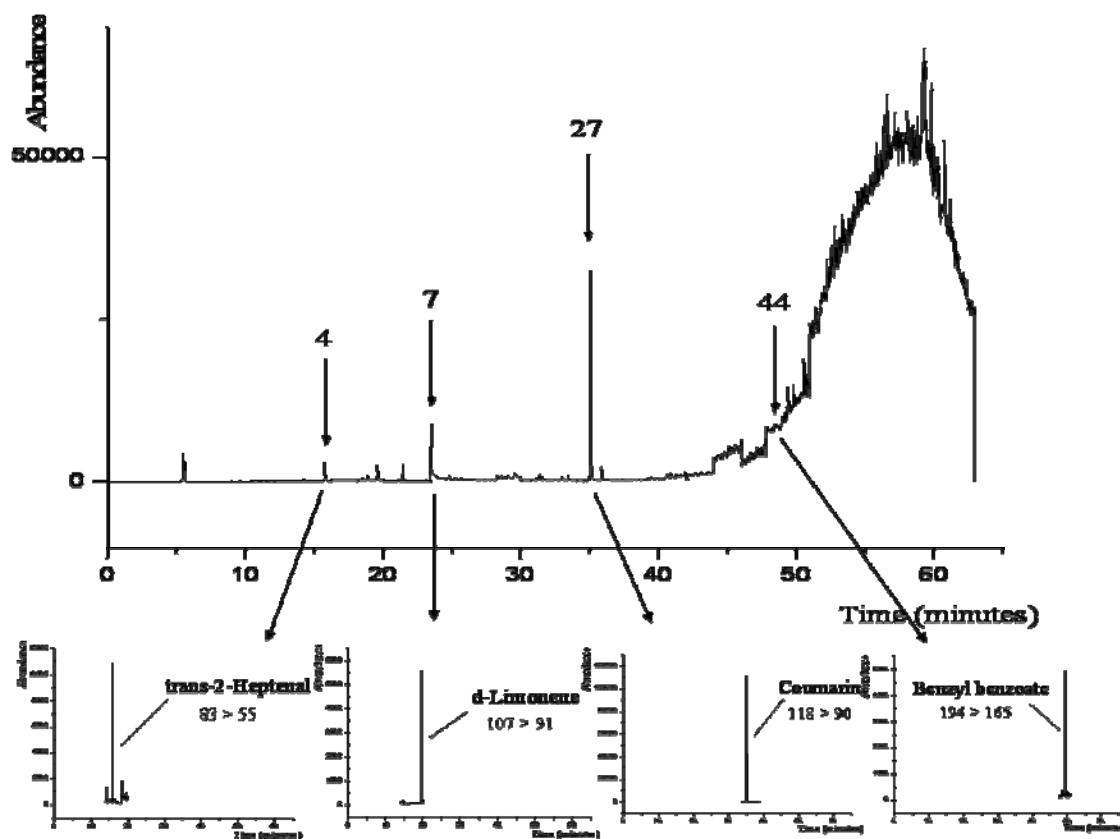
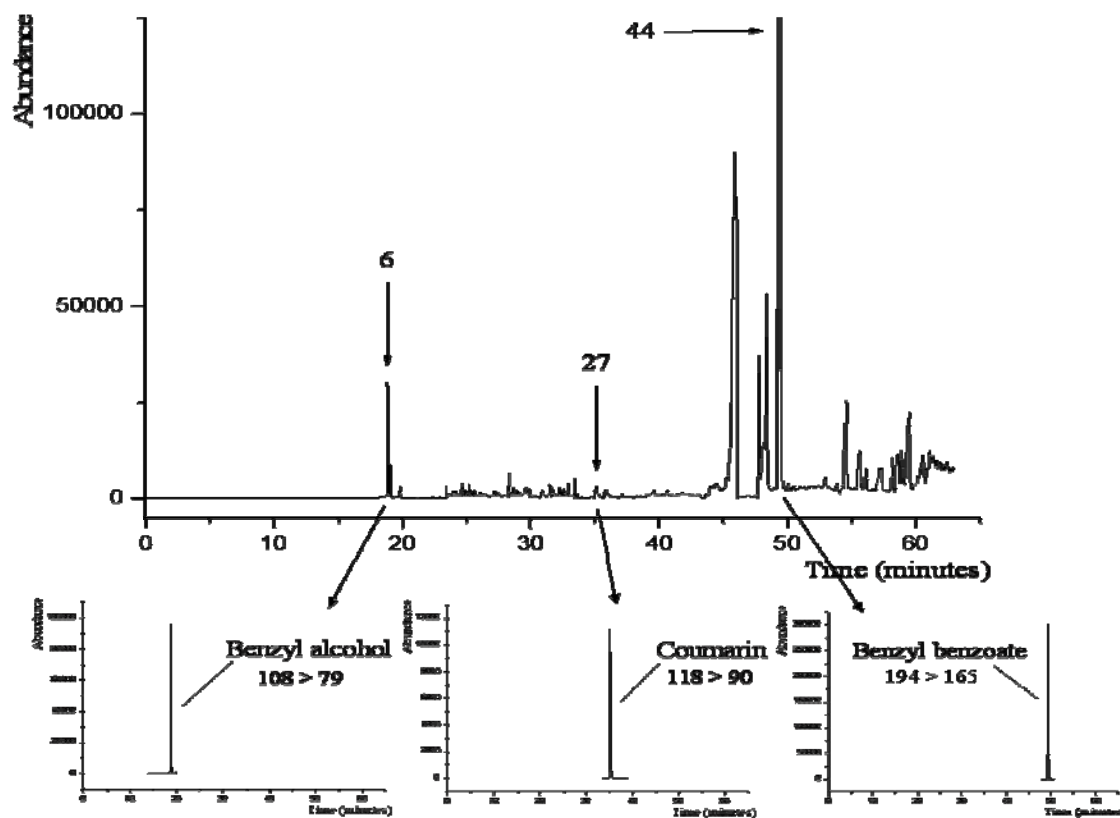


Table 1 Chemical abstract service (CAS) number, suppliers, purities and GC-MS/MS parameters of the analytes

