

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

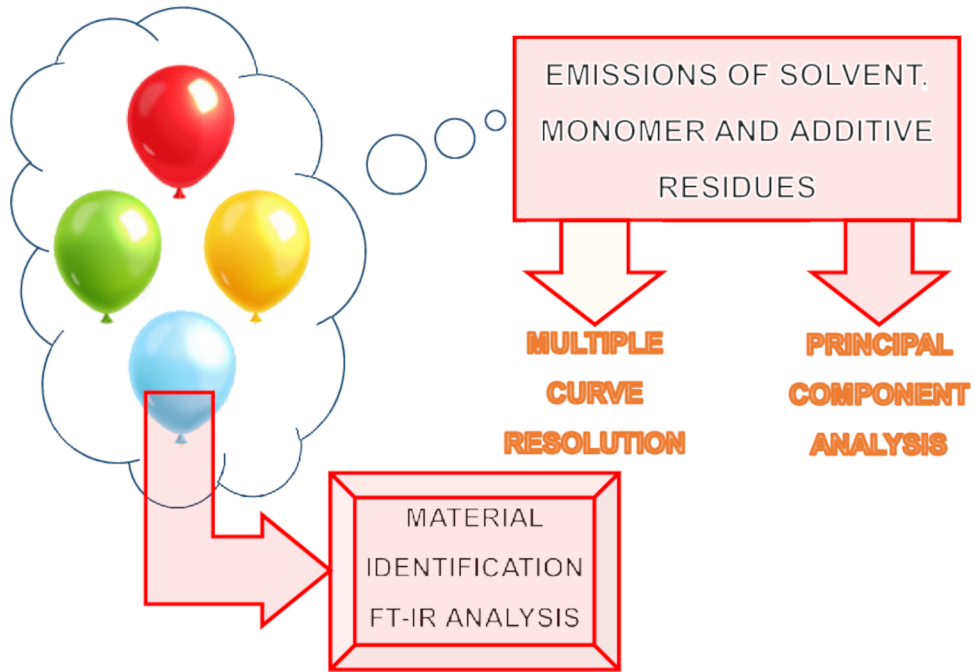
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2 **phase from latex balloons**

3

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

19

20 **Abstract**

21 This study describes the VOCs emissions from commercially available latex balloons. Nine
22 compounds are determined to be emitted from 13 types of balloons of different colors and
23 imprints in 30 and 60°C. The average values of total volatile organic compounds (TVOCs)
24 emitted from studied samples ranged from 0.054 up to 7.18 $\mu\text{g}\cdot\text{g}^{-1}$ and from 0.27 up to 36.13
25 $\mu\text{g}\cdot\text{g}^{-1}$ for 30°C and 60°C, respectively. The dataset is treated with principal component
26 analysis (PCA) and multiple curve resolution (MCR) to characterize its internal patterns. Here
27 two groups on compounds are recognized – the first one related to balloon material, the
28 second one being emissions of compounds previously adsorbed on balloon material. The
29 toxicity assessment of MCR modeled balloons' emissions was performed by toxic unit (TU)
30 approach. The obtained TUs were summed to give toxicity emission assessment. The
31 incorporation of TUs allows to identify the balloons with the most toxic emissions– imprinted
32 ones in 60°C. The compounds of the highest TUs are hexanal and benzene. FTIR analysis
33 shows that all balloons are made of the same polymeric material – isoprene, so all differences
34 in emissions are related to different additives like pigments, imprints or these responsible for
35 opaqueness. Analyzing the obtained research results it was noticed that latex balloons might
36 be considered as an important source of emission of aliphatic and monoaromatic
37 hydrocarbons to the gaseous phase.

