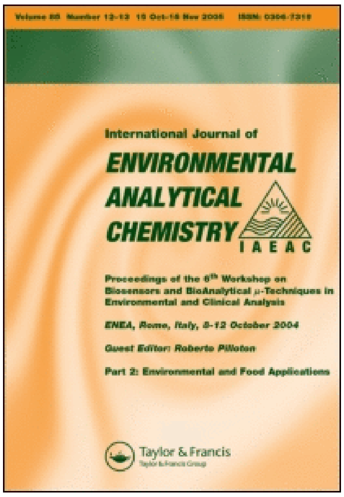

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# Chemical emissions from toys - the case of stink blasters

Salvatore Tirendi[a]; Otmar Geiss[a]; Josefa Barrero-Moreno[a]; Dimitrios Kotzias[a]
[a] European Commission, Joint Research Centre - Institute for Health and Consumer Protection, Ispra, Italy

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# Chemical emissions from toys – the case of stink blasters

Salvatore Tirendi*, Otmar Geiss, Josefa Barrero-Moreno and Dimitrios Kotzias

*European Commission, Joint Research Centre – Institute for Health and Consumer Protection, Ispra, Italy*

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The aim of the present study was to characterise and quantify the emissions of volatile organic compounds that can be released into the air from stink blasters (a toy in human shape that releases malodorous substances after squeezing the head) and to evaluate possible health risks, particularly for children. Although the stink blasters are intended for outdoor use, a hypothetical indoor use (e.g. a child's room) has been considered relevant for exposure assessment studies. The emissions of the items were investigated in environmental chambers and their content was assessed by chemical extraction. In addition to these preliminary experiments and in order to evaluate airborne exposure to cyclohexanone, the stink blasters were placed in the Indoortron facility, a 30 $m^3$ volume walk-in type environmental chamber, and tested for emissions after squeezing several times under 'real world setting' conditions (23°C, 50% relative humidity, 0.5 air changes per hour). The amount of chemicals released was determined by applying two different techniques and time series analysis of the air inside the chamber sampled on Tenax TA tubes and DNPH cartridges, followed by thermal desorption gas chromatography mass spectrometry and HPLC–UV, respectively. The main resulting compounds emitted were cyclohexanone and toluene, with concentrations reaching values of 25 and 32 $\mu g\,m^{-3}$, respectively. These levels are much lower than established permissible exposure limits. Measured toluene levels are also below the chronic inhalation reference limit value (300 $\mu g\,m^{-3}$) set for this compound by the California Environmental Protection Agency (Cal EPA). However, such a value is not set for cyclohexanone, so attention should be given to chronic exposures at low concentration levels, in particular for sensitive sub-groups such as children.

**Keywords:** cyclohexanone; RAPEX; environmental chamber; VOCs; carbonyls; stink blasters; Indoortron

## 1. Introduction

It is widely accepted nowadays that the quality of indoor air plays a significant role in total human exposure to air pollutants [1]. Through the Environment and Health Strategy [2] and Action Plan [3] and more recently through its Health and Consumer Policy Strategy, the European Commission promotes research on the health impacts of environmental factors, including consumer products, and strongly supports efforts to identify the strength of indoor sources and reduce indoor emissions to improve human health

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*Corresponding author. Email: Salvatore.tirendi@jrc.it

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and well-being [4,5]. In its opinion on air quality risk assessment [6], the Scientific Committee on Health and Environmental Risks (SCHER) of the European Commission's Directorate General for Health and Consumer Protection (DG SANCO) expressed the necessity for further research on the characterisation of chemical emissions from consumer products that could have an impact on health. The SCHER recognised that data on levels of emissions in realistic usage situations is needed, in view of the large part of the population handling such products and the limited availability of information to this regard.

Some studies with tests in environmental chambers of various dimensions have been carried out on the characterisation of emissions from various consumer products [7–13] (building materials, paints, carpets, air fresheners, office equipment) under 'real world settings' i.e. as they are commonly used in confined environments. However, studies on the characterisation of chemicals emitted from toys by environmental chamber testing are very rare.