| No. | Compounds                                       | Retention time (min) | CAS        | Suppliers         | Purities                     | Target MRM <sup>a</sup> (m/z) | Qualifier MRM (m/z) | Linear ranges (mg/L) | Correlation coefficients |
|-----|-------------------------------------------------|----------------------|------------|-------------------|------------------------------|-------------------------------|---------------------|----------------------|--------------------------|
| 1   | Ethyl acrylate <sup>b</sup>                     | 8.17                 | 140-88-5   | Fluka             | 99.5%(GC)                    | 99 > 77 (0.4v, 4)             | 99 > 81 (0.4v, 4)   | 0.2-50               | 0.9990                   |
| 2   | Methyl trans-2-butenolate <sup>b</sup>          | 9.97                 | 623-43-8   | Alfa Aesar        | 98%                          | 85 > 57 (0.3v, 3)             | 100 > 69 (0.4v, 3)  | 0.05-20              | 0.9995                   |
| 3   | 5-Methyl-2,3-hexanedione <sup>b</sup>           | 12.30                | 13706-86-0 | TCI               | ≥95%                         | 85 > 57 (0.5v, 3)             | 85 > 41 (0.5v, 3)   | 0.02-10              | 0.9996                   |
| 4   | trans-2-Heptenal <sup>b</sup>                   | 16.34                | 18829-55-5 | Aldrich           | 97%                          | 83 > 55 (0.4v, 4)             | 95 > 79 (0.4v, 5)   | 0.05-10              | 0.9993                   |
| 5   | trans-2-Hexenal dimethyl acetal <sup>b</sup>    | 17.58                | 18318-83-7 | Accustandard      | 96%(GC/MS)                   | 113 > 71 (0.6v, 3)            | 113 > 97 (0.6v, 3)  | 0.2-20               | 0.9968                   |
| 6   | Benzyl alcohol <sup>b</sup>                     | 18.93                | 100-51-6   | Sigma             | ≥99.8%                       | 108 > 79 (0.6v, 3)            | 91 > 65 (0.4v, 4)   | 0.005-5              | 0.9995                   |
| 7   | d-Limonene <sup>c</sup>                         | 19.65                | 5989-27-5  | Fluka             | ≥96%(GC)                     | 107 > 91 (0.6v, 3)            | 136 > 94 (0.5v, 3)  | 0.05-10              | 0.9992                   |
| 8   | Dimethyl citraconate <sup>b</sup>               | 20.53                | 617-54-9   | TCI               | 99%(GC)                      | 127 > 99 (0.4v, 4)            | 127 > 69 (0.4v, 4)  | 0.005-5              | 0.9993                   |
| 9   | trans-2-Hexenal diethyl acetal <sup>b</sup>     | 21.33                | 67746-30-9 | Accustandard      | 94%                          | 127 > 85 (0.7v, 3)            | 127 > 98 (0.8v, 3)  | 0.5-10               | 0.9943                   |
| 10  | Linalool <sup>c</sup>                           | 21.51                | 78-70-6    | Fluka             | ≥95%(GC)                     | 93 > 77 (0.6v, 4)             | 121 > 93 (0.4v, 3)  | 0.02-10              | 0.9994                   |
| 11  | Benzyl cyanide <sup>b</sup>                     | 21.87                | 140-29-4   | Fluka             | ≥98%(GC)                     | 117 > 90 (0.4v, 4)            | 90 > 63 (0.9v, 4)   | 0.002-5              | 0.9985                   |
| 12  | Diethyl maleate <sup>b</sup>                    | 22.93                | 141-05-9   | Aldrich           | 97%                          | 127 > 99 (0.4v, 4)            | 127 > 82 (0.5v, 4)  | 0.01-10              | 0.9995                   |
| 13  | Methyl heptene carbonate <sup>c</sup>           | 24.29                | 111-12-6   | Fluka             | ≥97%(GC)                     | 123 > 93 (0.7v, 4)            | 123 > 67 (0.5v, 4)  | 0.05-20              | 0.9996                   |
| 14  | 4-Methoxyphenol <sup>b</sup>                    | 24.70                | 150-76-5   | Alfa Aesar        | ≥98%                         | 124 > 109 (0.6v, 4)           | 109 > 81 (0.6v, 3)  | 0.01-20              | 0.9988                   |
| 15  | Citronellol <sup>c</sup>                        | 25.98                | 106-22-9   | Fluka             | 90-95%(GC)                   | 95 > 67 (0.4v, 4)             | 128 > 81 (0.7v, 3)  | 0.05-20              | 0.9991                   |
| 16  | Citral <sup>b</sup> Isomer1                     | 26.41                | 5392-40-5  | Fluka             | ≥95%(GC) cis+trans           | 137 > 95 (0.5v, 3)            | 137 > 109 (0.4v, 3) | 0.2-20               | 0.9996                   |
|     | Citral Isomer2                                  | 27.62                |            |                   |                              | 137 > 95 (0.5v, 3)            | 137 > 109 (0.4v, 3) |                      |                          |
| 17  | Geraniol <sup>b</sup>                           | 27.06                | 106-24-1   | Fluka             | ≥96%(GC)                     | 93 > 65 (1.2v, 4)             | 123 > 81 (0.7v, 5)  | 0.5-20               | 0.9986                   |
| 18  | Cinnamal <sup>b</sup>                           | 27.36                | 104-55-2   | Aldrich           | ≥98%                         | 131 > 103 (0.7v, 4)           | 131 > 77 (0.8v, 4)  | 0.01-20              | 0.9999                   |
| 19  | 4-Ethoxy-phenol <sup>b</sup>                    | 27.71                | 622-62-8   | Aldrich           | 99%                          | 138 > 110 (0.6v, 3)           | 110 > 82 (0.6v, 3)  | 0.02-20              | 0.9995                   |
| 20  | Anisyl alcohol <sup>c</sup>                     | 27.82                | 105-13-5   | Fluka             | ≥98%(GC)                     | 138 > 109 (0.5v, 4)           | 109 > 94 (0.7v, 5)  | 0.02-20              | 0.9990                   |
| 21  | Hydroxy-citronellal <sup>b</sup>                | 28.10                | 107-75-5   | Acros             | 98%                          | 95 > 67 (0.4v, 4)             | 121 > 93 (0.7v, 3)  | 0.5-50               | 0.9991                   |
| 22  | 4-tert-Butylphenol <sup>b</sup>                 | 28.66                | 98-54-4    | Acros             | 97%                          | 135 > 107 (0.6v, 3)           | 107 > 77 (0.6v, 3)  | 0.005-5              | 0.9995                   |
| 23  | Cinnamyl alcohol <sup>b</sup>                   | 29.12                | 104-54-1   | Fluka             | ≥97%(GC)                     | 92 > 65 (1.0v, 4)             | 115 > 89 (0.7v, 4)  | 0.1-20               | 0.9986                   |
| 24  | 4-Phenyl-3-buten-2-one <sup>b</sup>             | 31.64                | 122-57-6   | Alfa Aesar        | ≥98%                         | 103 > 77 (0.5v, 4)            | 131 > 103 (0.4v, 3) | 0.02-10              | 0.9996                   |
| 25  | Eugenol <sup>b</sup>                            | 31.91                | 97-53-0    | Fluka             | ≥99%(GC)                     | 164 > 149 (0.6v, 3)           | 164 > 131 (0.7v, 3) | 0.2-20               | 0.9992                   |
| 26  | Dihydrocoumarin <sup>b</sup>                    | 32.51                | 119-84-6   | Acros             | 99%                          | 120 > 91 (0.6v, 4)            | 148 > 120 (0.8v, 4) | 0.005-5              | 0.9991                   |
| 27  | Coumarin <sup>b</sup>                           | 35.17                | 91-64-5    | Fluka             | ≥97%                         | 118 > 90 (0.4v, 3)            | 146 > 118 (0.8v, 3) | 0.005-5              | 0.9987                   |
| 28  | Isoeugenol <sup>b</sup>                         | 36.23                | 97-54-1    | Dr.Ehrenstorfer   | 99%                          | 164 > 149 (0.6v, 4)           | 164 > 131 (0.7v, 4) | 0.2-20               | 0.9985                   |
| 29  | 2,4-Dihydroxy-3-methylbenzaldehyde <sup>b</sup> | 36.83                | 6248-20-0  | Bephar            | ≥96%                         | 151 > 67 (1.2v, 4)            | 151 > 95 (1.2v, 4)  | 0.2-10               | 0.9768                   |
| 30  | alpha-iso-Methyllionone <sup>c</sup>            | 38.54                | 127-51-5   | Fluka             | ≥85%                         | 135 > 79 (0.8v, 4)            | 135 > 107 (0.4v, 4) | 0.01-10              | 0.9999                   |
| 31  | Lilial <sup>c</sup>                             | 39.95                | 80-54-6    | TCI               | ≥95%(GC)                     | 189 > 131 (1.0v, 3)           | 147 > 129 (0.8v, 4) | 0.01-20              | 0.9999                   |
| 32  | Pseudoionone <sup>b</sup> Isomer1               | 40.16                | 141-10-6   | Aldrich           | ≥90%(GC, mixture of isomers) | 109 > 79 (0.6v, 4)            | 149 > 93 (0.7v, 4)  | 0.2-20               | 0.9995                   |
|     | Pseudoionone Isomer2                            | 42.34                |            |                   |                              | 109 > 79 (0.6v, 4)            | 149 > 93 (0.7v, 4)  |                      |                          |
| 33  | 6-Methylcoumarin <sup>b</sup>                   | 40.88                | 92-48-8    | Aldrich           | ≥99%(GC)                     | 160 > 132 (0.4v, 4)           | 132 > 103 (1.6v, 4) | 0.02-20              | 0.9993                   |
| 34  | 7-Methylcoumarin <sup>b</sup>                   | 40.88                | 2445-83-2  | Aldrich           | ≥98%                         | 160 > 132 (0.4v, 4)           | 132 > 103 (1.6v, 4) |                      |                          |
| 35  | Diphenylamine <sup>b</sup>                      | 43.62                | 122-39-4   | Acros             | 99%                          | 169 > 140 (3.2v, 3)           | 169 > 115 (3.2v, 3) | 0.005-5              | 0.9998                   |
| 36  | 4-(p-Methoxyphenyl)-3-buten-2-one <sup>b</sup>  | 44.50                | 943-88-4   | Matrix Scientific | ≥95%                         | 161 > 133 (0.6v, 3)           | 176 > 145 (0.6v, 4) | 0.02-10              | 0.9983                   |
| 37  | Amyl cinnamal <sup>b</sup>                      | 45.09                | 122-40-7   | Aldrich           | 97%                          | 203 > 145 (1.2v, 4)           | 203 > 129 (1.6v, 4) | 0.05-20              | 0.9991                   |
| 38  | Lylal <sup>b</sup>                              | 45.47                | 31906-04-4 | Accustandard      | 97.7%(GC/MS)                 | 136 > 107 (0.4v, 3)           | 136 > 79 (0.7v, 3)  | 0.5-50               | 0.9996                   |
| 39  | Amylcinnamyl alcohol <sup>b</sup>               | 46.57                | 101-85-9   | Fluka             | 85%                          | 133 > 115 (0.7v, 4)           | 187 > 130 (0.7v, 3) | 0.5-50               | 0.9997                   |
| 40  | Farnesol <sup>c</sup> Isomer1                   | 47.28                | 4602-84-0  | Fluka             | ≥90%(GC, sum of isomers)     | 93 > 77 (0.4v, 4)             | 107 > 91 (0.5v, 4)  | 1-50                 | 0.9963                   |
|     | Farnesol Isomer2                                | 47.81                |            |                   |                              | 93 > 77 (0.4v, 4)             | 107 > 91 (0.5v, 4)  |                      |                          |
|     | Farnesol Isomer3                                | 48.24                |            |                   |                              | 93 > 77 (0.4v, 4)             | 107 > 91 (0.5v, 4)  |                      |                          |
| 41  | 7-Methoxycoumarin <sup>b</sup>                  | 47.37                | 531-59-9   | Aldrich           | ≥98%                         | 148 > 133 (0.7v, 3)           | 176 > 148 (0.8v, 3) | 0.05-20              | 0.9989                   |
| 42  | 1-(p-Methoxyphenyl)-1-penten-3-one <sup>b</sup> | 48.64                | 104-27-8   | Accustandard      | 100%(GC/FID)                 | 161 > 133 (0.6v, 4)           | 190 > 161 (1.4v, 4) | 0.01-10              | 0.9997                   |
| 43  | Hexyl cinnamaldehyde <sup>c</sup>               | 49.08                | 101-86-0   | Aldrich           | ≥95%                         | 145 > 117 (0.7v, 4)           | 129 > 102 (1.7v, 5) | 0.05-20              | 0.9999                   |
| 44  | Benzyl benzoate <sup>c</sup>                    | 49.46                | 120-51-4   | Fluka             | ≥99%(GC)                     | 194 > 165 (1.7v, 3)           | 105 > 77 (0.6v, 3)  | 0.02-20              | 0.9992                   |