38

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

41

42 **1. Introduction**

43

44 Nowadays, almost every synthetic material consists a wide spectrum of additives, such as
45 antistatic agents, ultraviolet radiation filters, antioxidants, plasticisers, stabilizers, lubricants
46 as well as pigments, colorants, fillers or nanofillers (Mitchell et al., 2014; Hahladakis et al.,
47 2018). Consequently, the harmful chemicals (such as formaldehyde, volatile organic
48 compounds (VOC), as well as semi-volatile organic compounds (SVOCs)) that might be
49 introduced in a synthetic materials manufacturing process, could be emitted to the gaseous
50 phase during their regular use (Wolkoff and Nielsen, 2001; Gallon et al., 2020). Mainly, the
51 chemical compounds released from synthetic materials arise from residues of reagents used
52 during polymerisation reaction (monomers, cross-linking agents, reaction initiators, solvents)
53 and the impurities present in employed wide spectrum of plastic additives (Böhm et al., 2012;
54 Rosenmai et al., 2017; Yan et al., 2017). This phenomenon concerns the various types of
55 everyday use large or small-scale indoor equipment (floor coverings, floor panels, furniture,
56 electronic devices, toys), as well as the wide spectrum of synthetic materials (copolymer
57 acrylonitrile-butadiene styrene (ABS), polyvinyl chloride (PVC), polypropylene (PP) and
58 polyethylene(PE)) intended to come into direct contact with food or human skin
59 (Kamarulzaman et al., 2019; Rubio et al., 2019). The quality of synthetic materials (which can
60 be defined by assessing the type and amount of emitted chemical compounds) is particularly
61 important in the case of products intended for direct use by children. As a result of the use of
62 synthetic materials by children, exposure to the harmful chemical compounds can take place
63 not only through the skin (touch), but also through the mucous membranes of the mouth
64 (saliva) and nose (inhalation). It is particularly important because they can lead to allergies
65 and skin irritation and also because most of toxic additives are endocrine disrupting
66 substances (EDS) whose adverse effect are particularly relevant during childhood. (Denk et
67 al., 2017; Wiedmer and Buettner, 2018; Even et al., 2019).

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

2



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

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

109

110 **2. Materials and methods**

111

112 **2.1 Characteristics of latex balloon samples**

113 Studies were performed on latex balloons delivered directly from the local manufacturer,
114 which is the member of European Balloon and Party Council (EBPC). Thirteen different types
115 of latex balloons were delivered in a separate packed batch. Each batch contained ten balloons
116 of the exactly same shape, colour (pigment type) and similar weight placed in polypropylene
117 zipper bags. Zipper bags with latex balloons were stored at the laboratory at room temperature
118 in a dark place (stored without access to light). To determine the emissions of potential
119 solvent, monomer or additives residues four randomly selected latex balloons were picked up
120 from a single batch and considered as a representative for the whole batch. Selected samples
121 of latex balloons were then weighed, suitably labelled, and placed inside the stainless-steel
122 tightly sealed microscale chamber. Because of the fact that delivered latex balloons varies in
123 terms of colour (pigment type), weight, shape and the presence of additional imprint, it was

3

124 obliged to introduce the appropriate samples identification system, which was enclosed in
125 Table 1. There was no need for a special treatment of studied samples – absence of cutting
126 and reducing the samples dimensions.

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

130

131 **2.2 FT-IR analysis conditions**

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

144

145 **2.3 Sampling protocol of solvent, monomer and additives residues emitted from** 146 **investigated latex balloons**

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

155 Samples of latex balloons were investigated employing mentioned above the μ -CTE™ 250
156 system at two temperatures: (i) 30°C – to investigate the basic emission of general solvents,
157 reagents and potential additives that might be emitted during regular use of studied latex
158 samples; (ii) at 60°C – a significantly higher temperature to assess the maximum emission
159 potential of studied latex samples and to investigate the presence of potential chemical
160 compounds that might be released from the surface of studied latex materials as a polymer or
161 additives thermal degradation products (temperature close to maximum operating temperature
162 range – 70 - 80°C). One analytical conditioning and sampling period contains the analysis of
163 four samples originating from the same batch of latex balloons. The inert gas flow rate
164 (nitrogen, 2.2) passed through the chamber was set up to $25 \pm 0.5\text{ mL}\cdot\text{min}^{-1}$ and the sampling

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165 conditioning time was 30 ± 1 min. The samples of analytes emitted from the studied latex
166 balloons to the gaseous phase were transported by the gas stream directly to the attached
167 stainless steel tube filled with Tenax TA sorption medium (60/80 mesh, O.D. \times L 1/4 in. \times 3
168 1/2 in., Merck KGaA, Darmstadt, Germany), each time conditioned (300°C for 30 min under
169 inert gas flow rate) before sampling stage.

