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Emissions and toxic units of solvent, monomer and additive residues released to gaseous phase from latex balloons

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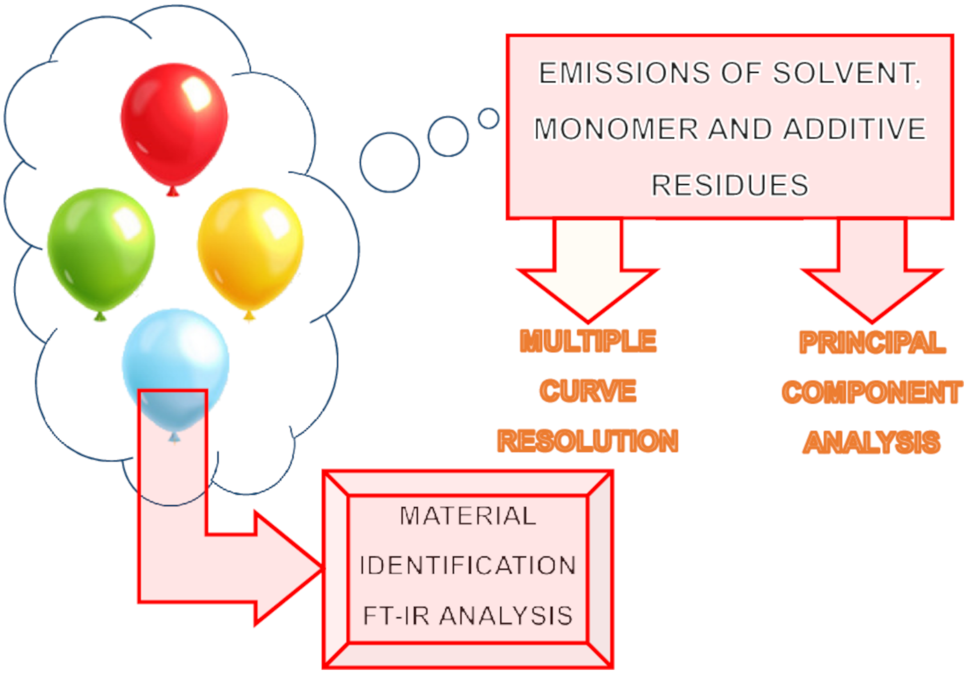
EMISSIONS OF SOLVENT, MONOMER AND ADDITIVE RESIDUES
MULTIPLE CURVE RESOLUTION
PRINCIPAL COMPONENT ANALYSIS
MATERIAL IDENTIFICATION FT-IR ANALYSIS

Emissions and toxic units of solvent, monomer and additive residues released to gaseous phase from latex balloons

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Capsule: The emitted compounds form two separate groups, suggesting two different emission sources: first related to latex material, the second one related to sorption-desorption processes

Abstract

This study describes the VOCs emissions from commercially available latex balloons. Nine compounds are determined to be emitted from 13 types of balloons of different colors and imprints in 30 and 60°C. The average values of total volatile organic compounds (TVOCs) emitted from studied samples ranged from 0.054 up to 7.18 $\mu g \cdot g^{-1}$ and from 0.27 up to 36.13 $\mu g \cdot g^{-1}$ for $30^{o}C$ and $60^{o}C$, respectively. The dataset is treated with principal component analysis (PCA) and multiple curve resolution (MCR) to characterize its internal patterns. Here two groups on compounds are recognized – the first one related to balloon material, the second one being emissions of compounds previously adsorbed on balloon material. The toxicity assessment of MCR modeled balloons' emissions was performed by toxic unit (TU) approach. The obtained TUs were summed to give toxicity emission assessment. The incorporation of TUs allows to identify the balloons with the most toxic emissions– imprinted ones in 60°C. The compounds of the highest TUs are hexanal and benzene. FTIR analysis shows that all balloons are made of the same polymeric material – isoprene, so all differences in emissions are related to different additives like pigments, imprints or these responsible for opaqueness. Analyzing the obtained research results it was noticed that latex balloons might be considered as an important source of emission of aliphatic and monoaromatic hydrocarbons to the gaseous phase.

Key words: latex balloons; solvent and monomer residues; emissions; multiple curve resolution; toxic units

1. Introduction

Nowadays, almost every synthetic material consists a wide spectrum of additives, such as antistatic agents, ultraviolet radiation filters, antioxidants, plasticisers, stabilizers, lubricants as well as pigments, colorants, fillers or nanofillers (Mitchell et al., 2014; Hahladakis et al., 2018). Consequently, the harmful chemicals (such as formaldehyde, volatile organic compounds (VOC), as well as semi-volatile organic compounds (SVOCs)) that might be introduced in a synthetic materials manufacturing process, could be emitted to the gaseous phase during their regular use (Wolkoff and Nielsen, 2001; Gallon et al., 2020). Mainly, the chemical compounds released from synthetic materials arise from residues of reagents used during polymerisation reaction (monomers, cross-linking agents, reaction initiators, solvents) and the impurities present in employed wide spectrum of plastic additives (Böhm et al., 2012; Rosenmai et al., 2017; Yan et al., 2017). This phenomenon concerns the various types of everyday use large or small-scale indoor equipment (floor coverings, floor panels, furniture, electronic devices, toys), as well as the wide spectrum of synthetic materials (copolymer acrylonitrile-butadiene styrene (ABS), polyvinyl chloride (PVC), polypropylene (PP) and polyethylene(PE)) intended to come into direct contact with food or human skin (Kamarulzaman et al., 2019; Rubio et al., 2019). The quality of synthetic materials (which can be defined by assessing the type and amount of emitted chemical compounds) is particularly important in the case of products intended for direct use by children. As a result of the use of synthetic materials by children, exposure to the harmful chemical compounds can take place not only through the skin (touch), but also through the mucous membranes of the mouth (saliva) and nose (inhalation). It is particularly important because they can lead to allergies and skin irritation and also because most of toxic additives are endocrine disrupting substances (EDS) whose adverse effect are particularly relevant during childhood. (Denk et al., 2017; Wiedmer and Buettner, 2018; Even et al., 2019).

One of the most common polymeric products that children over 3 years of age might have direct contact with are party balloons, mainly made of natural rubber latex (NRL). The NR is made from the latex of *Hevea brasiliensis* tree (occurring in tropical countries such as Thailand, Malaysia, and India), and mainly consists of cis-1,4-polyisoprene (up to 94% of the material weight) and about 6% non-rubber (non-isoprene) compounds such as lipids (range from 1.5 to 3% w/w), proteins and polypeptides (up to 2% w/w), carbohydrates (up to 0.4% w/w) and inorganic salts (up to 0.2% w/w) (Nimpaiboon and Sakdapipanich, 2013; Sukmak et al., 2020). As an alternative source of liquid latex, characterized by a lower allergenic potential, the *Parthenium argentatum* (known as Guayule, occurring in North American and Mexican desert shrub) might also be considered. The appropriate elastic, ductility and strength properties of this material are obtained in the course of rubber vulcanisation process (Altkofer et al., 2005; Critchley and Pemberton, 2020). During the manufacturing process of materials made of NRL, for instance party balloons or medical gloves, a number of additional chemicals, such as reaction accelerators, activators, as well as vulcanizing and anti-oxidant agents, are introduced. As it was observed in the early 1990s, the use of materials made of

NRL such as medical gloves, latex-containing medical products or devices, caused in their users allergic reactions ranging from urticarial to rhinoconjunctivitis, asthma, and anaphylaxis (Tommaso et al., 2019). Since that time, allergic problems resulting from the application of NRL accessories have become the subject of interest of the scientific and media world (Palosuo et al., 2011). In general, the skin allergic reaction might be associated with the sensitivity to chemical additives used in NRL material manufacturing process (Lauren Charous et al., 2002). For this reason it is highly recommended to investigate not only the quality of NRL medical products, but also other NRL products that have direct contact with human tissues, such as mentioned earlier party balloons, for which the manufacturing process is similar to that of medical gloves. However, the quality of party balloons and the emission potential of chemical compounds is very important due to their field of application. In general, party balloons should be filled with air or helium delivered from a manual or automatic pump or directly from a gas container. In fact, for regular use, the party balloons filling process is performed by the mouth, which causes direct contact of the material with the oral mucosa, thus increasing the risk of an allergic reaction. It is extremely important when the person using the NRL party balloons is a child just over 3 years of age (manufacturers state balloons are inappropriate for children under three years old).