|    |                                                        |       |          |            |          |                     |                     |         |        |
|----|--------------------------------------------------------|-------|----------|------------|----------|---------------------|---------------------|---------|--------|
| 45 | 4-tert-Butyl-3-methoxy-2,6-dinitrotoluene <sup>b</sup> | 52.23 | 83-66-9  | TCI        | ≥95%     | 253 > 219 (0.6v, 5) | 253 > 121 (1.3v, 5) | 0.2-50  | 0.9985 |
| 46 | Benzyl salicylate <sup>b</sup>                         | 53.47 | 118-58-1 | Fluka      | ≥99%(GC) | 91 > 65 (0.4v, 3)   | 228 > 210 (0.8v, 3) | 0.2-10  | 0.9850 |
| 47 | 7-Ethoxy-4-methylcoumarin <sup>b</sup>                 | 56.21 | 87-05-8  | Alfa Aesar | 98%      | 204 > 148 (1.9v, 4) | 148 > 91 (1.1v, 4)  | 0.1-10  | 0.9988 |
| 48 | Benzyl cinnamate <sup>c</sup>                          | 60.61 | 103-41-3 | Fluka      | ≥98%(GC) | 131 > 103 (0.7v, 3) | 192 > 115 (1.1v, 4) | 0.05-20 | 0.9984 |

<sup>a</sup> Precursor > quantifier (excitation voltage, isolation window), MRM: multiple reaction monitoring.

<sup>b</sup> Banned compound according to the Toys Safety Directive 2009/48/EC. However, the presence of traces of these fragrances shall be allowed provided that such presence is technically unavoidable under good manufacturing practice and does not exceed 100 mg/kg.

<sup>c</sup> According to 2009/48/EC, the compound requires declaration when contents of 100 mg/kg in the material are exceeded.

Accepted Article

Table 2 Recoveries, LOD, LOQ, intraday and interday repeatabilities for 48 fragrance allergens in plush toys