170

171 **2.4 Thermal desorption and final determination systems working parameters**

172 The analytical technique employed at the stage of thermal desorption of analytes collected on
173 the applied sorption medium was two-stage thermal desorption (TD) system (Markes Series 2
174 Thermal Desorption Systems; UNITY/TD-100). In brief, after the sampling stage the stainless
175 steel tubes were placed in a TD heating unit and maintained in elevated temperature 295°C for
176 15 min under the inert gas flow rate (helium, $50\text{ mL}\cdot\text{min}^{-1}$), which transfers the analytes
177 directly to the microtrap (multibed glass tube cooled down to 0°C). After this, the valve was
178 switched and the inert gas (helium flow rate $2.0\text{ mL}\cdot\text{min}^{-1}$) was passed through the microtrap
179 (rapidly heated up to 300°C and maintained for 5 min) and the analytes were transported
180 directly to the fused silica capillary column (J&W, DB-1 $30\text{ m} \times 0.32\text{ mm} \times 5\text{ }\mu\text{m}$). The
181 separation, preliminary identification and quantitative determination was performed with the
182 use of gas chromatograph (Agilent Technologies 7820A GC System) with flame ionization
183 detector (FID working temperature – 250°C). The GC-FID was connected with the TD unit by
184 transfer line, constantly heated up to 180°C . The GC oven working was: initial temperature –
185 45°C maintained for 1 min, next ramped $15^\circ\text{C}\cdot\text{min}^{-1}$ up to 120°C , and held for 2 min, then
186 increased with the rate $10^\circ\text{C}\cdot\text{min}^{-1}$ up to 250°C and held for 5 min. The inert GC gas constant
187 flow (He, 5.0) rate – $2.0\text{ mL}\cdot\text{min}^{-1}$. In order to perform better identification of the main
188 emitted chemical compounds from the studied samples of latex balloons the TD-GC-MS
189 system was employed, under the following working parameters: (i) TD unit (Unity v.2,
190 Markes International Ltd.) – the analytes thermal extraction process was performed in similar
191 conditions to mentioned TD-GC-FID system; (ii) GC (Agilent Technologies 6890) column
192 and oven working parameters – GC column ($60\text{ m} \times 0.25\text{ mm} \times 1\text{ }\mu\text{m}$, J&W DB-5MS, USA);
193 helium gas flow rate – $1.5\text{ mL}\cdot\text{min}^{-1}$, oven program: initial temperature – 50°C maintained for
194 1 min and next ramped $10^\circ\text{C}\cdot\text{min}^{-1}$ up to 280 and held for 10 min; (iii) MS (5873 Network
195 Mass Selective Detector, Agilent Technologies) working parameters - ion source temperature:
196 230°C , the quadrupole mass analyser temperature: 150°C , and the GC-MS transfer line
197 temperature: 280°C , MS working mode – SCAN, monitored mass range (m/z) – 35 - 450.

198

199 **2.5 Calibration and QA/QC protocol characteristic**

200 The amount of chemical compounds considered as solvent and reagent residues emitted from
201 the exanimated latex party balloon was assessed with the use of the calibration of the TD-GC-
202 FID employing the external standard (ESTD) method. Based on the commercially available
203 reference standard solution (EPA VOC Mix 2, Supelco, USA) containing defined type and
204 amount of VOCs (13 monoaromatic hydrocarbons dissolved in methanol at a concentration of
205 $2000\text{ }\mu\text{g}\cdot\text{mL}^{-1}$ each), hexanal analytical standard (1 mL, Supelco, USA) and n-undecane