The aim of the research is to investigate the emission of VOCs from party balloons mainly made of natural rubber latex which were delivered directly from the manufacturer. The potential sources of emitted compounds are discussed and with the aim of chemometric tools the risk assessment is performed. To our best knowledge it is the first study on the VOCs emissions from commercially available balloons. We identify the compounds emitted and determine the emission. The novelty lies also in the application of the combination of multiple curve resolution with toxicity units to assess, which of the VOCs from total flux contribute more to the health problems. This study widens the understanding of chemical hazards sources in humans everyday exposure.

2. Materials and methods

2.1 Characteristics of latex balloon samples

Studies were performed on latex balloons delivered directly from the local manufacturer, which is the member of European Balloon and Party Council (EBPC). Thirteen different types of latex balloons were delivered in a separate packed batch. Each batch contained ten balloons of the exactly same shape, colour (pigment type) and similar weight placed in polypropylene zipper bags. Zipper bags with latex balloons were stored at the laboratory at room temperature in a dark place (stored without access to light). To determine the emissions of potential solvent, monomer or additives residues four randomly selected latex balloons were picked up from a single batch and considered as a representative for the whole batch. Selected samples of latex balloons were then weighed, suitably labelled, and placed inside the stainless-steel tightly sealed microscale chamber. Because of the fact that delivered latex balloons varies in terms of colour (pigment type), weight, shape and the presence of additional imprint, it was obliged to introduce the appropriate samples identification system, which was enclosed in Table 1. There was no need for a special treatment of studied samples – absence of cutting and reducing the samples dimensions.

The total number of investigated samples of latex balloons for the type and amount of potential solvent, reagents and additives residues emitted from their surface was 52. The average weight of all analysed latex balloon samples was 3.37 ± 0.60 g.

2.2 FT-IR analysis conditions

In order to identify the main polymer, its preliminary quality and potential additives that might be used during its manufacturing process, the Fourier transform infrared spectroscopy (FT-IR) analysis was performed. The FT-IR analysis of studied latex balloon samples was recorded with a Nicolet Spectrometer IR200 from Thermo Scientific (Waltham, MA, USA). The system was equipped with an ATR attachment with a diamond crystal. Measurements were performed with 1 cm^{-1} resolution in the range from 4000 to 400 cm^{-1} and 64 scans. Four representatives of latex balloons that differ significantly by the colour (pigment type) and shape, were randomly selected for FT-IR analysis. Obtained IR results were paralleled to spectra in the Hummel Polymer Sample Library database, which encloses the IR spectra of the most commonly used polymers and other materials. In addition, the manual evaluation and the comparison with the literature IR spectra, was also performed to obtain the very reliable analytical information about studied material (Arjunan et al., 2001; Dghim et al., 2015).

2.3 Sampling protocol of solvent, monomer and additives residues emitted from investigated latex balloons

The emissions of solvents, monomers and additives residues released from studied latex balloons were assess with the use of microscale stationary emission chamber - the Micro-Chamber/Thermal Extractor™ (µ-CTE™ 250, Markes International, Inc). Detailed information about the characteristics of this analytical equipment, its operating range and overall working parameters were specified in previously published papers (Marć et al., 2017; Marć and Zabiegała, 2017; Marć, 2020). There was no need to apply a specific sample preparation procedure and the studied latex balloons were placed inside a chamber without previously cutting (whole latex balloon was placed inside a single chamber).

Samples of latex balloons were investigated employing mentioned above the µ-CTE™ 250 system at two temperatures: (i) 30°C – to investigate the basic emission of general solvents, reagents and potential additives that might be emitted during regular use of studied latex samples; (ii) at 60°C – a significantly higher temperature to assess the maximum emission potential of studied latex samples and to investigate the presence of potential chemical compounds that might be released from the surface of studied latex materials as a polymer or additives thermal degradation products (temperature close to maximum operating temperature range – 70-80°C). One analytical conditioning and sampling period contains the analysis of four samples originating from the same batch of latex balloons. The inert gas flow rate (nitrogen, 2.2) passed through the chamber was set up to 25 ± 0.5 $mL \cdot min^{-1}$ and the sampling conditioning time was 30 ± 1 min. The samples of analytes emitted from the studied latex balloons to the gaseous phase were transported by the gas stream directly to the attached stainless steel tube filled with Tenax TA sorption medium (60/80 mesh, O.D. × L 1/4 in. × 3 1/2 in., Merck KGaA, Darmstadt, Germany), each time conditioned ($300^{o}C$ for 30 min under inert gas flow rate) before sampling stage.

2.4 Thermal desorption and final determination systems working parameters

The analytical technique employed at the stage of thermal desorption of analytes collected on the applied sorption medium was two-stage thermal desorption (TD) system (Markes Series 2 Thermal Desorption Systems; UNITY/TD-100). In brief, after the sampling stage the stainless steel tubes were placed in a TD heating unit and maintained in elevated temperature $295^{o}C$ for 15 min under the inert gas flow rate (helium, 50 $mL\cdot min^{-1}$), which transfers the analytes directly to the microtrap (multibed glass tube cooled down to $0^{o}C$). After this, the valve was switched and the inert gas (helium flow rate 2.0 $mL\cdot min^{-1}$) was passed through the microtrap (rapidly heated up to $300^{o}C$ and maintained for 5 min) and the analytes were transported directly to the fused silica capillary column (J&W, DB-1 30 m × 0.32 mm × 5 µm). The separation, preliminary identification and quantitative determination was performed with the use of gas chromatograph (Agilent Technologies 7820A GC System) with flame ionization detector (FID working temperature – $250^{o}C$). The GC-FID was connected with the TD unit by transfer line, constantly heated up to $180^{o}C$. The GC oven working was: initial temperature – $45^{o}C$ maintained for 1 min, next ramped $15^{o}C\cdot min^{-1}$ up to $120^{o}C$, and held for 2 min, then increased with the rate $10^{o}C\cdot min^{-1}$ up to $250^{o}C$ and held for 5 min. The inert GC gas constant flow (He, 5.0) rate – 2.0 $mL\cdot min^{-1}$. In order to perform better identification of the main emitted chemical compounds from the studied samples of latex balloons the TD-GC-MS system was employed, under the following working parameters: (i) TD unit (Unity v.2, Markes International Ltd.) – the analytes thermal extraction process was performed in similar conditions to mentioned TD-GC-FID system; (ii) GC (Agilent Technologies 6890) column and oven working parameters – GC column (60 m × 0.25 mm × 1 µm, J&W DB-5MS, USA); helium gas flow rate – 1.5 $mL\cdot min^{-1}$, oven program: initial temperature – $50^{o}C$ maintained for 1 min and next ramped $10^{o}C\cdot min^{-1}$ up to 280 and held for 10 min; (iii) MS (5873 Network Mass Selective Detector, Agilent Technologies) working parameters - ion source temperature: 230°C, the quadrupole mass analyser temperature: 150°C, and the GC-MS transfer line temperature: 280°C, MS working mode – SCAN, monitored mass range (m/z) – 35 - 450.