Tanaka-Kagawa *et al.* [14] have recently investigated TVOCs emitted from some consumer products (including some toys) by a small chamber test method under conditions of 28°C, 50% relative humidity (RH) and 0.5 air changes per hour. As background, we refer to the Rapid Alarm System for Non Food Products (RAPEX), which Member States use to communicate products that do not comply with EU legislation, thus allowing a rapid exchange of information within the European Union on the dangers arising from the use of consumer products. Several notifications to RAPEX have been issued concerning the presence of the compound cyclohexanone [15], of concern for human health, in stink blasters. The aim of this study was to assess the release into the air of cyclohexanone and other specific volatile organic compounds (VOCs) [16,17], whose properties could raise concern for human health. Two complementary approaches were considered when designing the experimental set-up, the first relates to chemical extraction of single parts of the toy with subsequent quantification of cyclohexanone, while the second procedure focused on the characterisation and quantification of VOCs that can be released into the air from stink blasters in environmental exposure chambers where the toy was placed. The amount of chemicals released (VOCs and carbonyls) was determined by applying two different techniques and time series analysis of the air inside the chamber sampled on Tenax TA tubes and DNPH cartridges, followed by thermal desorption gas chromatography mass spectrometry and HPLC–UV, respectively. Both methods were applied for quantification of cyclohexanone.

## 2. Experimental

### 2.1 *Chemicals and materials*

All reagents were of analytical reagent grade unless otherwise stated; methanol and acetonitrile were of HPLC grade (Sigma-Aldrich, St Louis, MO). Deionised water was obtained from a Millipore Milli-Q system (Millipore Corp., Bedford, MA, USA). 2,4-dinitrophenylhydrazide derivatives were purchased from Supelco (Sigma-Aldrich Srl, Milan, Italy). The Solid Phase Extraction (SPE) cartridges used for extract clean up of were Strata-X polymeric RP sorbent 200 mg/6 mL, (Phenomenex, Torrance, CA, USA). Thermally desorbible Tenax TA tubes for sampling were purchased at Supelco. Carbonyls were sampled on Sep-Pak DNPH Silica Cartridges (360 mg) purchased at Waters (Waters Corp., Milford, MA, USA).

## 2.2 *Apparatus*

### 2.2.1 *Environmental chambers*

Emission tests were carried out at 23°C, 50% RH using small (0.45 $m^3$) and large (30 $m^3$) environmental chambers. The toy under study was placed inside the chamber and a remote-controlled pneumatic device was used for squeezing its head, causing the release of chemicals into the air of the chamber. The glass environmental chamber of 0.45 $m^3$ was used in static mode (without exchange of air internally). The stainless steel walk-in type chamber (Indoortron facility) was used in dynamic mode (0.5 air changes per hour). VOCs and low molecular aldehydes were determined by sampling air on TENAX TA tubes and Sep-Pak DNPH-Silica cartridges followed by TD GCMS and HPLC–DAD analysis, respectively. Cyclohexanone was analysed by GC/MS against external calibration in selected ion mode (SIM, *m*/*z* 98 and *m*/*z* 55). Quantification was done with a HPLC/DAD system against external calibration. The air volume sampled for VOCs was within the 1–2 L range at a sampling flow rate of 100 mL $min^{-1}$. Carbonyls, including cyclohexanone, were sampled at a flow of approximately 1.5 L $min^{-1}$ for a total of 100 L. Before each experiment, the quality of air inside the chambers was controlled by taking blank air samples and analysing them.

### 2.2.2 *Chromatographic analysis*

The extracts were analysed by GC–FID while standard methods ISO 16000-6 and ISO 16000-3 were used for the analysis of VOCs and low molecular weight carbonyls in the air, respectively.