5

206 reference substance for GC (5 mL, Supelco, USA), the calibration curves were elaborated. To
207 perform the calibration procedure, seven calibration reference solutions (for seven-point
208 calibration curve) in 1 mL of methanol were prepared, containing approx. from 1 ng up to 500
209 ng of each of measured monoaromatic hydrocarbons. The whole calibration protocol was
210 carried out with the use of specific type of laboratory tool (device that gives a possibility to
211 introduce a defined amount of calibration solution directly onto the clean sorption medium),
212 in details labelled in former studies (Zabiegała et al., 2011; Marć et al., 2014a; Marć et al.,
213 2014b). The Tenax Ta stainless steel tubes containing defined mass of selected VOCs were
214 analysed under the same equipment conditions and working parameters as the real samples.
215 Each point representing the defined calibration curve was repeated three times. The evaluated
216 correlation coefficients (R^2) of the prepared calibration curves for defined range of
217 monoaromatic hydrocarbons were approx. from 0.952 for benzene to 0.999 for styrene. As for
218 the aliphatic hydrocarbons identified on GC-MS system (n-dodecane and n-tridecane), the
219 obtained chromatograms on GC-MS system were compared with chromatograms obtained
220 with the use of GC-FID system and their amounts were calculated based FID response factors
221 and determined calibration curve of n-undecane. The TVOC values were calculated according
222 to the commonly used protocol which defines it as a the sum of all organic compounds,
223 eluting between n-hexane and n-hexadecane (analytical window) on non-polar or slightly
224 polar stationary phases of the GC column using GC-FID and quantifying as toluene
225 equivalents (ECA-IAQ, 1997; Massold et al., 2005). The TVOC parameter is a screening
226 factor that might define the impact on the emissions of non-aromatic hydrocarbons that might
227 be emitted from the studied samples of latex balloons as a thermal degradation of basic
228 polymer.

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

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

245

246 **2.6. Chemometric analysis and toxicity mixture assessment**



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

252

$$253 \quad \mathbf{D} = \mathbf{UV}^T + \mathbf{E} \quad (1)$$

254

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

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

273 The toxicity assessment of MCR modeled balloons' emissions is performed by toxic unit
274 (TU) approach. The TU is a concentration addition approach, which is based on the endpoint
275 of acute or chronic toxicity tests. The concentration of a substance is expressed as a
276 proportion of the response (LC50 inhalation toxicity towards rodents in this study) (Brown,
277 1968). The proportional toxicity (toxic unit) of each compound is obtained by dividing its
278 concentration in the balloon emission by its LC50 value. Then, the obtained TUs are summed
279 to give toxicity emission assessment.

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

283

284 **3. Results and discussion**

285

286 **3.1 FT-IR analysis of studied latex balloons**



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

297

298 **3.2 The emissions of solvent, monomer and additives residues from studied latex** 299 **balloons**

300 Detailed information about the results (contains the range of minimum and maximum values)
301 of emissions of the aliphatic and monoaromatic hydrocarbons (as a representatives of solvent,
302 monomer and additive residues) liberated to the gaseous phase from the studied samples of
303 latex balloons, as well as the values of calculated TVOC parameter were listed in the Table 3.
304 First of all, considering the data listed in the Table 3 it might be observed a clear relation
305 between the temperature and the emission levels. The increase of latex balloon samples
306 conditioning temperature affects significantly the emission of the most of determined
307 chemical compounds (excluding ethylbenzene and in some cases hexanal). Generally, the
308 presence of this phenomenon might be observed comparing the average values of TVOC
309 parameter. For emission experiment temperature 30°C , the average value of TVOC parameter
310 for all of studied samples ranged from 0.054 up to $7.2 \mu\text{g}\cdot\text{g}^{-1}$ for latex balloon samples
311 labelled as ORANGE_WG_2 and ORANGE_BLACK_IMPRINT_10, respectively. As for the
312 conditioning temperature equal 60°C , the average value of TVOC parameter for all of studied
313 samples ranged from 0.27 up to $36.11 \mu\text{g}\cdot\text{g}^{-1}$ which also corresponds to the latex balloon
314 samples labelled as ORANGE_WG_2 and ORANGE_BLACK_IMPRINT_11, respectively.
315 Moreover, in both temperature ranges it might be observed that latex balloon samples with an
316 additional imprint were characterised by highest values of TVOC parameter in comparison to
317 plane latex balloons (without the additional imprint). This might lead to the conclusion that
318 the application of additional imprint on the latex balloon surface contains an additional source
319 of emission of chemical compounds to the gaseous phase (mainly volatile organic
320 compounds). In addition, considering the data listed in the Table 3 it might be noticed that the
321 screening parameter defined as TVOC might be significantly use for quick and easy
322 comparison of the polymeric and synthetic materials, which might be characterised by the
323 different shape, pigment and applied additives.