2.5 Calibration and QA/QC protocol characteristic

The amount of chemical compounds considered as solvent and reagent residues emitted from the exanimated latex party balloon was assessed with the use of the calibration of the TD-GC-FID employing the external standard (ESTD) method. Based on the commercially available reference standard solution (EPA VOC Mix 2, Supelco, USA) containing defined type and amount of VOCs (13 monoaromatic hydrocarbons dissolved in methanol at a concentration of 2000 $\mu g\cdot mL^{-1}$ each), hexanal analytical standard (1 mL, Supelco, USA) and n-undecane reference substance for GC (5 mL, Supelco, USA), the calibration curves were elaborated. To perform the calibration procedure, seven calibration reference solutions (for seven-point calibration curve) in 1 mL of methanol were prepared, containing approx. from 1 ng up to 500 ng of each of measured monoaromatic hydrocarbons. The whole calibration protocol was carried out with the use of specific type of laboratory tool (device that gives a possibility to introduce a defined amount of calibration solution directly onto the clean sorption medium), in details labelled in former studies (Zabiegała et al., 2011; Marć et al., 2014a; Marć et al., 2014b). The Tenax Ta stainless steel tubes containing defined mass of selected VOCs were analysed under the same equipment conditions and working parameters as the real samples. Each point representing the defined calibration curve was repeated three times. The evaluated correlation coefficients (R^2) of the prepared calibration curves for defined range of monoaromatic hydrocarbons were approx. from 0.952 for benzene to 0.999 for styrene. As for the aliphatic hydrocarbons identified on GC-MS system (n-dodecane and n-tridecane), the obtained chromatograms on GC-MS system were compared with chromatograms obtained with the use of GC-FID system and their amounts were calculated based FID response factors and determined calibration curve of n-undecane. The TVOC values were calculated according to the commonly used protocol which defines it as a the sum of all organic compounds, eluting between n-hexane and n-hexadecane (analytical window) on non-polar or slightly polar stationary phases of the GC column using GC-FID and quantifying as toluene equivalents (ECA-IAQ, 1997; Massold et al., 2005). The TVOC parameter is a screening factor that might define the impact on the emissions of non-aromatic hydrocarbons that might be emitted from the studied samples of latex balloons as a thermal degradation of basic polymer.

Following the principles of good laboratory practice, the calculated masses of detected monoraomatic and aliphatic hydrocarbons, as well as TVOC parameter were corrected for the blank field value assessed for the entire measuring set. The blank values were evaluated after every measuring period. In addition, after each of sampling period and blank field value measurement, the emission chambers were conditioned at temperature 100^oC for 30 min to remove potential analytes residues or chamber impurities and to reduce to minimum the potential wall-memory effect. The blank field tests were carried out under the same conditions as for the analysis of real samples.

The recovery values of monoaromatic hydrocarbons retained on the sorption medium were assessed based on the application of defined mass of analytes (form reference solution) on a clean sorption bed. Next, the sorption tube was introduced to the TD unit and analytes were thermally extracted, separated and determined under the same TD-GC-FID conditions as for the real samples. As a result, the average recovery values of monoarometic hydrocarbons do not exceed ± 5%. The method detection limits (MDL) were evaluated based the signal-to-noise ratio. The assessed values of method quantification limits (MQLs) calculated as 3 × MDL ranged from $0.088\ ng \cdot g^{-1}$ for benzene to $0.098\ ng \cdot g^{-1}$ for styrene.

2.6. Chemometric analysis and toxicity mixture assessment

Principal component analysis (PCA) is well known chemometric technique for dimensionality reduction (Navarro et al., 2010). PCA looks for the components (latent factors) that describe the major variance sources present in a particular data set (Jolliffe, 2002). To extract the components associated with major part of data variance PCA decomposes the data matrix (D) as the product of two orthogonal factor matrices U and V^T (eq. 1).

$$D = UV^T + E \tag{1}$$

where **D** is the data matrix of dimensions (I, J): I is the number of samples (balloon series No in this study), J is the number of variables (detected volatile organic compounds). **U** is the matrix of principal component sample scores of dimension (I, N), where N is the number of principal components. $\mathbf{V}^\mathbf{T}$ is the matrix of loadings with dimension (N, J). **E** is the residual matrix with the same dimensions like data matrix (**D**). The two matrices **U** (scores) and $\mathbf{V}^\mathbf{T}$ (loadings) contain the useful information about hidden relationships within the data set and could be used for the identification of sources contributed to the balloons' emissions. However, the score and loadings profiles obtained by PCA could not be used as source profiles since they have negative values. The original scores and loadings matrixes obtained by PCA could not be used directly for source apportionment. They need a transformation leading to non-negativity solution. The most used approach is absolute principal component scores (APCS) proposed by Thurston and Spengler (1985). The non-negativity is obtained by introducing of "zero day" (in current study it could be "zero emission") for correction of principal component scores.

Similarly to PCA, Multivariate curve resolution (MCR) decomposes the data matrix into two factor matrices using alternating least squares optimization (Tauler, 1995) but the method provides non-negative solutions without using orthogonal constraints which leads to physically meaningful emission sources.

The toxicity assessment of MCR modeled balloons' emissions is performed by toxic unit (TU) approach. The TU is a concentration addition approach, which is based on the endpoint of acute or chronic toxicity tests. The concentration of a substance is expressed as a proportion of the response (LC50 inhalation toxicity towards rodents in this study) (Brown, 1968). The proportional toxicity (toxic unit) of each compound is obtained by dividing its concentration in the balloon emission by its LC50 value. Then, the obtained TUs are summed to give toxicity emission assessment.

All chemometric analysis calculations were performed under MATLAB R2018b using PLS Toolbox 8.7 (Eigenvector Research Inc, Manson, WA, USA) and MCR-ALS Toolbox (Jaumot et al., 2015).

3. Results and discussion

3.1 FT-IR analysis of studied latex balloons

In order to identify the main polymer material and possible solvents, reagents and additives residues the FT-IR analysis was performed and the results of these studies are shown in Figure 1. Considering the data show in Figure 1 it might be observed that all of studied latex balloon samples were characterised by similar IR spectra. Because of this it might be concluded that analysed latex balloons are generally made of the same type and quality of polymeric material, and slight differences might occur from the application of different type of pigment or due to the presence of gloss on the surface of the studied material. The detailed information about the vibration types and assignments of various IR bands obtained for selected samples of latex balloons (frequencies are recorded with an accuracy of ± 1 cm^{-1}) was enclosed in Table 2.

3.2 The emissions of solvent, monomer and additives residues from studied latex balloons

Detailed information about the results (contains the range of minimum and maximum values) of emissions of the aliphatic and monoaromatic hydrocarbons (as a representatives of solvent, monomer and additive residues) liberated to the gaseous phase from the studied samples of latex balloons, as well as the values of calculated TVOC parameter were listed in the Table 3.

First of all, considering the data listed in the Table 3 it might be observed a clear relation between the temperature and the emission levels. The increase of latex balloon samples conditioning temperature affects significantly the emission of the most of determined chemical compounds (excluding ethylbenzene and in some cases hexanal). Generally, the presence of this phenomenon might be observed comparing the average values of TVOC parameter. For emission experiment temperature $30^{o}C$, the average value of TVOC parameter for all of studied samples ranged from 0.054 up to 7.2 $\mu g \cdot g^{-1}$ for latex balloon samples labelled as ORANGE_WG_2 and ORANGE_BLACK_IMPRINT_10, respectively. As for the conditioning temperature equal $60^{o}C$, the average value of TVOC parameter for all of studied samples ranged from 0.27 up to 36.11 $\mu g \cdot g^{-1}$ which also corresponds to the latex balloon samples labelled as ORANGE_WG_2 and ORANGE_BLACK_IMPRINT_11, respectively. Moreover, in both temperature ranges it might be observed that latex balloon samples with an additional imprint were characterised by highest values of TVOC parameter in comparison to plane latex balloons (without the additional imprint). This might lead to the conclusion that the application of additional imprint on the latex balloon surface contains an additional source of emission of chemical compounds to the gaseous phase (mainly volatile organic compounds). In addition, considering the data listed in the Table 3 it might be noticed that the screening parameter defined as TVOC might be significantly use for quick and easy comparison of the polymeric and synthetic materials, which might be characterised by the different shape, pigment and applied additives.