**GC-FID analysis:** The GC separation was performed with an Agilent 6890N gas chromatographic system in combination with a flame ionisation detector (Agilent Technologies, Inc., Santa Clara, CA). The column employed was a J&W Scientific DB-WAX (30 m, 0.25 mm ID, 0.5 μm film). Gas chromatographic parameters: injector/detector temperature, 250°C; constant flow mode, 1.2 mL $min^{-1}$ He, split ratio, 1:50; injection volume, 2 μL. Oven program initial temperature, 80°C; ramp, 20°C $min^{-1}$ up to 220°C; hold 220°C for 8 min; total runtime, 15 min.

**TD–GCMS analysis:** A TM650 thermal desorber (Perkin Elmer, Boston, MA, USA) equipped with a TENAX TA cold trap of 100 mg coupled to a HP7890A gas chromatograph and HP5975C inert mass spectrometer system (Agilent Technologies, Inc., Santa Clara, CA, USA) was used for the analysis of VOCs in air samples taken from the environmental test chamber, applying the ISO 16000-6 standard method. The capillary column used was a DB-5-MS (30 m, 0.25 mm, 1 μm film; J&W Scientific, Folsom, CA, USA); the oven temperature was as follows: 10°C (2 min) at 4°C $min^{-1}$ to 220°C, at 15°C $min^{-1}$ to 260°C (1.5 min). The transfer line temperature was set at 280°C. Helium was used as carrier gas at 15 psi (constant pressure mode).

**HPLC–UV analysis:** The HPLC consisted of an Agilent Series 1100 system (Agilent Technologies, Inc., Santa Clara, CA, USA), composed of a G1312A binary pump, a G1379A degassing device, a G1329A Autosampler and a G1315B Diode Array Detector set at 360 nm. The chromatographic separation was performed on a Waters Nova-Pak C18, 60A, 4 μm (3.9 × 300 $mm^2$) column (Waters Corp., Milford, MA, USA). The flow rate was 1 mL $min^{-1}$; the injection volume was 25 μL. The mobile phase consisted of acetonitrile/water gradient as shown in Table 1.

Table 1. HPLC Gradient composition over time.

| Time (min) | Vol (%) acetontrile | Time (min) | Vol (%) acetontrile |
|---|---|---|---|
| 1 | 60 | 19 | 76 |
| 5 | 62 | 20 | 78 |
| 10 | 62.5 | 22 | 80 |
| 11 | 62.7 | 24 | 83 |
| 12 | 63 | 25 | 85 |
| 13 | 63.5 | 26 | 88 |
| 14 | 70 | 28 | 90 |
| 16 | 72 | 30 | 95 |
| 18 | 74 | 40 | 95 |

## 2.3 *Procedures*

### 2.3.1 *Analysis of toys*

Stink blasters are a particular kind of toy with human shape that releases malodorous substances after the head is squeezed [18]. In the present study, eight stink blasters were subjected to analysis for their content of cyclohexanone and emissions (four items subjected to bulk analysis by extraction, two specimens studied in the small chamber for characterisation of emissions and two toys studied in the large chamber simulating an indoor environment). The analysed toys were manufactured in China and purchased from Italian stores. The toys were selected based on market availability, each item providing a characteristic smell. They are composed of a body and an impregnated sponge, covered by cotton, located inside the head. The sponge is imbued with a mixture emitting the characteristic odorous compound.

### 2.3.2 *Extraction and determination of cyclohexanone from stink blasters*

Approximately 5 g material was weighed into a 250 mL round bottom flask and 100 mL methanol was added. The single parts of the body were refluxed for 2 h and afterwards methanol was evaporated up to 5 mL using a Rotavapour (bath temperature 55°C). The extract was transferred to a 100 mL recipient and 45 mL of Milli-Q water were added. An unfilterable milky suspension formed. This suspension was cleaned up by SPE. Clean up of the extracts was performed as follows: the column was conditioned with 6 mL methanol and equilibrated with 6 mL of water. The extract was loaded and washed with 6 mL of 10% methanol. After drying for 1 min, 6 mL of methanol were used as eluting agent. Flow rates for conditioning and equilibration up to 12–24 mL $\mathrm{min}^{-1}$. Flow rates for sampling loading, washing and elution up to 4–8 mL $\mathrm{min}^{-1}$. The extract was collected in a 20 mL volumetric flask, brought to volume with methanol and shaken thoroughly. A total volume of 100 µL of the 2-fluorotoluene internal standard solution was added to the volumetric flask. This solution was analysed by GC–FID.