| No. | Compounds                                 | LOD<br>(mg/kg) | LOQ<br>(mg/kg) | Recovery in plush toys % (intraday repeatability, n=6, % RSD) |            |             |             |            | interday repeatability,<br>n=4 (% RSD) |     |
|-----|-------------------------------------------|----------------|----------------|---------------------------------------------------------------|------------|-------------|-------------|------------|----------------------------------------|-----|
|     |                                           |                |                | 0.4mg/kg                                                      | 4mg/kg     | 40mg/kg     | 100mg/kg    | 200mg/kg   | 100mg/kg                               |     |
| 1   | Ethyl acrylate                            | 1.0            | 4.0            |                                                               | 98.5 (6.2) | 95.0 (2.8)  | 99.6 (2.5)  |            |                                        | 4.0 |
| 2   | Methyl trans-2-butenate                   | 0.5            | 2.0            |                                                               | 97.4 (3.5) | 96.2 (5.3)  | 95.9 (2.4)  |            |                                        | 5.8 |
| 3   | 5-Methyl-2,3-hexanedione                  | 0.1            | 0.4            | 97.9 (4.6)                                                    |            | 100.9 (2.2) | 97.9 (1.7)  |            |                                        | 4.2 |
| 4   | trans-2-Heptenal                          | 0.4            | 1.0            |                                                               | 95.8 (5.0) | 101.5 (2.4) | 99.3 (1.9)  |            |                                        | 6.1 |
| 5   | trans-2-Hexenal dimethyl acetal           | 1.0            | 4.0            |                                                               | 95.3 (3.8) | 110.4 (3.6) | 109.1 (4.1) |            |                                        | 3.3 |
| 6   | Benzyl alcohol                            | 0.04           | 0.1            | 96.2 (2.4)                                                    |            | 95.5 (3.4)  | 97.1 (2.3)  |            |                                        | 4.6 |
| 7   | d-Limonene                                | 0.4            | 1.0            |                                                               | 95.1 (3.1) | 98.3 (2.7)  | 95.9 (2.8)  |            |                                        | 6.9 |
| 8   | Dimethyl citraconate                      | 0.04           | 0.1            | 93.7 (6.1)                                                    |            | 96.1 (2.7)  | 98.8 (3.4)  |            |                                        | 4.9 |
| 9   | trans-2-Hexenal diethyl acetal            | 4.0            | 10             |                                                               |            | 104.7 (3.8) | 97.5 (2.7)  | 95.2 (6.4) |                                        | 3.5 |
| 10  | Linalool                                  | 0.1            | 0.4            | 92.2 (6.0)                                                    |            | 102.3 (3.3) | 94.8 (2.5)  |            |                                        | 6.0 |
| 11  | Benzyl cyanide                            | 0.01           | 0.04           | 90.3 (2.9)                                                    |            | 97.2 (4.1)  | 95.5 (1.7)  |            |                                        | 5.9 |
| 12  | Diethyl maleate                           | 0.05           | 0.2            | 85.7 (4.9)                                                    |            | 95.6 (5.8)  | 97.1 (4.3)  |            |                                        | 8.4 |
| 13  | Methyl heptene carbonate                  | 0.4            | 1.0            |                                                               | 92.0 (4.0) | 97.7 (5.1)  | 102.6 (4.7) |            |                                        | 6.7 |
| 14  | 4-Methoxyphenol                           | 0.05           | 0.2            | 94.7 (5.2)                                                    |            | 95.0 (3.6)  | 97.8 (2.7)  |            |                                        | 5.1 |
| 15  | Citronellol                               | 0.4            | 1.0            |                                                               | 92.1 (4.8) | 94.6 (2.7)  | 96.3 (4.5)  |            |                                        | 4.9 |
| 16  | Citral                                    | 1.0            | 4.0            |                                                               | 85.7 (6.1) | 99.2 (2.4)  | 100.4 (2.1) |            |                                        | 5.2 |
| 17  | Geraniol                                  | 4              | 10             |                                                               |            | 97.2 (1.8)  | 94.2 (4.5)  | 91.6 (2.7) |                                        | 7.3 |
| 18  | Cinnamal                                  | 0.05           | 0.2            | 96.1 (2.9)                                                    |            | 102.0 (2.1) | 100.5 (2.5) |            |                                        | 7.0 |
| 19  | 4-Ethoxy-phenol                           | 0.1            | 0.4            | 90.9 (4.3)                                                    |            | 101.1 (2.8) | 98.0 (3.7)  |            |                                        | 6.4 |
| 20  | Anisyl alcohol                            | 0.1            | 0.4            | 95.2 (4.6)                                                    |            | 105.0 (3.1) | 96.6 (2.4)  |            |                                        | 3.5 |
| 21  | Hydroxy-citronellal                       | 4              | 10             |                                                               |            | 100.9 (2.7) | 99.8 (1.2)  | 92.7 (6.6) |                                        | 4.9 |
| 22  | 4-tert-Butylphenol                        | 0.04           | 0.1            | 98.5 (5.3)                                                    |            | 96.8 (2.5)  | 101.5 (3.0) |            |                                        | 7.7 |
| 23  | Cinnamyl alcohol                          | 0.5            | 2.0            |                                                               | 93.2 (4.8) | 103.4 (2.3) | 97.4 (1.9)  |            |                                        | 3.2 |
| 24  | 4-Phenyl-3-buten-2-one                    | 0.1            | 0.4            | 93.8 (2.3)                                                    |            | 99.4 (2.8)  | 97.3 (1.5)  |            |                                        | 3.7 |
| 25  | Eugenol                                   | 1.0            | 4.0            |                                                               | 96.4 (4.0) | 97.3 (2.9)  | 106.8 (4.4) |            |                                        | 6.5 |
| 26  | Dihydrocoumarin                           | 0.04           | 0.1            | 94.1 (2.4)                                                    |            | 101.3 (2.7) | 97.4 (3.8)  |            |                                        | 4.2 |
| 27  | Coumarin                                  | 0.04           | 0.1            | 92.0 (3.6)                                                    |            | 98.0 (2.3)  | 93.1 (2.0)  |            |                                        | 8.7 |
| 28  | Isoeugenol                                | 1.0            | 4.0            |                                                               | 90.4 (3.7) | 105.5 (4.2) | 96.1 (2.8)  |            |                                        | 8.0 |
| 29  | 2,4-Dihydroxy-3-methylbenzaldehyde        | 1.0            | 4.0            |                                                               | 86.5 (7.5) | 100.6 (3.6) | 106.5 (7.3) |            |                                        | 7.7 |
| 30  | alpha-iso-Methylionone                    | 0.05           | 0.2            | 88.6 (3.7)                                                    |            | 100.0 (1.8) | 99.9 (3.2)  |            |                                        | 5.6 |
| 31  | Lilial                                    | 0.05           | 0.2            | 94.6 (4.6)                                                    |            | 99.1 (2.2)  | 98.7 (2.4)  |            |                                        | 5.8 |
| 32  | Pseudoionone                              | 1.0            | 4.0            |                                                               | 93.3 (4.6) | 103.1 (4.7) | 99.6 (1.5)  |            |                                        | 7.0 |
| 33  | 6-Methylcoumarin                          | 0.1            | 0.4            | 93.5 (4.0)                                                    |            | 94.1 (1.8)  | 93.7 (3.1)  |            |                                        | 4.2 |
| 34  | 7-Methylcoumarin                          |                |                |                                                               |            |             |             |            |                                        |     |
| 35  | Diphenylamine                             | 0.04           | 0.1            | 91.9 (4.3)                                                    |            | 93.5 (2.5)  | 104.3 (2.5) |            |                                        | 6.9 |
| 36  | 4-(p-Methoxyphenyl)-3-buten-2-one         | 0.1            | 0.4            | 90.0 (5.5)                                                    |            | 102.2 (3.2) | 98.6 (1.7)  |            |                                        | 4.2 |
| 37  | Amyl cinnamal                             | 0.4            | 1.0            |                                                               | 93.4 (5.9) | 101.0 (3.7) | 99.1 (1.9)  |            |                                        | 4.6 |
| 38  | Lylal                                     | 4.0            | 10             |                                                               |            | 96.2 (3.2)  | 94.6 (2.7)  | 93.7 (4.3) |                                        | 7.8 |
| 39  | Amylcinnamyl alcohol                      | 4.0            | 10             |                                                               |            | 96.1 (2.1)  | 98.7 (3.3)  | 93.2 (6.1) |                                        | 6.0 |
| 40  | Farnesol                                  | 5.0            | 20             |                                                               |            | 94.2 (5.4)  | 100.3 (5.7) | 94.7 (2.6) |                                        | 5.5 |
| 41  | 7-Methoxycoumarin                         | 0.4            | 1.0            |                                                               | 91.0 (3.6) | 99.1 (4.5)  | 95.7 (2.6)  |            |                                        | 4.5 |
| 42  | 1-(p-Methoxyphenyl)-1-penten-3-one        | 0.05           | 0.2            | 91.1 (1.4)                                                    |            | 99.8 (3.4)  | 98.6 (1.8)  |            |                                        | 8.7 |
| 43  | Hexyl cinnamaldehyde                      | 0.4            | 1.0            |                                                               | 90.2 (4.4) | 98.9 (3.0)  | 98.2 (3.3)  |            |                                        | 7.2 |
| 44  | Benzyl benzoate                           | 0.1            | 0.4            | 96.1 (3.0)                                                    |            | 105.4 (3.9) | 101.7 (2.1) |            |                                        | 4.6 |
| 45  | 4-tert-Butyl-3-methoxy-2,6-dinitrotoluene | 1.0            | 4.0            |                                                               | 88.4 (6.7) | 95.2 (3.8)  | 104.0 (2.7) |            |                                        | 7.4 |
| 46  | Benzyl salicylate                         | 1.0            | 4.0            |                                                               | 94.5 (6.9) | 96.3 (2.7)  | 100.2 (5.0) |            |                                        | 8.5 |
| 47  | 7-Ethoxy-4-methylcoumarin                 | 0.5            | 2.0            |                                                               | 91.6 (4.6) | 100.4 (3.3) | 98.3 (2.1)  |            |                                        | 6.3 |
| 48  | Benzyl cinnamate                          | 0.4            | 1.0            |                                                               | 96.8 (4.5) | 97.9 (4.3)  | 96.4 (3.6)  |            |                                        | 5.2 |

Table 3 Recoveries, LOD, LOQ, intraday and interday repeatabilities for 48 fragrance allergens in paper toys