Taking into account the chemical structure of applied polymeric material (linear polymer structure) to manufacture the studied latex balloons and combine this information with the FT-IR analysis (Figure 1 and Table 2) and Table 3 it might be observed that the significant impact on the values of TVOC parameter have the aliphatic hydrocarbons, such as undecane, dodecane and tridecane. It is mainly associated with the chemical structure of synthetic materials and their emission might be caused by the thermal degradation of the structure of polymeric material applied in studied balloon samples. For this reason, the emission of monoaromatic hydrocarbons from the surface of studied latex balloons samples might be considered as a residual. Especially, it might be observed at the conditioning temperature equal to 30°C, in which the emission of ethylbenzene was below LOD and the emission of other monoaromatic hydrocarbons was at the very low level. From all of the determined monoaromatic hydrocarbons, in both temperature ranges, toluene and p,m-xylene were characterised by the highest emission rate. It might be caused by the fact that toluene and in some cases p,m-xylene might be used as the general solvents in the manufacturing process of latex balloons, as well as during the pigment and other additives application process. As a consequence, the impurities that might occur in mentioned solvents (even up to 1%) such as benzene or styrene might be introduced to the final synthetic product and be emitted into the gaseous phase during its regular use.

However, most of potential impurities and contaminants that are volatile and might be introduced during the latex balloons manufacturing process might be removed from them during their washing (with a cleaning agent) and drying stage. Despite the fact that the main synthetic material is the same, it might be observed a clear dissimilarities between studied samples (both at 30°C and 60°C). It is mainly associated with the different pigment application, the additive that gives the final material a specific gloss as well as the additional imprint application. Following the literature data, the emission fluctuations (defined by the type and the amount of the emitted chemical compounds) under real conditions (in indoor environment) might also by caused by the presence of atmospheric oxygen, moisture, light irradiation especially for the most reactive compounds such as styrene and hexanal. This issue is also associated with the emission investigations which are accelerated by raising the temperature (Kagi et al., 2009; Nohr et al., 2015). However, the use of described µ-CTE™ 250 system was supplied by dry nitrogen with no light irradiation, not affecting the overall emission results.

3.3 Chemometric analysis and toxicity mixture assessment

More information on the emissions of VOC from balloons can be obtained with application of chemometric tools. The results of PCA are presented in the Figure 2. The first principal component (PC1) explains 58.89% of initial dataset variability, while the second principal component (PC2) carries 17.40% of initial variability. Each of the remaining principal components carry less than 10% of variability so they are not further considered. The investigation of the PC1 factor loadings shows the following grouping of VOCs: sum of para and meta xylenes, styrene, tridecane, ethylbenzene, dodecane, undecane with higher factor loadings, and benzene, toluene and hexanal with lower factor loadings. This is an indication that compounds assigned to these two groups are emitted from different sources. Considering the structures of VOCs present in the first group and the structure of polymeric material it can be concluded that the compounds from first group are emitted from the material of balloon.

The probable source of emission of remaining three compounds is their sorption during balloons storage and their release from the surface of material during thermal desorption.

The second type of information can be obtained from PCA factor scores interpretation. Firstly, objects located in lower left corner of the plane are characterized by low emission of both groups of compounds. These objects are balloons treated with thermal desorption at 30°C. For objects 9, 10, 11, 12 and 13 the change of desorption temperature from 30 to 60°C results in much higher emission of compounds mainly from the first group - meta xylenes, styrene, tridecane, ethylbenzene, dodecane, undecane. These objects are balloons with imprints, that is potential cause of high emissions of these hydrocarbons. For the remaining objects there is an increase in emission of compounds from both groups (shift upwards and to the right).

The results of PCA (Figure 2) are in good agreement with MCR results (Figure 3). The first component in both analyses, PC1 for PCA and S1 for MCR, are characterized by high factor loadings of p,m-xylene, styrene, tridecane, ethylbenzene, dodecane and undecane. In the MCR score plot (Figure 3B) the first component reflects the temperature dependences of balloons' emissions from 30 to 60°C. According to the MCR modelled emissions the balloons could be classified in three groups. The first group consists of balloons 1-8 at 30°C and their emissions are characterized by the contributions of the second component (C2). The second group is formed by the balloons 9-13 (30°C) and balloons 1-8 (60°C). The content of this group indicates that the imprinted balloons have similar emission pattern at 30°C to the non-printed balloons at 60°C. The emission pattern is characterized by the contributions of both components with prevalence of the C2. The emission pattern of the third group consisting of balloons 9-13 (60°C) is strongly dominated by the first component (C1). This group is also clearly outlined in PCA score plot (Figure 2B).

For estimation of the toxicity of balloons' emissions toxic units model is implemented. The concentrations of emitted compounds are weighted by LC50 inhalation toxicity towards rodents. The calculated TUs of balloons' emissions with contributions of both MCR components (TU1 and TU2) are presented in Figure 4. The emissions from balloons 1-8 at 30°C are characterized by rather lower TUs , compared to other emissions. The emission toxicity of this group of balloons is based on compounds related to the second MCR component like benzene, toluene and hexanal. The emissions of imprinted balloons at 30°C (balloons 9-13) and non-printed ones at 60°C (balloons 1-8) cause much higher TUs than emissions from balloons from the first group. The toxicity emission pattern of the second group is dominated (from 80 to 90%) by the compounds related to the first MCR component like para and meta xylenes, styrene, tridecane, ethylbenzene, dodecane and undecane. The emission expressed in TUs from 9-13 balloons at 60°C is 3 to 8 times higher in comparison to other balloons emissions. Similarly to the previous group the main contribution to the emission toxicity is based again on the compounds related to the first MCR component.

As the emission profiles were not measured, the future studies will be focused on changes of emission in time at different temperatures. The other limitation is lack of calculation of VOCs concentrations nor they TUs to the exposure, which should be considered in the future work.

The limitation of the study is lack of knowledge on the exact composition of balloon material (the type and quality of basic reagents and additives, as well as the detailed description of each stage of studied materials manufacturing process), which is not stated by the manufacturer, so the relation between investigated material and VOCs emission can be the topic for the future studies.

4. Conclusions

Latex balloons should be considered as one of the source of emission of aliphatic and monoaromatic hydrocarbons. Due to the fact that the main type of polymer from which the NRL party balloons were made is of natural origin, the presence of VOCs might be a direct result of their natural occurrence - biological VOCs from natural source of liquid latex. Additionally, determined chemical compounds could come from the contamination of additives introduced in the technological process at the stage of preparation of the final NRL product.

The emitted compounds form two separate groups, suggesting two different emission sources – first related to latex material, the second one related to sorption-desorption processes on the surface of the balloon. The shape and applied pigment and especially imprints might be considered as the general factor that impact the emission level of determined chemical compounds. The temperature has a significant impact on the emissions of determined chemical compounds. The emission of carcinogenic compounds such as benzene should be monitored in the future in more detailed studies.

5. Conflict of interest

The authors declare that they have no conflict of interest.

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7. Figure and Table captions

Figure 1. The results of the FT-IR analysis of selected latex balloon samples, differs in a shape and applied pigment: ORANGE_WG_2 - Regular latex balloons, orange without gloss ; DARK_GREEN_G_5 - Regular latex balloons, glossy, dark green, shaded; BLACK_WG_6 - Regular latex balloons, black, matt, without gloss; COLORLESS_LATEX_8 - Regular latex balloons, colorless, pure latex balloons.

Figure 2. Principal component analysis (PCA) results – factor scores (A) and factor loadings (B).

Figure 3. Multiple curve resolution (MCR) results – factor loadings (A); factor scores (B) first emission from 1-13 balloons in 30°C then from 1-13 balloons in 60°C

Figure 4. Toxicity assessment of MCR modelled emissions (TU1 and TU2 represent the contributions of the first and second MCR components, respectively).