324 Taking into account the chemical structure of applied polymeric material (linear polymer
325 structure) to manufacture the studied latex balloons and combine this information with the
326 FT-IR analysis (Figure 1 and Table 2) and Table 3 it might be observed that the significant
327 impact on the values of TVOC parameter have the aliphatic hydrocarbons, such as undecane,

328 dodecane and tridecane. It is mainly associated with the chemical structure of synthetic
329 materials and their emission might be caused by the thermal degradation of the structure of
330 polymeric material applied in studied balloon samples. For this reason, the emission of
331 monoaromatic hydrocarbons from the surface of studied latex balloons samples might be
332 considered as a residual. Especially, it might be observed at the conditioning temperature
333 equal to 30°C, in which the emission of ethylbenzene was below LOD and the emission of
334 other monoaromatic hydrocarbons was at the very low level. From all of the determined
335 monoaromatic hydrocarbons, in both temperature ranges, toluene and p,m-xylene were
336 characterised by the highest emission rate. It might be caused by the fact that toluene and in
337 some cases p,m-xylene might be used as the general solvents in the manufacturing process of
338 latex balloons, as well as during the pigment and other additives application process. As a
339 consequence, the impurities that might occur in mentioned solvents (even up to 1%) such as
340 benzene or styrene might be introduced to the final synthetic product and be emitted into the
341 gaseous phase during its regular use.

342 However, most of potential impurities and contaminants that are volatile and might be
343 introduced during the latex balloons manufacturing process might be removed from them
344 during their washing (with a cleaning agent) and drying stage. Despite the fact that the main
345 synthetic material is the same, it might be observed a clear dissimilarities between studied
346 samples (both at 30°C and 60°C). It is mainly associated with the different pigment
347 application, the additive that gives the final material a specific gloss as well as the additional
348 imprint application. Following the literature data, the emission fluctuations (defined by the
349 type and the amount of the emitted chemical compounds) under real conditions (in indoor
350 environment) might also be caused by the presence of atmospheric oxygen, moisture, light
351 irradiation especially for the most reactive compounds such as styrene and hexanal. This issue
352 is also associated with the emission investigations which are accelerated by raising the
353 temperature (Kagi et al., 2009; Nohr et al., 2015). However, the use of described μ -CTE™
354 250 system was supplied by dry nitrogen with no light irradiation, not affecting the overall
355 emission results.

356

357 **3.3 Chemometric analysis and toxicity mixture assessment**

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

9

369 The probable source of emission of remaining three compounds is their sorption during
370 balloons storage and their release from the surface of material during thermal desorption.
371 The second type of information can be obtained from PCA factor scores interpretation.
372 Firstly, objects located in lower left corner of the plane are characterized by low emission of
373 both groups of compounds. These objects are balloons treated with thermal desorption at
374 30°C. For objects 9, 10, 11, 12 and 13 the change of desorption temperature from 30 to 60°C
375 results in much higher emission of compounds mainly from the first group - meta xylenes,
376 styrene, tridecane, ethylbenzene, dodecane, undecane. These objects are balloons with
377 imprints, that is potential cause of high emissions of these hydrocarbons. For the remaining
378 objects there is an increase in emission of compounds from both groups (shift upwards and to
379 the right).