### 2.3.3 *Emission of cyclohexanone in small environmental chamber from stink blasters: preliminary experiments*

The amount of cyclohexanone emitted into the air was evaluated after placing the stink blaster in an environmental chamber of 0.45 $m^3$, in static mode (no air exchange) at 23°C.

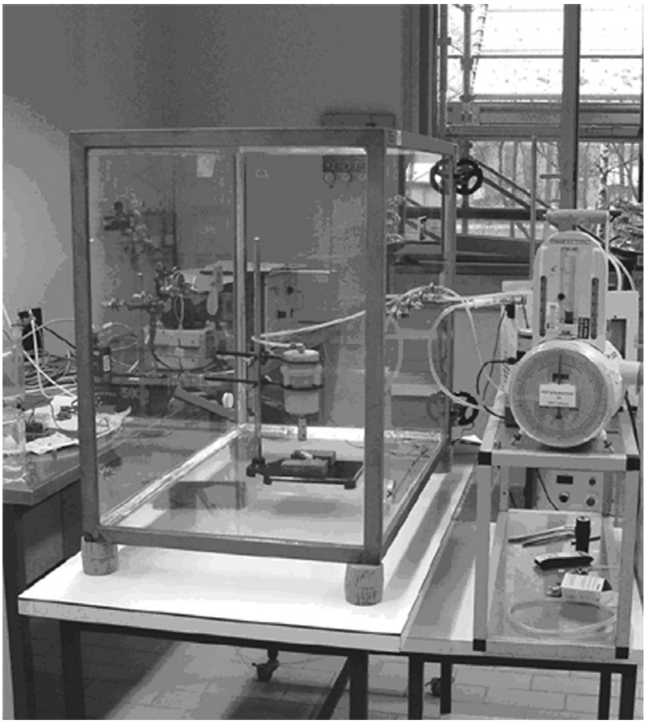

Figure 1. Experimental set-up in the 0.45 $m^3$ environmental test chamber.

The head of the toy was repeatedly squeezed by a remote-controlled pneumatic device to emit the characteristic odour, as shown in Figure 1. The toy was left inside the chamber for 24 h without any further squeezing. The air was analysed at defined intervals. Quantification was performed by GC–MS using SIM.

### 2.3.4 *Emission of cyclohexanone in the environmental walk-in test chamber (Indoortron)*

Simulation of a real scenario was carried out in the Indoortron walk-in environmental chamber. The physical parameters set inside the chamber were 23°C temperature, 50% RH and an air exchange rate of 0.5. The toys were left inside the chamber for 24 h after squeezing the head pneumatically eight times. VOCs and low molecular aldehydes were determined at defined intervals by sampling on TENAX TA tubes and Sep-Pak DNPH-Silica cartridges followed by TD GCMS and HPLC–DAD analysis, respectively. Cyclohexanone was analysed by GC/MS against external calibration in SIM ($m/z$ 98 and $m/z$ 55). Quantification was done with a HPLC/DAD system against external calibration.