Table 1. General information about the analyzed samples of latex balloons delivered directly form the manufacturer.

Table 2. Assignments of various IR bands for representatives of studied samples of latex balloons (frequencies are recorded with an accuracy of ± 1 cm^{-1}) .

Table 3. The selected aliphatic and monoaromatic hydrocarbons emitted from the investigated latex balloon samples.

Table 1. General information about the analyzed samples of latex balloons delivered directly form the manufacturer.

Sample	**Sample acronym**	**Average mass ± SD [g] (n = 4)**	**Brief description**
Balloon Series 1	ORANGE_G_1	3.618 ± 0.030	Regular latex balloons, glossy orange
Balloon Series 2	ORANGE_WG_2	3.702 ± 0.087	Regular latex balloons, orange without gloss
Balloon Series 3	SMALL_ORANGE_WG_3	1.959 ± 0.014	Small latex balloons, orange without gloss
Balloon Series 4	SMALL_GREEN_WG_4	2.519 ± 0.047	Small latex balloons, green without gloss, matt
Balloon Series 5	DARK_GREEN_G_5	3.593 ± 0.036	Regular latex balloons, glossy, dark green, shaded
Balloon Series 6	BLACK_WG_6	3.681 ± 0.061	Regular latex balloons, black, matt, without gloss
Balloon Series 7	WHITE_WG_7	2.595 ± 0.038	Regular latex balloons, without gloss, matt, white
Balloon Series 8	COLORLESS_LATEX_8	3.643 ± 0.020	Regular latex balloons, colorless, pure latex balloons
Balloon Series 9	ORANGE_WHITE_IMPRINT_9	3.657 ± 0.083	Regular latex balloons, orange with white imprint
Balloon Series 10	ORANGE_BLACK IMPRINT_10	3.661 ± 0.057	Regular latex balloons, orange with black imprint 1
Balloon Series 11	ORANGE_BLACK_IMPRINT_11	3.785 ± 0.109	Regular latex balloons, orange with black imprint 2
Balloon Series 12	BLACK_WHITE_IMPRINT_12	3.711 ± 0.053	Regular latex balloons, black with white imprint
Balloon Series 13	BLACK_WHITE_POWDER_13	3.707 ± 0.034	Regular latex balloons, matt, black covered with white powder

Table 1. Assignments of various IR bands for representatives of studied samples of latex balloons (frequencies are recorded with an accuracy of ± 1 cm^{-1}) .

Wavenumber (cm^{-1})	**Vibration type and assignment**	**Studied sample type**
2960 (s)	=C-H stretching vibrations	commercially available latex balloons delivered directly from the manufacturer
2916 (s)	C-H asymmetrical stretching	
2850 (s)	C-H symmetrical stretching	
1574 (w) and 1537 (w)	C=C stretching vibrations	
1421-1445 (m)	C-H asymmetric deformation	
1375 (m)	C-H symmetric deformation	
1003-1016 (s)	-C-C stretching or wagging vibrations	
850-840 (s)	C-H out off-plane banding vibrations in the –CH=CH-	
567 (w)	C-C skeleton vibration	
s – strong; m – medium; w – weak		

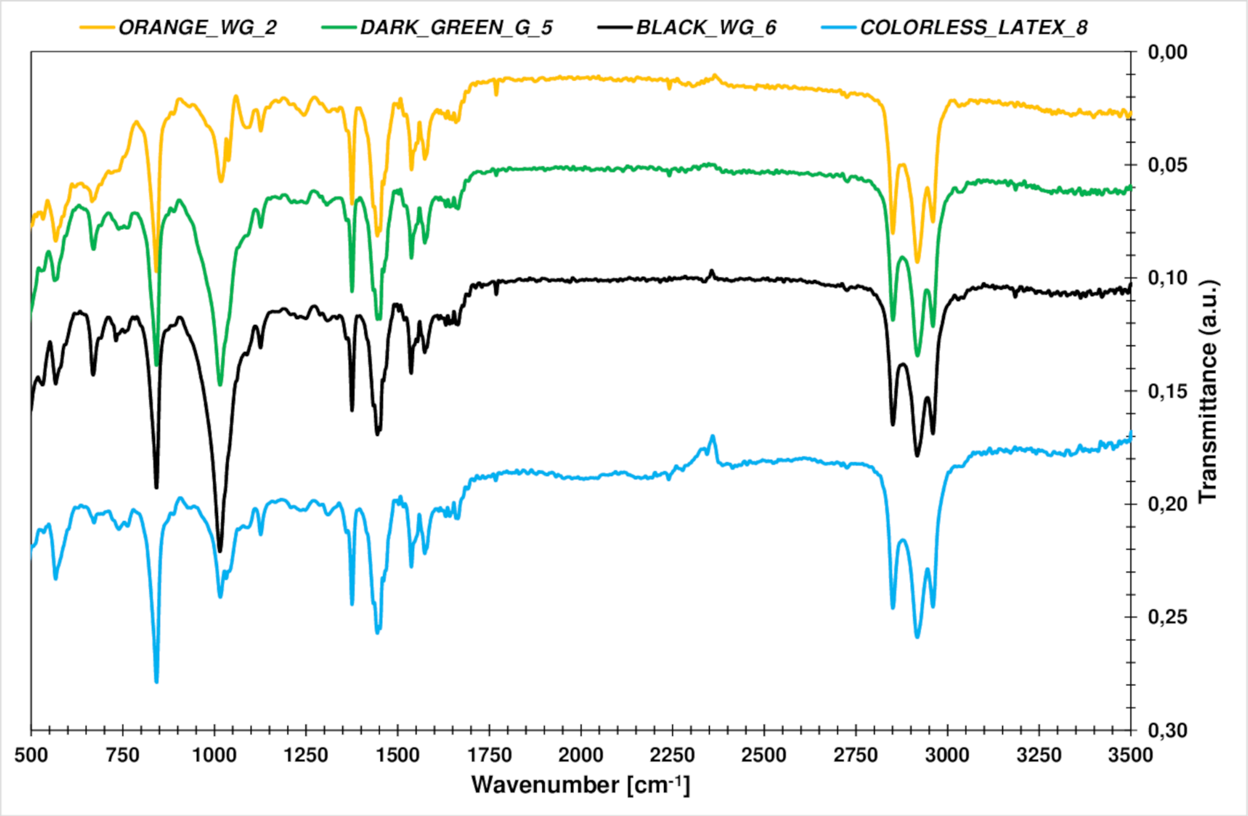
Table 3. The selected aliphatic and monoaromatic hydrocarbons emitted from the investigated latex balloon samples.