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

393 For estimation of the toxicity of balloons' emissions toxic units model is implemented. The
394 concentrations of emitted compounds are weighted by LC50 inhalation toxicity towards
395 rodents. The calculated TUs of balloons' emissions with contributions of both MCR
396 components (TU1 and TU2) are presented in Figure 4. The emissions from balloons 1-8 at
397 30°C are characterized by rather lower TUs, compared to other emissions. The emission
398 toxicity of this group of balloons is based on compounds related to the second MCR
399 component like benzene, toluene and hexanal. The emissions of imprinted balloons at 30°C
400 (balloons 9-13) and non-printed ones at 60°C (balloons 1-8) cause much higher TUs than
401 emissions from balloons from the first group. The toxicity emission pattern of the second
402 group is dominated (from 80 to 90%) by the compounds related to the first MCR component
403 like para and meta xylenes, styrene, tridecane, ethylbenzene, dodecane and undecane. The
404 emission expressed in TUs from 9-13 balloons at 60°C is 3 to 8 times higher in comparison to
405 other balloons emissions. Similarly to the previous group the main contribution to the
406 emission toxicity is based again on the compounds related to the first MCR component.

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

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

415

416 **4. Conclusions**

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

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

431

432 **5. Conflict of interest**

433

434 The authors declare that they have no conflict of interest.

435

436 **6. References**

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540

541 **7. Figure and Table captions**

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

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

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

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

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

555 **Table 2.** Assignments of various IR bands for representatives of studied samples of latex
556 balloons (frequencies are recorded with an accuracy of $\pm 1 \text{ cm}^{-1}$).

557 **Table 3.** The selected aliphatic and monoaromatic hydrocarbons emitted from the
558 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 \pm SD [g] (n = 4)	Brief description
Balloon Series 1	ORANGE_G_1	3.618 \pm 0.030	Regular latex balloons, glossy orange
Balloon Series 2	ORANGE_WG_2	3.702 \pm 0.087	Regular latex balloons, orange without gloss
Balloon Series 3	SMALL_ORANGE_WG_3	1.959 \pm 0.014	Small latex balloons, orange without gloss
Balloon Series 4	SMALL_GREEN_WG_4	2.519 \pm 0.047	Small latex balloons, green without gloss, matt
Balloon Series 5	DARK_GREEN_G_5	3.593 \pm 0.036	Regular latex balloons, glossy, dark green, shaded
Balloon Series 6	BLACK_WG_6	3.681 \pm 0.061	Regular latex balloons, black, matt, without gloss
Balloon Series 7	WHITE_WG_7	2.595 \pm 0.038	Regular latex balloons, without gloss, matt, white
Balloon Series 8	COLORLESS_LATEX_8	3.643 \pm 0.020	Regular latex balloons, colorless, pure latex balloons
Balloon Series 9	ORANGE_WHITE_IMPRINT_9	3.657 \pm 0.083	Regular latex balloons, orange with white imprint
Balloon Series 10	ORANGE_BLACK_IMPRINT_10	3.661 \pm 0.057	Regular latex balloons, orange with black imprint 1
Balloon Series 11	ORANGE_BLACK_IMPRINT_11	3.785 \pm 0.109	Regular latex balloons, orange with black imprint 2
Balloon Series 12	BLACK_WHITE_IMPRINT_12	3.711 \pm 0.053	Regular latex balloons, black with white imprint
Balloon Series 13	BLACK_WHITE_POWDER_13	3.707 \pm 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 $\pm 1 \text{ cm}^{-1}$).

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 of plane banding vibrations in the -CH=CH-	
567 (w)	C-C skeleton vibration	
<i>s – strong; m – medium; w – weak</i>		

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

Latex balloons seasoning temperature: 30°C											
Smample 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