| No. | Compounds                                 | LOD<br>(mg/kg) | LOQ<br>(mg/kg) | Recovery in paper toys % (intraday repeatability, n=6, % RSD) |             |             |             |             | interday repeatability,<br>n=4 (% RSD) |
|-----|-------------------------------------------|----------------|----------------|---------------------------------------------------------------|-------------|-------------|-------------|-------------|----------------------------------------|
|     |                                           |                |                | 0.4mg/kg                                                      | 4mg/kg      | 40mg/kg     | 100mg/kg    | 200mg/kg    |                                        |
| 1   | Ethyl acrylate                            | 1.0            | 4.0            |                                                               | 94.4 (5.1)  | 97.3 (3.8)  | 98.9 (2.1)  |             | 6.4                                    |
| 2   | Methyl trans-2-butenate                   | 0.5            | 2.0            |                                                               | 93.8 (6.0)  | 103.2 (4.6) | 99.3 (3.1)  |             | 7.7                                    |
| 3   | 5-Methyl-2,3-hexanedione                  | 0.1            | 0.4            | 93.7 (3.8)                                                    |             | 97.4 (2.7)  | 98.6 (2.3)  |             | 4.9                                    |
| 4   | trans-2-Heptenal                          | 0.4            | 1.0            |                                                               | 95.3 (5.7)  | 101.7 (3.8) | 99.8 (2.0)  |             | 5.4                                    |
| 5   | trans-2-Hexenal dimethyl acetal           | 1.0            | 4.0            |                                                               | 94.4 (3.8)  | 106.5 (8.3) | 103.1 (5.9) |             | 5.8                                    |
| 6   | Benzyl alcohol                            | 0.04           | 0.1            | 93.1 (3.2)                                                    |             | 104.5 (4.6) | 97.6 (3.0)  |             | 5.2                                    |
| 7   | d-Limonene                                | 0.4            | 1.0            |                                                               | 92.8 (4.3)  | 95.7 (3.5)  | 96.2 (5.0)  |             | 6.7                                    |
| 8   | Dimethyl citraconate                      | 0.04           | 0.1            | 88.9 (5.7)                                                    |             | 101.1 (3.4) | 94.8 (4.8)  |             | 9.2                                    |
| 9   | trans-2-Hexenal diethyl acetal            | 4.0            | 10             |                                                               |             | 108.3 (6.7) | 99.4 (5.5)  | 103.9 (1.8) | 6.0                                    |
| 10  | Linalool                                  | 0.1            | 0.4            | 90.4 (3.7)                                                    |             | 106.5 (2.4) | 98.0 (2.7)  |             | 4.6                                    |
| 11  | Benzyl cyanide                            | 0.01           | 0.04           | 97.4 (2.4)                                                    |             | 103.6 (5.1) | 97.3 (5.0)  |             | 6.9                                    |
| 12  | Diethyl maleate                           | 0.05           | 0.2            | 94.0 (5.6)                                                    |             | 97.8 (2.5)  | 105.4 (5.2) |             | 7.3                                    |
| 13  | Methyl heptene carbonate                  | 0.4            | 1.0            |                                                               | 92.0 (4.0)  | 98.4 (3.2)  | 102.5 (2.6) |             | 4.0                                    |
| 14  | 4-Methoxyphenol                           | 0.05           | 0.2            | 90.6 (2.4)                                                    |             | 104.3 (3.7) | 98.0 (4.2)  |             | 4.5                                    |
| 15  | Citronellol                               | 0.4            | 1.0            |                                                               | 95.5 (3.3)  | 96.7 (2.9)  | 97.7 (3.5)  |             | 5.2                                    |
| 16  | Citral                                    | 1.0            | 4.0            |                                                               | 98.2 (6.9)  | 102.2 (4.0) | 102.0 (4.3) |             | 7.0                                    |
| 17  | Geraniol                                  | 4              | 10             |                                                               |             | 96.0 (2.6)  | 95.9 (5.2)  | 97.8 (2.2)  | 8.5                                    |
| 18  | Cinnamal                                  | 0.05           | 0.2            | 100.4 (4.2)                                                   |             | 98.3 (2.9)  | 100.5 (4.1) |             | 3.8                                    |
| 19  | 4-Ethoxy-phenol                           | 0.1            | 0.4            | 96.0 (7.5)                                                    |             | 95.3 (3.1)  | 103.3 (4.4) |             | 5.9                                    |
| 20  | Anisyl alcohol                            | 0.1            | 0.4            | 94.0 (5.4)                                                    |             | 101.1 (2.6) | 98.5 (5.8)  |             | 4.6                                    |
| 21  | Hydroxy-citronellal                       | 4              | 10             |                                                               |             | 100.4 (3.4) | 101.6 (5.2) | 101.2 (3.5) | 7.2                                    |
| 22  | 4-tert-Butylphenol                        | 0.04           | 0.1            | 95.8 (4.8)                                                    |             | 105.3 (3.6) | 96.7 (7.3)  |             | 6.8                                    |
| 23  | Cinnamyl alcohol                          | 0.5            | 2.0            |                                                               | 94.6 (3.0)  | 97.1 (4.5)  | 95.6 (3.4)  |             | 5.1                                    |
| 24  | 4-Phenyl-3-buten-2-one                    | 0.1            | 0.4            | 108.8 (5.0)                                                   |             | 102.4 (2.9) | 99.2 (2.8)  |             | 6.9                                    |
| 25  | Eugenol                                   | 1.0            | 4.0            |                                                               | 98.4 (5.7)  | 96.6 (6.9)  | 104.9 (4.0) |             | 4.1                                    |
| 26  | Dihydrocoumarin                           | 0.04           | 0.1            | 105.2 (5.9)                                                   |             | 102.7 (2.6) | 101.9 (3.6) |             | 6.3                                    |
| 27  | Coumarin                                  | 0.04           | 0.1            | 94.3 (4.5)                                                    |             | 105.5 (2.5) | 105.0 (5.0) |             | 5.3                                    |
| 28  | Isoeugenol                                | 1.0            | 4.0            |                                                               | 94.2 (4.3)  | 97.8 (5.1)  | 102.2 (6.0) |             | 8.9                                    |
| 29  | 2,4-Dihydroxy-3-methylbenzaldehyde        | 1.0            | 4.0            |                                                               | 103.8 (5.3) | 104.8 (8.9) | 101.8 (6.4) |             | 7.0                                    |
| 30  | alpha-iso-Methylionone                    | 0.05           | 0.2            | 96.1 (4.1)                                                    |             | 101.4 (2.9) | 99.2 (3.8)  |             | 5.1                                    |
| 31  | Lilial                                    | 0.05           | 0.2            | 94.1 (3.6)                                                    |             | 100.5 (2.8) | 100.7 (4.3) |             | 4.8                                    |
| 32  | Pseudoionone                              | 1.0            | 4.0            |                                                               | 93.1 (8.3)  | 100.8 (2.2) | 99.2 (4.4)  |             | 4.2                                    |
| 33  | 6-Methylcoumarin                          | 0.1            | 0.4            | 95.9 (3.5)                                                    |             | 98.1 (4.5)  | 104.6 (6.4) |             | 7.4                                    |
| 34  | 7-Methylcoumarin                          |                |                |                                                               |             |             |             |             |                                        |
| 35  | Diphenylamine                             | 0.04           | 0.1            | 97.6 (3.4)                                                    |             | 103.7 (4.9) | 97.4 (3.9)  |             | 5.5                                    |
| 36  | 4-(p-Methoxyphenyl)-3-buten-2-one         | 0.1            | 0.4            | 100.7 (5.6)                                                   |             | 103.0 (1.3) | 101.9 (4.6) |             | 7.3                                    |
| 37  | Amyl cinnamal                             | 0.4            | 1.0            |                                                               | 99.8 (5.3)  | 103.3 (3.6) | 99.0 (3.6)  |             | 3.7                                    |
| 38  | Lylal                                     | 4.0            | 10             |                                                               |             | 106.1 (5.3) | 101.6 (4.7) | 102.7 (2.8) | 8.3                                    |
| 39  | Amylcinnamyl alcohol                      | 4.0            | 10             |                                                               |             | 104.5 (3.6) | 99.0 (2.3)  | 102.9 (2.9) | 6.7                                    |
| 40  | Farnesol                                  | 5.0            | 20             |                                                               |             | 97.7 (5.5)  | 103.0 (5.9) | 105.4 (4.3) | 6.6                                    |
| 41  | 7-Methoxycoumarin                         | 0.4            | 1.0            |                                                               | 94.2 (4.1)  | 95.8 (5.5)  | 98.5 (4.0)  |             | 4.7                                    |
| 42  | 1-(p-Methoxyphenyl)-1-penten-3-one        | 0.05           | 0.2            | 101.8 (2.3)                                                   |             | 101.6 (3.5) | 100.7 (3.8) |             | 5.6                                    |
| 43  | Hexyl cinnamaldehyde                      | 0.4            | 1.0            |                                                               | 95.7 (2.0)  | 101.4 (3.7) | 102.1 (3.8) |             | 6.5                                    |
| 44  | Benzyl benzoate                           | 0.1            | 0.4            | 95.7 (3.0)                                                    |             | 100.4 (3.5) | 96.4 (3.2)  |             | 6.4                                    |
| 45  | 4-tert-Butyl-3-methoxy-2,6-dinitrotoluene | 1.0            | 4.0            |                                                               | 94.3 (3.5)  | 97.8 (3.5)  | 99.2 (2.9)  |             | 7.1                                    |
| 46  | Benzyl salicylate                         | 1.0            | 4.0            |                                                               | 102.2 (5.4) | 98.1 (4.2)  | 97.8 (4.7)  |             | 9.1                                    |
| 47  | 7-Ethoxy-4-methylcoumarin                 | 0.5            | 2.0            |                                                               | 100.3 (1.6) | 102.7 (4.0) | 101.8 (4.6) |             | 6.8                                    |
| 48  | Benzyl cinnamate                          | 0.4            | 1.0            |                                                               | 89.3 (4.9)  | 102.2 (3.5) | 98.8 (5.5)  |             | 8.0                                    |