## 3. Results and discussion

The aims of this study were to assess the release into the air of cyclohexanone and other specific VOCs, whose properties could raise concern for human health, and also to gather data for further exposure assessment via inhalation to the chemicals released

Table 2. Panel A: cyclohexanone content in different parts of toy 02A; Panel B: cyclohexanone content in different toys.

| Panel (A) | |
|---|---|
| Toy 02A | Concentration of cyclohexanone in each part (g/100 g) |
| Sponge | 0.09 |
| Head | 0.09 |
| Neck | 0.03 |
| Body | 0.02 |

| Panel (B) | |
|---|---|
| ID Sample | Cyclohexanone (g/100 g) |
| Toy 02A | 0.18 |
| Toy 02B | 0.05 |
| Toy 03C | 0.17 |
| Toy 04D | 0.06 |

by stink blasters. For the purpose, a typical indoor environment in terms of size of the room, air exchange rate, temperature and RH as might be possibly found in a child's room was set up. Additionally, the content of cyclohexanone in the toy was evaluated by extraction.

### 3.1 *Extraction of single body parts and whole figures*

Cyclohexanone was determined qualitatively and quantitatively in the extracts of the toys after clean up with SPE Strata-X polymeric RP sorbent. Recovery experiments of the clean-up step were carried out by spiking SPE cartridges with known amounts of cyclohexanone and resulted in values around 104%. Table 2 (Panel A) shows the amount of cyclohexanone found in different parts of the body, the sponge and head being the two parts of the toy containing the highest amount of cyclohexanone. The presence of the compound, in minor quantities, in the other parts analysed, suggests an eventual chemical diffusion from the sponge and subsequent absorption throughout the toy's surface. The results obtained show that the content of cyclohexanone in whole articles is less than 0.2% (Panel B).

### 3.2 *Emissions from whole figures placed in the 0.45 m$^3$ environmental chamber*

The toys were placed inside the chamber and the head was squeezed several times. Between each squeeze, 0.1 L samples were drawn on TENAX TA tubes (flow 100 mL min$^{-1}$). Approximately 2-min time elapsed between two squeezes. Figure 2 shows that the cyclohexanone emission value increases when the toy is squeezed and can reach values close to 1000 µg m$^{-3}$. The concentration of cyclohexanone in the air increases over time even without any further squeezing, reaching 5 mg m$^{-3}$ after 24 h. This fact suggests that the cyclohexanone contained in the sponge and body parts is released in the environment and therefore additional emissions of cyclohexanone might be due to diffusion of this chemical (from the interior parts) and/or volatilisation from the toy surface. Apart from cyclohexanone, the following volatile organic compounds were identified to be emitted

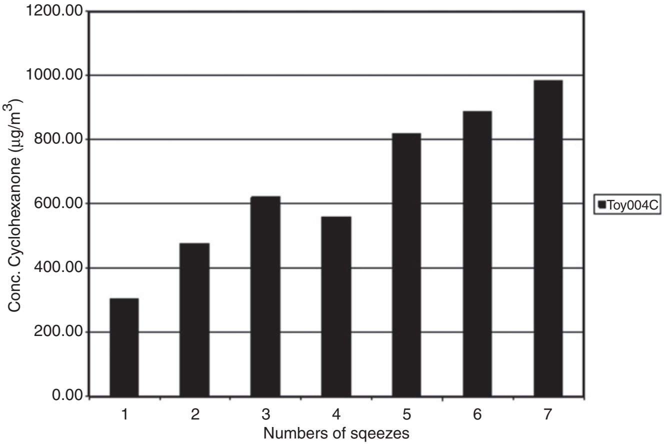

Figure 2. Cyclohexanone emitted from stink blasters in the small environmental chamber.

Table 3. Levels of cyclohexanone and toluene found in air samples taken at the Indoortron (by sampling on Tenax TA tubes and DNPH cartridges).