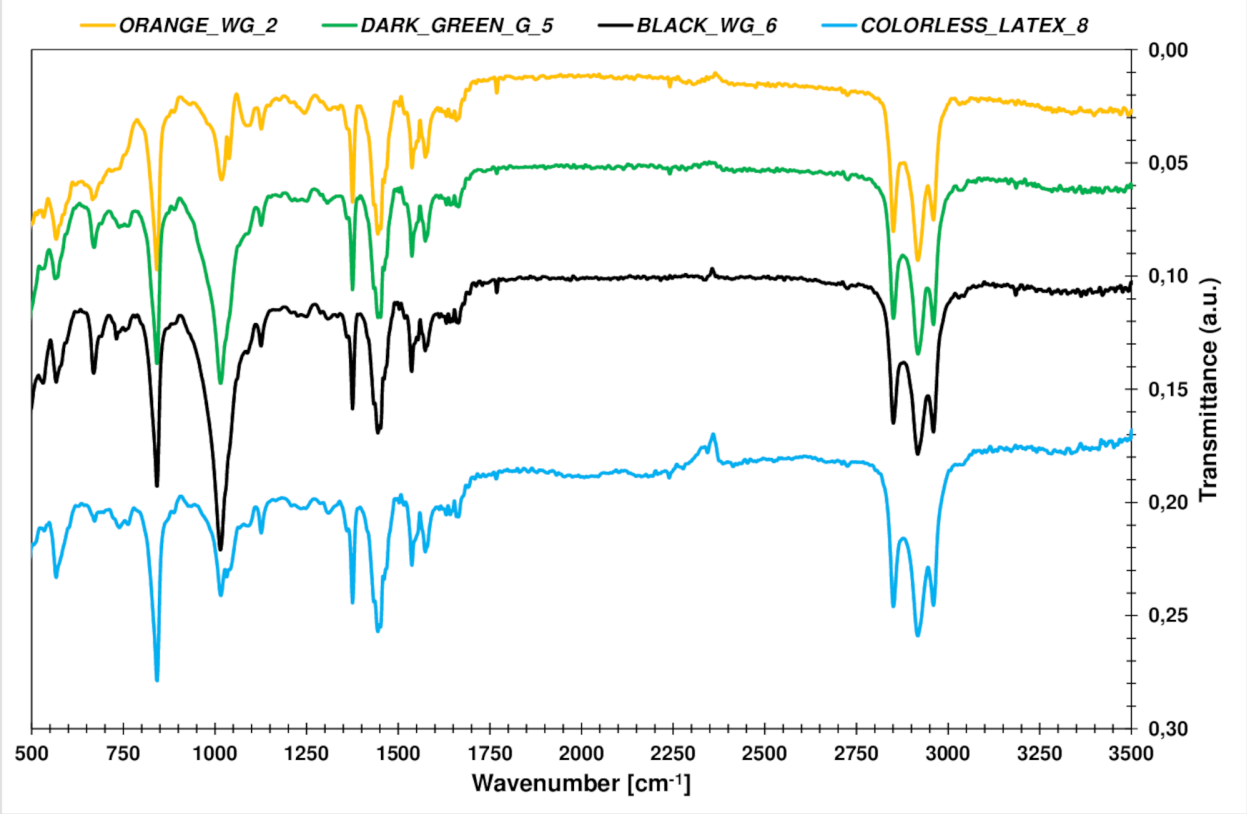


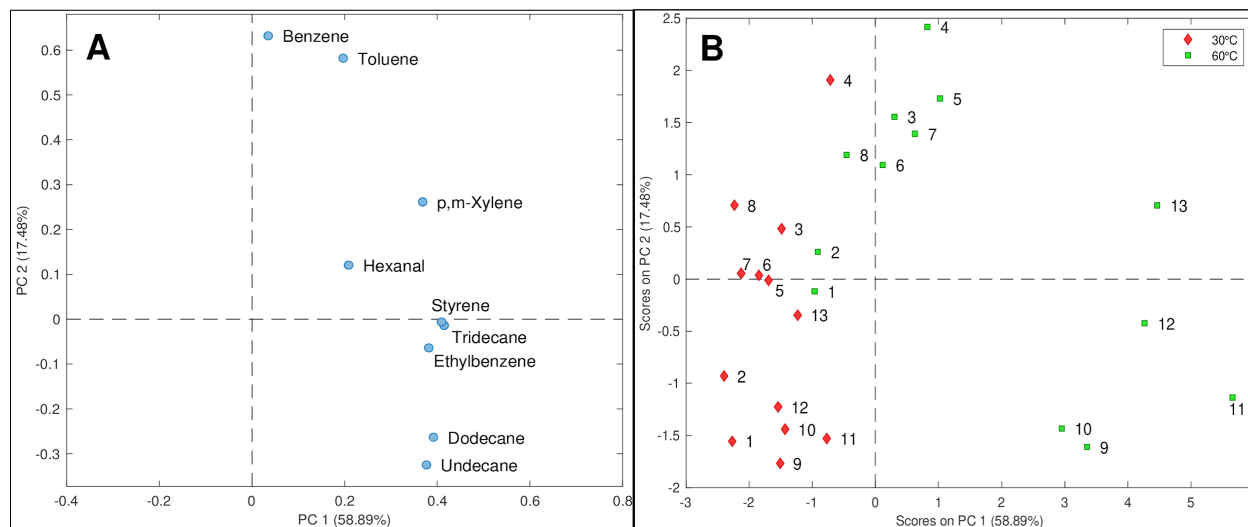
	Min	5.12	2.87	3.7	2.03	2.04	5.27	-	0.45	-	122
	Max	6.53	3.97	6.4	3.93	2.30	6.61	-	0.82	-	212
ORANGE_WHITE_IMPRINT_9	Average	6.4	70.6	50.2	8.0	0.071	3.00	0.142	1.37	1.41	59.7·10 ²
	Stand. Dev.	1.1	3.9	4.2	1.2	0.011	0.85	0.011	0.37	0.33	2.8·10 ²
	Min	4.9	65.4	45.7	7.3	0.06	2.21	0.13	1.02	1.19	56.7·10 ²
	Max	7.4	74.7	55.8	9.7	0.08	3.82	0.15	1.71	1.89	63.2·10 ²
ORANGE_BLACK_IMPRINT_10	Average	6.98	87	85	10.7	0.46	3.80	0.37	1.08	1.23	71.8·10 ²
	Stand. Dev.	0.65	16	18	2.1	0.16	0.78	-	0.17	0.67	13.0·10 ²
	Min	6.19	64	59.8	8.6	0.36	2.96	0.37	0.95	0.68	54.9·10 ²
	Max	7.63	100	101.1	13.6	0.69	4.72	0.37	1.33	2.20	86.3·10 ²
ORANGE_BLACK_IMPRINT_11	Average	9.74	92.3	110	15.0	0.381	3.72	0.26	1.07	1.34	71.7·10 ²