Table 4 Recoveries, LOD, LOQ, intraday and interday repeatabilities for 48 fragrance allergens in plastic toys

| No. | Compounds                                 | LOD<br>(mg/kg) | LOQ<br>(mg/kg) | Recovery in plastic toys /% (intraday repeatability, n=6, % RSD) |             |            |            |            |             | interday repeatability,<br>n=4 (% RSD) |           |
|-----|-------------------------------------------|----------------|----------------|------------------------------------------------------------------|-------------|------------|------------|------------|-------------|----------------------------------------|-----------|
|     |                                           |                |                | 0.1 mg/kg                                                        | 1.0 mg/kg   | 5.0 mg/kg  | 10 mg/kg   | 20 mg/kg   | 50 mg/kg    | 100 mg/kg                              | 100 mg/kg |
| 1   | Ethyl acrylate                            | 4.0            | 10             |                                                                  |             |            | 91.1 (2.8) |            | 87.2 (2.2)  | 93.9 (2.6)                             | 5.1       |
| 2   | Methyl trans-2-butenate                   | 2.0            | 5.0            |                                                                  |             | 97.2 (1.6) |            |            | 95.9 (2.7)  | 95.6 (0.7)                             | 4.3       |
| 3   | 5-Methyl-2,3-hexanedione                  | 0.2            | 0.5            |                                                                  | 90.0 (2.3)  |            |            |            | 81.2 (1.6)  | 94.7 (2.6)                             | 6.1       |
| 4   | trans-2-Heptenal                          | 0.1            | 0.25           |                                                                  | 88.2 (1.8)  |            |            |            | 88.3 (3.1)  | 88.5 (3.6)                             | 4.8       |
| 5   | trans-2-Hexenal dimethyl acetal           | 0.4            | 1.0            |                                                                  | 93.0 (4.8)  |            |            |            | 83.1 (9.8)  | 96.3 (5.0)                             | 9.8       |
| 6   | Benzyl alcohol                            | 0.02           | 0.05           | 98.0 (5.5)                                                       |             |            |            |            | 95.0 (4.3)  | 96.2 (3.7)                             | 5.6       |
| 7   | d-Limonene                                | 2.0            | 5.0            |                                                                  |             | 93.6 (4.0) |            |            | 90.3 (3.6)  | 88.4 (2.7)                             | 6.5       |
| 8   | Dimethyl citraconate                      | 0.02           | 0.05           | 92.7 (5.8)                                                       |             |            |            |            | 91.7 (4.3)  | 92.0 (4.9)                             | 7.0       |
| 9   | trans-2-Hexenal diethyl acetal            | 5.0            | 20             |                                                                  |             |            |            | 92.7 (3.2) | 89.4 (7.2)  | 84.4 (4.8)                             | 8.4       |
| 10  | Linalool                                  | 0.04           | 0.1            | 94.2 (6.5)                                                       |             |            |            |            | 92.8 (4.1)  | 93.5 (2.6)                             | 6.0       |
| 11  | Benzyl cyanide                            | 0.005          | 0.02           | 89.9 (5.0)                                                       |             |            |            |            | 93.3 (3.6)  | 91.1 (2.5)                             | 4.5       |
| 12  | Diethyl maleate                           | 0.02           | 0.05           | 89.4 (8.2)                                                       |             |            |            |            | 92.0 (3.8)  | 97.1 (3.4)                             | 6.9       |
| 13  | Methyl heptene carbonate                  | 0.1            | 0.25           |                                                                  | 94.9 (5.7)  |            |            |            | 90.9 (6.6)  | 93.7 (5.2)                             | 10.5      |
| 14  | 4-Methoxyphenol                           | 0.02           | 0.05           | 93.0 (6.4)                                                       |             |            |            |            | 95.4 (3.8)  | 90.0 (3.0)                             | 6.0       |
| 15  | Citronellol                               | 0.1            | 0.25           |                                                                  | 87.5 (5.1)  |            |            |            | 95.0 (3.8)  | 94.7 (3.4)                             | 7.5       |
| 16  | Citral                                    | 0.4            | 1.0            |                                                                  | 99.4 (3.6)  |            |            |            | 90.8 (6.1)  | 90.2 (3.6)                             | 5.5       |
| 17  | Geraniol                                  | 1.0            | 2.5            |                                                                  |             |            | 85.3 (2.8) |            | 98.5 (2.0)  | 89.4 (5.5)                             | 6.8       |
| 18  | Cinnamal                                  | 0.02           | 0.05           |                                                                  | 89.5 (3.3)  |            |            |            | 91.0 (3.7)  | 95.8 (4.0)                             | 6.5       |
| 19  | 4-Ethoxy-phenol                           | 0.1            | 0.25           |                                                                  | 96.3 (1.7)  |            |            |            | 97.2 (5.4)  | 92.8 (3.6)                             | 5.8       |
| 20  | Anisyl alcohol                            | 0.1            | 0.25           |                                                                  | 93.7 (4.8)  |            |            |            | 91.5 (5.0)  | 96.3 (4.0)                             | 5.6       |
| 21  | Hydroxy-citronellal                       | 1.0            | 2.5            |                                                                  |             |            | 96.3 (4.9) |            | 96.2 (1.8)  | 94.3 (3.6)                             | 4.3       |
| 22  | 4-tert-Butylphenol                        | 0.02           | 0.05           | 90.9 (4.2)                                                       |             |            |            |            | 95.0 (2.2)  | 98.1 (4.7)                             | 5.0       |
| 23  | Cinnamyl alcohol                          | 0.2            | 0.5            |                                                                  | 93.2 (4.0)  |            |            |            | 95.5 (4.5)  | 91.9 (2.7)                             | 7.6       |
| 24  | 4-Phenyl-3-buten-2-one                    | 0.04           | 0.1            | 98.6 (3.1)                                                       |             |            |            |            | 93.0 (3.0)  | 97.1 (2.1)                             | 5.3       |
| 25  | Eugenol                                   | 0.4            | 1.0            |                                                                  | 94.4 (4.6)  |            |            |            | 90.7 (5.2)  | 92.5 (3.9)                             | 7.1       |
| 26  | Dihydrocoumarin                           | 0.02           | 0.05           | 92.0 (4.8)                                                       |             |            |            |            | 99.0 (3.6)  | 94.1 (5.1)                             | 7.9       |
| 27  | Coumarin                                  | 0.02           | 0.05           | 90.2 (5.6)                                                       |             |            |            |            | 95.0 (2.4)  | 97.3 (4.9)                             | 7.1       |
| 28  | Isoeugenol                                | 0.4            | 1.0            |                                                                  | 88.7 (4.7)  |            |            |            | 94.3 (5.0)  | 97.1 (2.6)                             | 6.1       |
| 29  | 2,4-Dihydroxy-3-methylbenzaldehyde        | 0.4            | 1.0            |                                                                  | 90.0 (2.4)  |            |            |            | 109.1 (6.2) | 94.3 (2.7)                             | 5.7       |
| 30  | alpha-iso-Methylionone                    | 0.02           | 0.05           | 88.7 (1.8)                                                       |             |            |            |            | 93.2 (3.7)  | 97.2 (3.9)                             | 12.9      |
| 31  | Lilial                                    | 0.02           | 0.05           | 93.1 (3.0)                                                       |             |            |            |            | 93.5 (4.2)  | 101.5 (4.6)                            | 8.1       |
| 32  | Pseudoionone                              | 0.4            | 1.0            |                                                                  | 99.5 (3.5)  |            |            |            | 96.9 (1.8)  | 97.7 (4.8)                             | 7.9       |
| 33  | 6-Methylcoumarin                          |                |                |                                                                  |             |            |            |            |             |                                        |           |
| 34  | 7-Methylcoumarin                          | 0.04           | 0.1            |                                                                  | 90.8 (4.5)  |            |            |            | 88.0 (4.2)  | 95.5 (3.4)                             | 6.3       |
| 35  | Diphenylamine                             | 0.02           | 0.05           | 94.5 (6.4)                                                       |             |            |            |            | 92.9 (6.2)  | 101.5 (4.6)                            | 9.9       |
| 36  | 4-(p-Methoxyphenyl)-3-butene-2-one        | 0.04           | 0.1            | 81.3 (7.0)                                                       |             |            |            |            | 89.7 (4.9)  | 96.2 (5.9)                             | 11.6      |
| 37  | Amyl cinnamal                             | 0.1            | 0.25           |                                                                  | 101.8 (3.6) |            |            |            | 92.9 (3.8)  | 97.2 (6.4)                             | 9.6       |
| 38  | Lylal                                     | 1.0            | 2.5            |                                                                  |             |            | 89.5 (2.2) |            | 83.3 (6.8)  | 84.3 (4.0)                             | 7.8       |
| 39  | Amylcinnamyl alcohol                      | 1.0            | 2.5            |                                                                  |             |            | 97.9 (5.8) |            | 98.6 (4.3)  | 97.0 (4.3)                             | 5.4       |
| 40  | Farnesol                                  | 2.0            | 5              |                                                                  |             |            | 93.5 (4.5) |            | 102.2 (3.7) | 96.3 (5.1)                             | 8.8       |
| 41  | 7-Methoxycoumarin                         | 0.1            | 0.25           |                                                                  | 91.4 (7.2)  |            |            |            | 96.8 (5.0)  | 95.1 (3.9)                             | 6.6       |
| 42  | 1-(p-Methoxyphenyl)-1-penten-3-one        | 0.1            | 0.25           |                                                                  | 95.3 (6.9)  |            |            |            | 90.3 (5.7)  | 95.2 (5.4)                             | 11.9      |
| 43  | Hexyl cinnamaldehyde                      | 0.2            | 0.5            |                                                                  | 96.1 (2.2)  |            |            |            | 92.6 (6.3)  | 97.5 (5.8)                             | 13.4      |
| 44  | Benzyl benzoate                           | 0.1            | 0.25           |                                                                  | 93.5 (5.0)  |            |            |            | 85.2 (4.2)  | 92.3 (5.4)                             | 7.2       |
| 45  | 4-tert-Butyl-3-methoxy-2,6-dinitrotoluene | 0.4            | 1.0            |                                                                  | 98.4 (4.2)  |            |            |            | 90.7 (5.0)  | 95.6 (4.3)                             | 6.9       |
| 46  | Benzyl salicylate                         | 0.4            | 1.0            |                                                                  | 103.3 (6.0) |            |            |            | 87.8 (4.1)  | 92.9 (3.7)                             | 5.8       |
| 47  | 7-Ethoxy-4-methylcoumarin                 | 0.2            | 0.5            |                                                                  | 90.2 (3.1)  |            |            |            | 85.5 (3.5)  | 87.6 (5.1)                             | 8.4       |
| 48  | Benzyl cinnamate                          | 0.1            | 0.25           |                                                                  | 95.6 (7.4)  |            |            |            | 91.1 (2.5)  | 86.4 (4.9)                             | 6.8       |