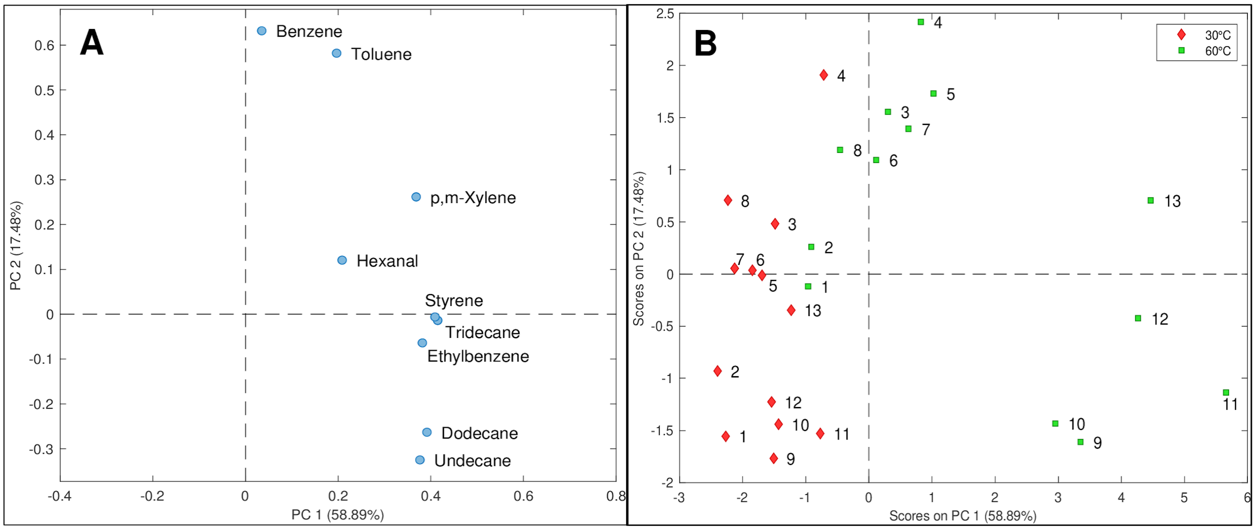
Latex balloons seasoning temperature: 30°C											
Smaple name	**Parameter**	**Hexanal [ng/g]**	**Undcane [ng/g]**	**Dodecane [ng/g]**	**Tridecane [ng/g]**	**Benzene [ng/g]**	**Toluene [ng/g]**	**Ethylbenzene [ng/g]**	**p,m-Xylene [ng/g]**	**Styrene [ng/g]**	**TVOC [ng/g]**
ORANGE_G_1	**Average**	8.7	4.6	4.3	2.4	0.30	0.38	<LOD	0.29	<LOD	60.6
	Stand. Dev.	1.3	1.3	2.1	1.5	0.30	0.18	-	0.04	-	5.6
	Min	6.6	3.6	3.0	1.5	0.02	0.13	-	0.25	-	56.8
	Max	9.5	6.4	7.4	4.5	0.72	0.51	-	0.32	-	68.8
ORANGE_WG_2	**Average**	6.19	3.55	3.64	1.95	0.96	0.96	<LOD	0.36	0.27	54.3
	Stand. Dev.	0.82	0.12	0.27	0.41	0.18	0.36	-	0.10	0.10	6.1
	Min	4.89	3.43	3.26	1.55	0.79	0.44	-	0.22	0.15	45.2
	Max	6.70	3.70	3.89	2.43	1.22	1.28	-	0.46	0.36	58.4
SMALL_ORANGE_WG_3	**Average**	10.7	6.07	7.06	5.1	1.90	3.8	<LOD	0.47	1.37	130
	Stand. Dev.	1.4	0.77	0.39	1.2	0.22	1.3	-	0.27	0.42	24
	Min	8.8	5.13	6.52	4.0	1.69	2.19	-	0.29	0.88	104
	Max	12.1	6.70	7.42	6.9	2.16	5.26	-	0.88	1.91	162
SMALL_GREEN_WG_4	**Average**	12.2	7.7	11.3	8.0	2.14	16.9	<LOD	1.85	1.29	241
	Stand. Dev.	1.9	3.0	4.9	5.4	0.65	2.6	-	0.59	0.40	47
	Min	11.0	5.2	7.9	4.7	1.29	14.79	-	1.35	0.74	204
	Max	15.0	12.1	18.5	16.1	2.78	20.33	-	2.71	1.58	308
DARK_GREEN_G_5	**Average**	7.58	4.55	6.94	4.58	0.95	11.4	<LOD	1.31	0.57	125
	Stand. Dev.	0.48	0.58	0.96	0.93	0.27	1.2	-	0.55	0.42	34
	Min	7.02	3.77	5.61	3.59	0.55	9.98	-	0.81	0.23	103
	Max	8.17	5.11	7.76	5.81	1.10	12.81	-	1.91	1.18	175
BLACK_WG_6	**Average**	6.73	3.72	8.3	6.8	1.28	8.44	<LOD	0.99	0.57	133.8
	Stand. Dev.	0.69	0.53	1.4	1.6	0.41	0.74	-	0.07	0.28	6.5
	Min	5.80	3.26	7.2	5.6	0.88	7.78	-	0.91	0.36	127.3
	Max	7.45	4.46	10.3	9.1	1.83	9.45	-	1.06	0.98	143.9
WHITE_WG_7	**Average**	6.9	4.27	6.87	5.10	1.39	7.8	<LOD	0.61	<LOD	479
	Stand. Dev.	1.3	0.28	0.40	0.99	0.20	1.5	-	0.24	-	33
	Min	5.4	3.89	6.48	4.04	1.16	5.99	-	0.33	-	441
	Max	8.3	4.55	7.43	6.44	1.60	9.51	-	0.91	-	521
COLORLESS_LATEX_8	**Average**	5.66	3.36	5.0	3.02	2.16	5.93	<LOD	0.64	<LOD	156
	Stand. Dev.	0.63	0.48	1.1	0.78	0.13	0.73	-	0.16	-	40