| | Tenax TA GC/MS | | DNPH HPLC/DAD | | Tenax TA GC/MS | |
|---|---|---|---|---|---|---|
| | Cyclohexanone | | | | Toluene | |
| Time elapsed from experiment start (h) | Toy 05A | Toy 01B | Toy 05A | Toy 01B | Toy 05A | Toy 01B |
| | Concentration ($\mu g\,m^{-3}$) | | | | | |
| 0.1 | 4.8 | 7.5 | | | 10.6 | 14.6 |
| 0.5 | 12.8 | 18.8 | 10.9 | 14.6 | 21.0 | 27.4 |
| 1 | 17.0 | 22.5 | | | 25.3 | 32.1 |
| 2 | 18.6 | 25.8 | | | 26.4 | 32.0 |
| 2.5 | | | 16.7 | 24.9 | | |
| 3 | 15.9 | 23.3 | | | 21.3 | 26.6 |
| 4.5 | | | 16.2 | 22.2 | | |
| 6 | 13.6 | 20.5 | | | 17.1 | 21.6 |
| 6.5 | | | 14.2 | 19.0 | | |
| 8 | 12.1 | 17.0 | | | 14.7 | 17.8 |
| 8.5 | | | 11.4 | 16.3 | | |
| 24 | 6.6 | 9.2 | 6.0 | 8.7 | 8.3 | 9.8 |

from the toys: toluene, *m*/*p*-xylene and propanediol, which were considered indicative chemicals for further monitoring in the real-size room experiment.

### 3.3 *Emissions from toys placed in the 30 m³ environmental chamber (Indoortron)*

Although the stink blasters are intended for outdoor use, a hypothetical indoor use (e.g. a child's room) was considered relevant for exposure assessment studies. The results obtained from the experiments using two different toys inside the Indoortron, simulating a more realistic scenario, indicates the presence of cyclohexanone and toluene as the

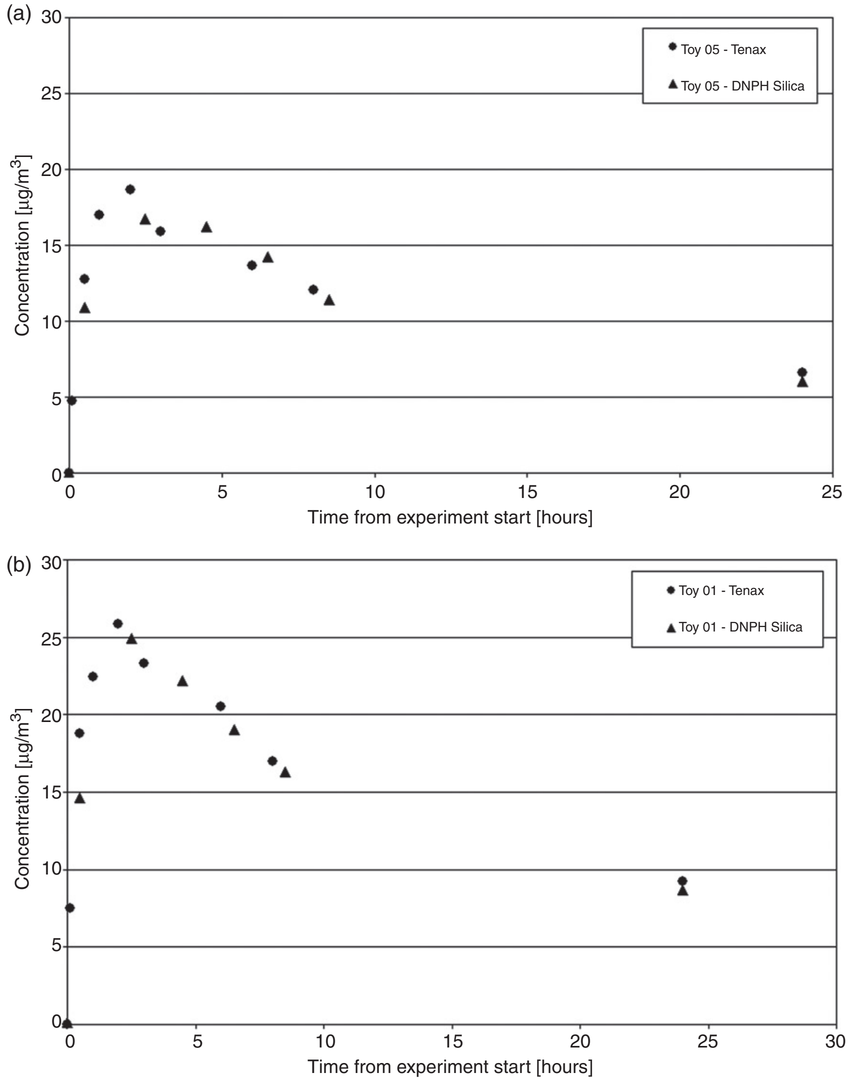

Figure 3. Concentration of cyclohexanone measured with both Tenax TA and DNPH-Silica (a) for toy 05A and (b) for toy 01B.