For ethyl acrylate, methyl trans-2-butenate, d-limonene, and trans-2-hexenal diethyl acetal, the solution was not concentrated via rotary evaporation (see section 3.3.2).

Table 5 Recoveries, LOD, LOQ, intraday and interday repeatabilities for 48 fragrance allergens in play clays

| No. | Compounds                                 | LOD<br>(mg/kg) | LOQ<br>(mg/kg) | Recovery in play clays /% (intraday repeatability, n=6, % RSD) |             |            |             |            |            | interday repeatability,<br>n=4 (% RSD) |           |
|-----|-------------------------------------------|----------------|----------------|----------------------------------------------------------------|-------------|------------|-------------|------------|------------|----------------------------------------|-----------|
|     |                                           |                |                | 0.1 mg/kg                                                      | 1.0 mg/kg   | 5.0 mg/kg  | 10 mg/kg    | 20 mg/kg   | 50 mg/kg   | 100 mg/kg                              | 100 mg/kg |
| 1   | Ethyl acrylate                            | 4.0            | 10             |                                                                |             |            | 104.0 (5.2) |            | 92.7 (2.4) | 95.3 (3.3)                             | 7.7       |
| 2   | Methyl trans-2-butenate                   | 2.0            | 5.0            |                                                                |             | 89.5 (2.3) |             |            | 93.5 (2.8) | 98.7 (1.5)                             | 8.4       |
| 3   | 5-Methyl-2,3-hexanedione                  | 0.2            | 0.5            |                                                                | 87.5 (2.5)  |            |             |            | 95.8 (1.9) | 89.4 (2.5)                             | 7.6       |
| 4   | trans-2-Heptenal                          | 0.1            | 0.25           |                                                                | 86.6 (1.1)  |            |             |            | 93.8 (5.1) | 85.6 (2.1)                             | 6.1       |
| 5   | trans-2-Hexenal dimethyl acetal           | 0.4            | 1.0            |                                                                | 101.8 (2.7) |            |             |            | 90.4 (3.8) | 103.6 (5.3)                            | 6.5       |
| 6   | Benzyl alcohol                            | 0.02           | 0.05           | 82.9 (3.2)                                                     |             |            |             |            | 88.9 (2.3) | 90.9 (4.6)                             | 5.8       |
| 7   | d-Limonene                                | 2.0            | 5.0            |                                                                |             | 95.3 (2.5) |             |            | 95.0 (3.1) | 92.6 (1.6)                             | 5.9       |
| 8   | Dimethyl citraconate                      | 0.02           | 0.05           | 92.2 (4.5)                                                     |             |            |             |            | 83.6 (4.8) | 84.1 (3.8)                             | 4.3       |
| 9   | trans-2-Hexenal diethyl                   | 5.0            | 20             |                                                                |             |            |             | 88.7 (7.2) | 90.2 (5.2) | 82.1 (10.5)                            | 12.2      |
| 10  | Linalool                                  | 0.04           | 0.1            | 90.1 (3.0)                                                     |             |            |             |            | 87.4 (0.7) | 87.1 (1.8)                             | 3.1       |
| 11  | Benzyl cyanide                            | 0.005          | 0.02           | 91.9 (3.4)                                                     |             |            |             |            | 86.6 (6.0) | 79.7 (3.8)                             | 5.1       |
| 12  | Diethyl maleate                           | 0.02           | 0.05           | 86.1 (4.3)                                                     |             |            |             |            | 84.6 (6.2) | 81.0 (3.5)                             | 5.8       |
| 13  | Methyl heptene carbonate                  | 0.1            | 0.25           |                                                                | 93.1 (2.2)  |            |             |            | 95.9 (3.2) | 99.0 (3.6)                             | 7.2       |
| 14  | 4-Methoxyphenol                           | 0.02           | 0.05           | 87.7 (3.9)                                                     |             |            |             |            | 94.9 (3.8) | 97.8 (2.5)                             | 5.8       |
| 15  | Citronellol                               | 0.1            | 0.25           |                                                                | 91.3 (1.7)  |            |             |            | 85.4 (1.5) | 89.5 (5.0)                             | 4.6       |
| 16  | Citral                                    | 0.4            | 1.0            |                                                                | 94.2 (3.3)  |            |             |            | 85.0 (2.7) | 86.1 (4.8)                             | 6.4       |
| 17  | Geraniol                                  | 1.0            | 2.5            |                                                                |             |            | 97.4 (3.0)  |            | 97.7 (1.4) | 93.5 (3.9)                             | 3.9       |
| 18  | Cinnamal                                  | 0.02           | 0.05           |                                                                | 87.5 (3.7)  |            |             |            | 85.3 (3.8) | 79.6 (3.1)                             | 5.7       |
| 19  | 4-Ethoxy-phenol                           | 0.1            | 0.25           |                                                                | 96.3 (2.7)  |            |             |            | 98.7 (3.2) | 101.4 (2.8)                            | 6.2       |
| 20  | Anisyl alcohol                            | 0.1            | 0.25           |                                                                | 91.4 (3.2)  |            |             |            | 92.3 (3.1) | 94.1 (3.0)                             | 8.3       |
| 21  | Hydroxy-citronellal                       | 1.0            | 2.5            |                                                                |             |            | 87.1 (5.3)  |            | 82.4 (4.6) | 81.7 (1.1)                             | 6.6       |
| 22  | 4-tert-Butylphenol                        | 0.02           | 0.05           | 90.8 (1.7)                                                     |             |            |             |            | 94.6 (3.0) | 95.8 (3.4)                             | 4.5       |
| 23  | Cinnamyl alcohol                          | 0.2            | 0.5            |                                                                | 93.5 (3.0)  |            |             |            | 94.4 (3.3) | 102.5 (2.9)                            | 7.0       |
| 24  | 4-Phenyl-3-buten-2-one                    | 0.04           | 0.1            | 83.5 (4.8)                                                     |             |            |             |            | 80.7 (3.6) | 85.7 (1.9)                             | 8.4       |
| 25  | Eugenol                                   | 0.4            | 1.0            |                                                                | 93.6 (2.7)  |            |             |            | 95.3 (4.1) | 106.6 (3.8)                            | 6.8       |
| 26  | Dihydrocoumarin                           | 0.02           | 0.05           | 93.4 (2.6)                                                     |             |            |             |            | 89.8 (3.7) | 90.4 (3.9)                             | 8.7       |
| 27  | Coumarin                                  | 0.02           | 0.05           | 90.8 (5.0)                                                     |             |            |             |            | 93.7 (4.0) | 93.9 (1.8)                             | 5.5       |
| 28  | Isoeugenol                                | 0.4            | 1.0            |                                                                | 91.9 (3.7)  |            |             |            | 95.8 (4.2) | 96.1 (4.3)                             | 7.3       |
| 29  | 2,4-Dihydroxy-3-methylbenzaldehyde        | 0.4            | 1.0            |                                                                | 92.0 (5.4)  |            |             |            | 97.4 (3.1) | 89.5 (3.6)                             | 11.4      |
| 30  | alpha-iso-Methyllionone                   | 0.02           | 0.05           | 97.0 (2.7)                                                     |             |            |             |            | 93.4 (3.5) | 100.4 (2.6)                            | 7.4       |
| 31  | Lilial                                    | 0.02           | 0.05           | 93.7 (3.0)                                                     |             |            |             |            | 93.0 (3.8) | 92.5 (4.5)                             | 6.7       |
| 32  | Pseudoionone                              | 0.4            | 1.0            |                                                                | 91.7 (1.3)  |            |             |            | 96.7 (2.5) | 93.2 (0.8)                             | 4.8       |
| 33  | 6-Methylcoumarin                          | 0.04           | 0.1            |                                                                | 95.6 (4.5)  |            |             |            | 95.9 (3.0) | 96.7 (5.1)                             | 6.0       |
| 34  | 7-Methylcoumarin                          |                |                |                                                                |             |            |             |            |            |                                        |           |
| 35  | Diphenylamine                             | 0.02           | 0.05           | 88.0 (6.8)                                                     |             |            |             |            | 86.2 (3.1) | 86.1 (2.8)                             | 4.7       |
| 36  | 4-(p-Methoxyphenyl)-3-buten-2-one         | 0.04           | 0.1            | 95.1 (1.9)                                                     |             |            |             |            | 88.1 (2.3) | 86.8 (2.9)                             | 5.1       |
| 37  | Amyl cinnamal                             | 0.1            | 0.25           |                                                                | 99.4 (7.3)  |            |             |            | 96.3 (2.9) | 94.8 (3.9)                             | 6.6       |
| 38  | Lylal                                     | 1.0            | 2.5            |                                                                |             |            | 91.7 (2.2)  |            | 85.0 (3.2) | 90.5 (1.4)                             | 4.4       |
| 39  | Amylcinnamyl alcohol                      | 1.0            | 2.5            |                                                                |             |            | 95.5 (2.3)  |            | 99.1 (3.6) | 98.0 (1.6)                             | 6.0       |
| 40  | Farnesol                                  | 2.0            | 5.0            |                                                                |             |            | 94.8 (4.0)  |            | 98.0 (4.2) | 99.5 (5.5)                             | 7.8       |
| 41  | 7-Methoxycoumarin                         | 0.1            | 0.25           |                                                                | 99.4 (1.1)  |            |             |            | 97.1 (3.4) | 94.3 (2.2)                             | 6.1       |
| 42  | 1-(p-Methoxyphenyl)-1-penten-3-one        | 0.1            | 0.25           |                                                                | 90.8 (2.9)  |            |             |            | 91.8 (6.4) | 79.5 (5.6)                             | 7.5       |
| 43  | Hexyl cinnamaldehyde                      | 0.2            | 0.5            |                                                                | 96.2 (3.1)  |            |             |            | 90.8 (5.1) | 85.6 (4.9)                             | 5.8       |
| 44  | Benzyl benzoate                           | 0.1            | 0.25           |                                                                | 95.8 (5.5)  |            |             |            | 93.7 (2.5) | 87.3 (2.1)                             | 4.5       |
| 45  | 4-tert-Butyl-3-methoxy-2,6-dinitrotoluene | 0.4            | 1.0            |                                                                | 94.8 (4.3)  |            |             |            | 90.5 (3.5) | 97.4 (4.4)                             | 6.9       |
| 46  | Benzyl salicylate                         | 0.4            | 1.0            |                                                                | 85.4 (2.8)  |            |             |            | 90.9 (4.4) | 93.2 (5.6)                             | 10.3      |
| 47  | 7-Ethoxy-4-methylcoumarin                 | 0.2            | 0.5            |                                                                | 88.7 (1.8)  |            |             |            | 82.2 (4.6) | 97.4 (2.7)                             | 9.7       |
| 48  | Benzyl cinnamate                          | 0.1            | 0.25           |                                                                | 94.2 (3.7)  |            |             |            | 83.0 (5.7) | 85.9 (3.9)                             | 7.8       |