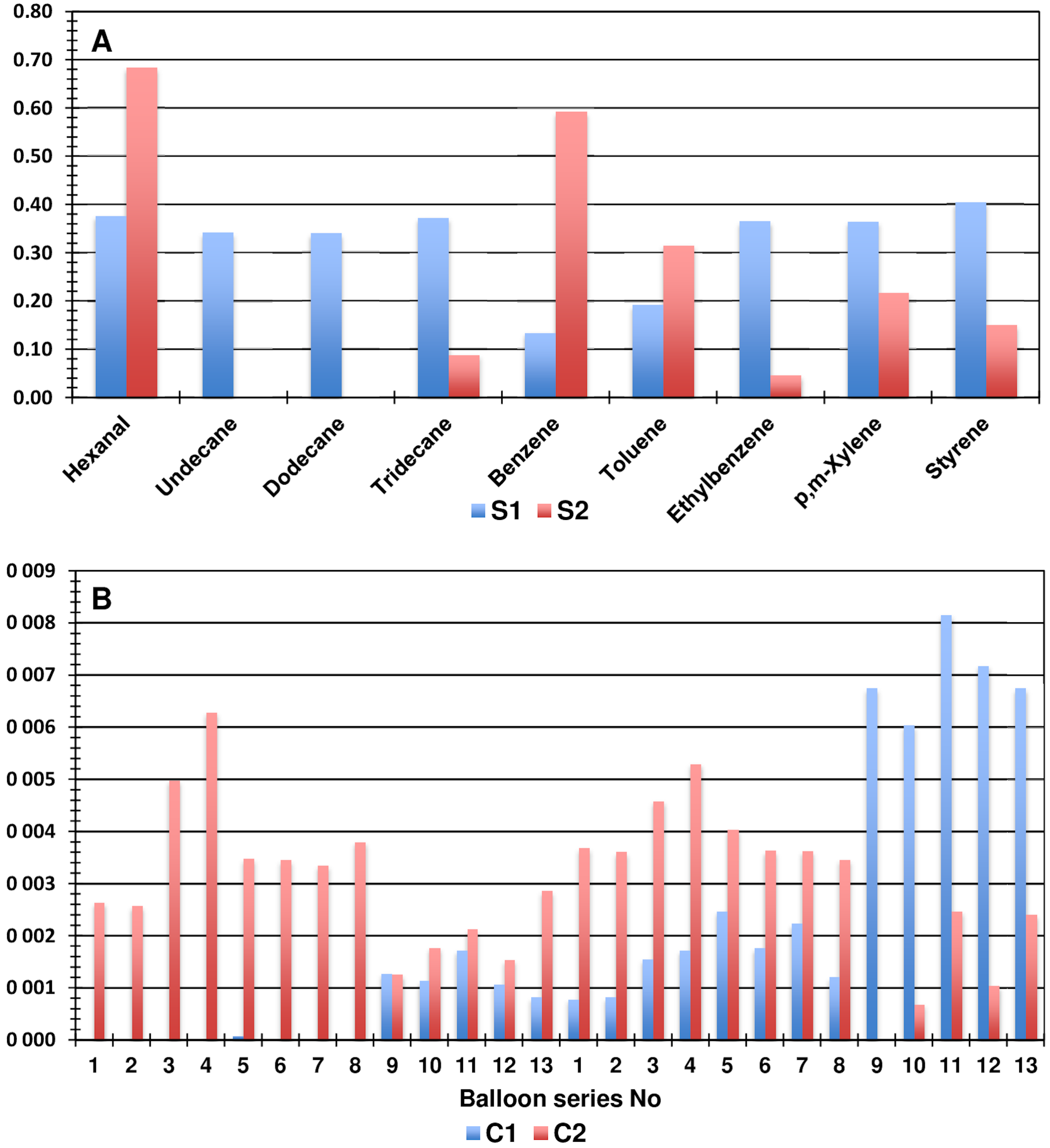
	Min	5.12	2.87	3.7	2.03	2.04	5.27	-	0.45	-	122
	Max	6.53	3.97	6.4	3.93	2.30	6.61	-	0.82	-	212
ORANGE_WHITE_IMPRINT_9	**Average**	6.4	70.6	50.2	8.0	0.071	3.00	0.142	1.37	1.41	$59.7\cdot10^2$
	Stand. Dev.	1.1	3.9	4.2	1.2	0.011	0.85	0.011	0.37	0.33	$2.8\cdot10^2$
	Min	4.9	65.4	45.7	7.3	0.06	2.21	0.13	1.02	1.19	$56.7\cdot10^2$
	Max	7.4	74.7	55.8	9.7	0.08	3.82	0.15	1.71	1.89	$63.2\cdot10^2$
ORANGE_BLACK_IMPRINT_10	**Average**	6.98	87	85	10.7	0.46	3.80	0.37	1.08	1.23	$71.8\cdot10^2$
	Stand. Dev.	0.65	16	18	2.1	0.16	0.78	-	0.17	0.67	$13.0\cdot10^2$
	Min	6.19	64	59.8	8.6	0.36	2.96	0.37	0.95	0.68	$54.9\cdot10^2$
	Max	7.63	100	101.1	13.6	0.69	4.72	0.37	1.33	2.20	$86.3\cdot10^2$
ORANGE_BLACK_IMPRINT_11	**Average**	9.74	92.3	110	15.0	0.381	3.72	0.26	1.07	1.34	$71.7\cdot10^2$
	Stand. Dev.	0.63	9.2	18	4.2	0.082	0.13	0.16	0.05	0.13	$5.9\cdot10^2$
	Min	9.19	80.8	94	11.5	0.28	3.54	0.11	1.04	1.24	$64.7\cdot10^2$
	Max	10.62	102.8	134	21.0	0.46	3.84	0.44	1.14	1.53	$78.9\cdot10^2$
BLACK_WHITE_IMPRINT_12	**Average**	5.6	57	59	8.1	0.40	5.3	0.21	2.19	1.01	$44.7\cdot10^2$
	Stand. Dev.	1.4	27	26	2.4	0.22	1.6	-	0.64	0.15	$22.1\cdot10^2$
	Min	4.1	23	22	4.6	0.17	3.72	0.21	1.58	0.87	$17.8\cdot10^2$
	Max	6.8	81	83	10.2	0.68	6.91	0.21	2.74	1.21	$64.4\cdot10^2$
BLACK_WHITE_POWDER_13	**Average**	7.48	54.5	63.3	8.73	0.982	8.18	0.083	2.24	0.98	$43.2\cdot10^2$
	Stand. Dev.	0.47	2.6	4.3	0.32	0.031	0.47	0.051	0.28	0.11	$1.4\cdot10^2$
	Min	6.89	51.6	57.9	8.36	0.94	7.79	0.04	1.96	0.85	$41.7\cdot10^2$
	Max	7.98	57.9	68.4	9.05	1.01	8.79	0.12	2.57	1.10	$44.7\cdot10^2$
Latex balloons seasoning temperature: 60°C											
Smaple name	**Parameter**	**Hexanal [ng/g]**	**Undcane [ng/g]**	**Dodecane [ng/g]**	**Tridecane [ng/g]**	**Benzene [ng/g]**	**Toluene [ng/g]**	**Ethylbenzene [ng/g]**	**p,m-Xylene [ng/g]**	**Styrene [ng/g]**	**TVOC [ng/g]**
ORANGE_G_1	**Average**	8.67	19.9	33	18	1.27	2.44	<LOD	3.27	0.80	330
	Stand. Dev.	0.91	1.7	13	12	0.35	0.48	-	0.44	0.21	35
	Min	7.60	18.3	23	11	1.03	1.85	-	2.76	0.54	294
	Max	9.51	21.8	51	36	1.78	2.91	-	3.80	1.04	367
ORANGE_WG_2	**Average**	7.00	15.7	21.7	11.7	1.57	3.76	<LOD	3.39	1.86	265
	Stand. Dev.	0.70	1.3	2.6	1.4	0.24	0.70	-	0.99	0.53	23
	Min	5.97	13.9	19.5	9.9	1.32	2.99	-	2.53	1.43	246
	Max	7.48	16.7	25.2	13.1	1.91	4.68	-	4.81	2.62	298
SMALL_ORANGE_WG_3	**Average**	8.3	29.1	47.2	27.3	2.34	8.9	<LOD	4.95	2.86	484