main components in the air samples; traces of other compounds (e.g. ethylbenzene and *m*/*p*-xylenes) were detected. The experiment started with squeezing head of the toy (eight times). From this point onwards, samples were drawn on TENAX TA and on DNPH-silica cartridges at various time intervals (differing between Tenax and DNPH-Silica due to different sampling times). The results are summarised in Table 3.

Figure 3 shows a good matching of the concentration found by plotting the results obtained by GC/MS analysis of the thermally desorbed Tenax TA tubes and HPLC/DAD analysis of the DNPH-covered silica cartridges.

Due to the air exchange inside the chamber, concentrations of cyclohexanone and toluene vary over the time of the experiment from the moment when the head was squeezed. Peak concentrations were observed after approximately 2 h, reaching around 1 $\mu g\,m^{-3}$ for toy 05A and around 25 $\mu g\,m^{-3}$ for toy 01B. After 24 h, the concentration of cyclohexanone decreased by 65% relatively to the peak concentration. Toluene concentrations reached the highest concentration after 2 h (26.4 $\mu g\,m^{-3}$ for toy 05A and 32.0 $\mu g\,m^{-3}$ for toy 01B). After 24 h, the concentrations decreased by 70% relatively to the peak concentration. The reduction of the chemical levels at 24 h revealed that the additional emissions of chemicals originated by diffusion and/or volatilisation are overcome by the exchange of air in the room. The chemical levels measured are much lower than permissible exposure limits of 80 and 750 $mg\,m^{-3}$ for cyclohexanone and toluene, respectively. In the case of toluene [17], the California Environmental Protection Agency (Cal EPA) has established 300 $\mu g\,m^{-3}$ as chronic inhalation reference limit estimate of daily exposure with no risk of adverse effects to the general human population (including sensitive subgroups) during a lifetime of exposure (cREL). The toluene levels measured in our studies (using 1 toy) are 10 times lower than the chronic inhalation reference value. The highest quantity found for cyclohexanone was in the order of 30 $\mu g\,m^{-3}$ after 2 h, which is much lower than the permissible exposure limits; however, there is no cREL value for this compound. Other chemicals found at trace levels in this study are xylenes and ethylbenzene, whose cREL values are 700 and 2000 $\mu g\,m^{-3}$, respectively, and propanediol which has no cREL value, thus attention should be given to chronic exposures at low concentration levels of individual compounds and chemical mixtures in particular for sensitive sub-groups e.g. children.

## 4. Conclusions

The toys analysed contain less than 0.2% of cyclohexanone as determined in this study by extraction. Cyclohexanone was found mainly in the sponge, which is placed inside the head, but also in the other parts of the body. The emission tests carried out in a small environmental chamber with no exchange of air have shown that cyclohexanone accumulates not only by squeezing the toy but also by diffusion, reaching concentrations up to 5000 $\mu g\,m^{-3}$ after 24 h. The full-scale experiments revealed that besides the main compounds cyclohexanone and toluene, traces of xylenes, ethylbenzene and propanediol were also identified as emitted from the toys. The highest concentration measured (peak concentrations 2 h after having squeezed the head of the toy) was 25.8 $\mu g\,m^{-3}$ for cyclohexanone and 32.1 $\mu g\,m^{-3}$ for toluene. These values are below the corresponding established permissible exposure limits. Toluene levels were also below the chronic inhalation reference limit, but such a type of value has not been set for cyclohexanone.

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