For ethyl acrylate, methyl trans-2-butenate, d-limonene, and trans-2-hexenal diethyl acetal, the solution was not concentrated via rotary evaporation (see section 3.3.2).

Table 6 List of commercial toys that could found at least one of the 48 fragrance allergens (S1: Sample 1).

| No. | Compounds              | Plush toys / (mg/kg) |      |     | Paper toys / (mg/kg) |      |      |       |      | Plastic toys / (mg/kg) |      |       |      | Play clays / (mg/kg) |      |       |      |      |
|-----|------------------------|----------------------|------|-----|----------------------|------|------|-------|------|------------------------|------|-------|------|----------------------|------|-------|------|------|
|     |                        | S1                   | S2   | S3  | S4                   | S5   | S6   | S7    | S8   | S9                     | S10  | S11   | S12  | S13                  | S14  | S15   | S16  | S17  |
| 4   | trans-2-Heptenal       |                      |      |     |                      |      |      |       |      |                        |      |       |      | 2.6                  | 1.9  | 1.9   |      | 0.4  |
| 6   | Benzyl alcohol         | 1.3                  | 50.8 |     |                      |      | 15.3 |       | 0.8  |                        | 0.7  | 44.2  |      | 1.2                  | 1.3  |       |      | 0.8  |
| 7   | d-Limonene             |                      |      |     |                      |      |      |       |      |                        |      |       |      | 21.9                 |      | 183.2 | 18.2 |      |
| 10  | Linalool               |                      |      |     |                      |      |      |       |      |                        |      |       |      | 4.4                  |      |       |      |      |
| 14  | 4-Methoxyphenol        |                      |      |     |                      | 14.5 |      |       |      | 8.9                    | 5.6  |       | 7.8  |                      |      |       |      |      |
| 18  | Cinnamal               |                      |      | 1.6 |                      |      |      | 1.9   |      |                        |      |       |      |                      |      |       |      |      |
| 20  | Anisyl alcohol         | 9.4                  |      |     |                      |      |      |       |      |                        | 3.0  |       |      |                      |      |       |      |      |
| 21  | Hydroxy-citronellal    |                      |      |     | 11.5                 |      |      |       |      |                        |      |       |      |                      |      |       |      |      |
| 22  | 4-tert-Butylphenol     |                      |      | 1.3 |                      |      |      | 15.0  |      | 0.3                    |      |       |      |                      |      |       |      |      |
| 23  | Cinnamyl alcohol       |                      |      |     | 93.0                 | 8.7  | 18.0 |       | 16.8 |                        |      |       |      |                      |      |       |      |      |
| 24  | 4-Phenyl-3-buten-2-one |                      |      |     | 6.7                  | 19.7 |      |       | 18.8 | 1.7                    |      |       |      |                      |      |       |      |      |
| 27  | Coumarin               |                      | 5.2  | 1.1 |                      |      |      | 6.8   |      |                        |      | 7.2   |      |                      |      | 40.0  | 5.1  | 0.6  |
| 30  | alpha-iso-Methylionone |                      |      |     |                      |      |      |       |      |                        |      |       |      |                      | 12.9 |       |      | 4.7  |
| 37  | Amyl cinnamal          |                      |      |     |                      |      |      |       |      |                        |      |       |      |                      | 32.1 |       |      | 13.9 |
| 40  | Farnesol               |                      |      |     |                      |      |      |       |      |                        |      |       | 54.2 |                      |      |       |      |      |
| 144 | Benzyl benzoate        | 8.2                  | 49.2 | 5.0 |                      |      |      | 245.0 |      |                        | 46.0 | 433.5 |      |                      |      | 7.4   |      |      |

Blank spaces mean that values are not detected or below LOQs.