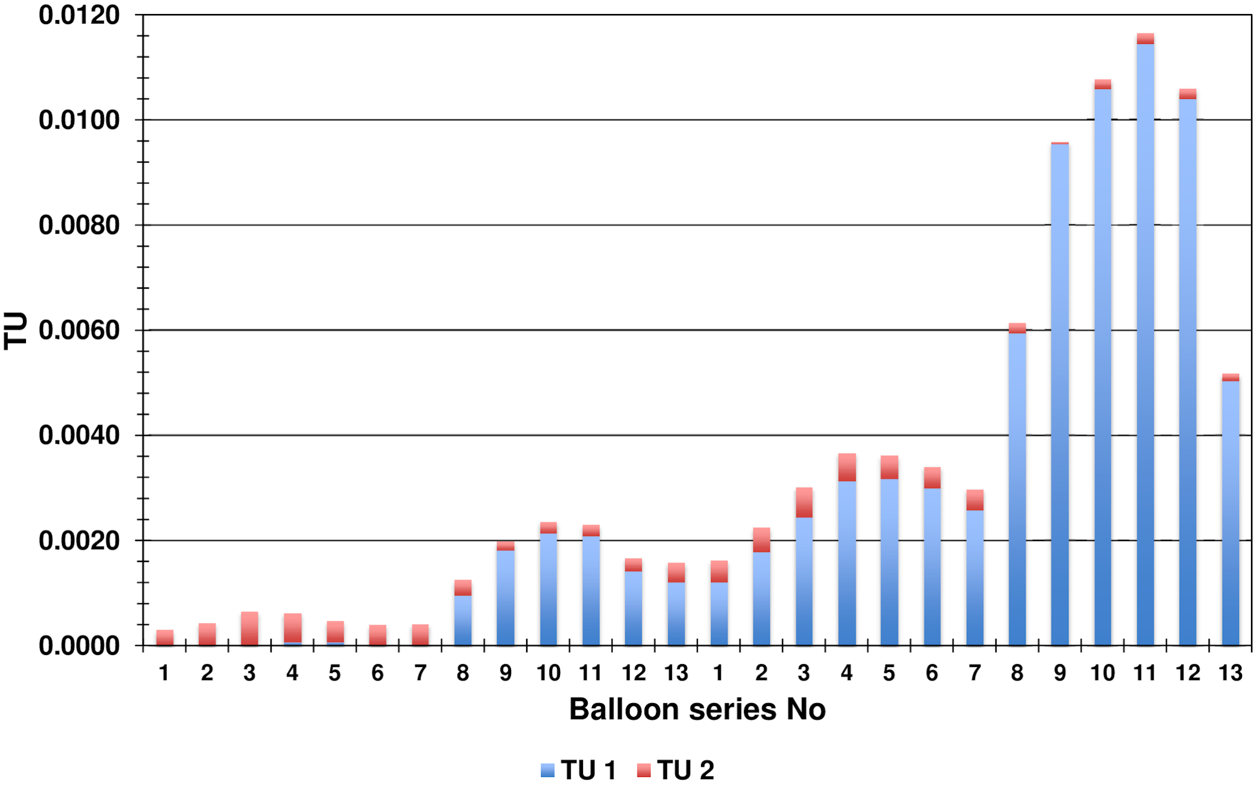
	Stand. Dev.	1.1	1.4	3.0	4.0	0.37	1.5	-	0.13	0.36	21
	Min	7.3	27.6	43.8	22.2	1.97	7.56	-	4.83	2.59	467
	Max	9.8	30.8	51.0	31.5	2.85	11.00	-	5.13	3.38	514
SMALL_GREEN_WG_4	**Average**	10.67	24.3	42.1	25.1	1.471	31.3	<LOD	4.94	2.26	472
	Stand. Dev.	0.92	2.7	4.2	3.4	0.074	3.3	-	0.62	0.53	56
	Min	9.35	22.5	38.9	20.2	1.40	28.62	-	4.49	1.58	423
	Max	11.44	28.4	47.8	27.7	1.56	35.43	-	5.83	2.74	551
DARK_GREEN_G_5	**Average**	8.58	21.8	39	25.5	1.19	28.1	0.60	4.92	1.88	412
	Stand. Dev.	0.83	2.4	11	7.7	0.22	2.8	0.15	0.38	0.43	32
	Min	7.50	19.4	26.1	16.6	0.92	24.23	0.38	4.41	1.26	389
	Max	9.44	25.1	51.8	35.2	1.43	30.77	0.70	5.30	2.22	457
BLACK_WG_6	**Average**	6.9	16.5	26.6	17.1	1.40	18.0	0.53	4.02	1.63	338
	Stand. Dev.	1.2	1.6	4.2	3.2	0.32	3.3	0.21	0.84	0.85	53
	Min	5.3	15.4	22.7	12.9	1.22	14.31	0.32	3.12	0.99	291
	Max	8.0	18.9	31.7	20.2	1.89	22.39	0.80	5.1	2.9	415
WHITE_WG_7	**Average**	7.16	24.9	48.0	34.7	1.481	19.8	0.35	5.1	1.8	690
	Stand. Dev.	0.55	1.6	4.4	3.9	0.059	1.8	0.14	0.50	0.21	12
	Min	6.37	23.6	43.7	31.2	1.41	17.21	0.22	4.57	1.61	683
	Max	7.62	27.2	53.3	40.2	1.55	21.29	0.53	5.56	2.12	707
COLORLESS_LATEX_8	**Average**	4.73	17.54	33.1	19.6	1.82	14.28	0.330	4.20	1.08	344
	Stand. Dev.	0.41	0.96	6.0	6.6	0.26	0.80	0.079	0.34	0.17	48
	Min	4.46	16.33	26.2	13.3	1.60	13.35	0.25	3.91	0.92	281
	Max	5.34	18.65	38.3	26.1	2.11	14.97	0.41	4.61	1.33	391
ORANGE_WHITE_IMPRINT_9	**Average**	7.18	379	318	41.8	0.69	8.4	0.96	5.1	4.49	$30.5\cdot10^3$
	Stand. Dev.	0.90	45	47	1.6	0.23	2.3	0.37	1.4	0.66	$3.0\cdot10^3$
	Min	6.37	346	279	40.4	0.38	5.75	0.63	3.73	3.76	$28.1\cdot10^3$
	Max	8.30	441	379	43.9	0.92	10.41	1.35	6.55	5.38	$34.6\cdot10^3$
ORANGE_BLACK_IMPRINT_10	**Average**	7.67	483	459	52.1	1.24	8.9	0.513	4.06	2.69	$34.5\cdot10^3$
	Stand. Dev.	0.78	45	93	9.5	0.49	1.5	0.091	0.35	0.37	$6.3\cdot10^3$
	Min	6.97	459	325	41.0	0.70	7.47	0.44	3.68	2.28	$26.1\cdot10^3$
	Max	8.70	551	527	63.9	1.80	10.38	0.64	4.38	3.16	$41.4\cdot10^3$
ORANGE_BLACK_IMPRINT_11	**Average**	17.9	416	667	93	1.16	10.06	0.712	4.76	4.15	$36.1\cdot10^3$
	Stand. Dev.	1.2	35	76	11	0.10	0.82	0.081	0.38	0.68	$3.3\cdot10^3$
	Min	16.8	394	592	82.4	1.02	9.34	0.61	4.33	3.34	$33.0\cdot10^3$

	Max	19.3	468	773	107.6	1.27	10.80	0.80	5.24	4.96	$40.4\cdot10^3$
BLACK_WHITE_IMPRINT_12	**Average**	9.3	319	343	52	0.96	15.0	1.22	7.4	3.87	$23.6\cdot10^3$
	Stand. Dev.	1.8	161	127	17	0.18	4.3	0.40	1.4	0.21	$10.1\cdot10^3$
	Min	7.5	148	188	31.9	0.76	11.05	0.85	6.10	3.68	$12.4\cdot10^3$
	Max	11.2	488	482	71.0	1.13	19.43	1.67	9.03	4.16	$34.6\cdot10^3$
BLACK_WHITE_POWDER_13	**Average**	10.10	348	372	52.5	1.67	20.82	0.96	7.2	4.24	$23.5\cdot10^3$
	Stand. Dev.	0.91	86	41	6.5	0.17	0.83	0.22	1.4	0.25	$1.9\cdot10^3$
	Min	9.05	290	319	44.5	1.49	19.95	0.75	6.03	4.08	$21.6\cdot10^3$
	Max	11.05	475	418	60.5	1.87	21.85	1.16	8.43	4.60	$25.6\cdot10^3$


ORANGE_WG_2
DARK_GREEN_G_5
BLACK_WG_6
COLORLESS_LATEX_8
Transmittance (a.u.)
0,00
0,05
0,10
0,15
0,20
0,25
0,30
500
750
1000
1250
1500
1750
2000
2250
2500
2750
3000
3250
3500
Wavenumber [cm-1]


A
Benzene
Toluene
p,m-Xylene
Hexanal
Styrene
Tridecane
Ethylbenzene
Dodecane
Undecane
PC 1 (58.89%)
PC 2 (17.48%)
-0.4
-0.2
0
0.2
0.4
0.6
0.8
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
B
30°C
60°C
Scores on PC 1 (58.89%)
Scores on PC 2 (17.48%)
-3
-2
-1
0
1
2
3
4
5
6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
1
2
3
4
5
6
7
8
9
10
11
12
13
1
2
3
4
5
6
7
8
9
10
11
12
13


A
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Hexanal
Undecane
Dodecane
Tridecane
Benzene
Toluene
Ethylbenzene
p,m-Xylene
Styrene
S1
S2
B
0 009
0 008
0 007
0 006
0 005
0 004
0 003
0 002
0 001
0 000
1
2
3
4
5
6
7
8
9
10
11
12
13
1
2
3
4
5
6
7
8
9
10
11
12
13
Balloon series No
C1
C2


0.0120
0.0100
0.0080
0.0060
0.0040
0.0020
0.0000
TU
1
2
3
4
5
6
7
8
9
10
11
12
13
1
2
3
4
5
6
7
8
9
10
11
12
13
Balloon series No
TU 1
TU 2

Highlights

- The VOCs emissions depend on latex balloon pigment and imprints presence
- The average values of emitted TVOCs at 30oC ranged from 0.051 up to 7.18 $\mu g \cdot g^{-1}$
- The average values of emitted TVOCs at 60oC ranged from 0.27 up to 31.13 $\mu g \cdot g^{-1}$
- PCA analysis showed that VOCs are from balloon material and desorption process
- MCR with toxic units identified the most hazardous VOCs – benzene and hexanal