	Stand. Dev.	0.63	9.2	18	4.2	0.082	0.13	0.16	0.05	0.13	5.9·10 ²
	Min	9.19	80.8	94	11.5	0.28	3.54	0.11	1.04	1.24	64.7·10 ²
	Max	10.62	102.8	134	21.0	0.46	3.84	0.44	1.14	1.53	78.9·10 ²
BLACK_WHITE_IMPRINT_12	Average	5.6	57	59	8.1	0.40	5.3	0.21	2.19	1.01	44.7·10 ²
	Stand. Dev.	1.4	27	26	2.4	0.22	1.6	-	0.64	0.15	22.1·10 ²
	Min	4.1	23	22	4.6	0.17	3.72	0.21	1.58	0.87	17.8·10 ²
	Max	6.8	81	83	10.2	0.68	6.91	0.21	2.74	1.21	64.4·10 ²
BLACK_WHITE_POWDER_13	Average	7.48	54.5	63.3	8.73	0.982	8.18	0.083	2.24	0.98	43.2·10 ²
	Stand. Dev.	0.47	2.6	4.3	0.32	0.031	0.47	0.051	0.28	0.11	1.4·10 ²
	Min	6.89	51.6	57.9	8.36	0.94	7.79	0.04	1.96	0.85	41.7·10 ²
	Max	7.98	57.9	68.4	9.05	1.01	8.79	0.12	2.57	1.10	44.7·10 ²
Latex balloons seasoning temperature: 60°C											
Smample 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

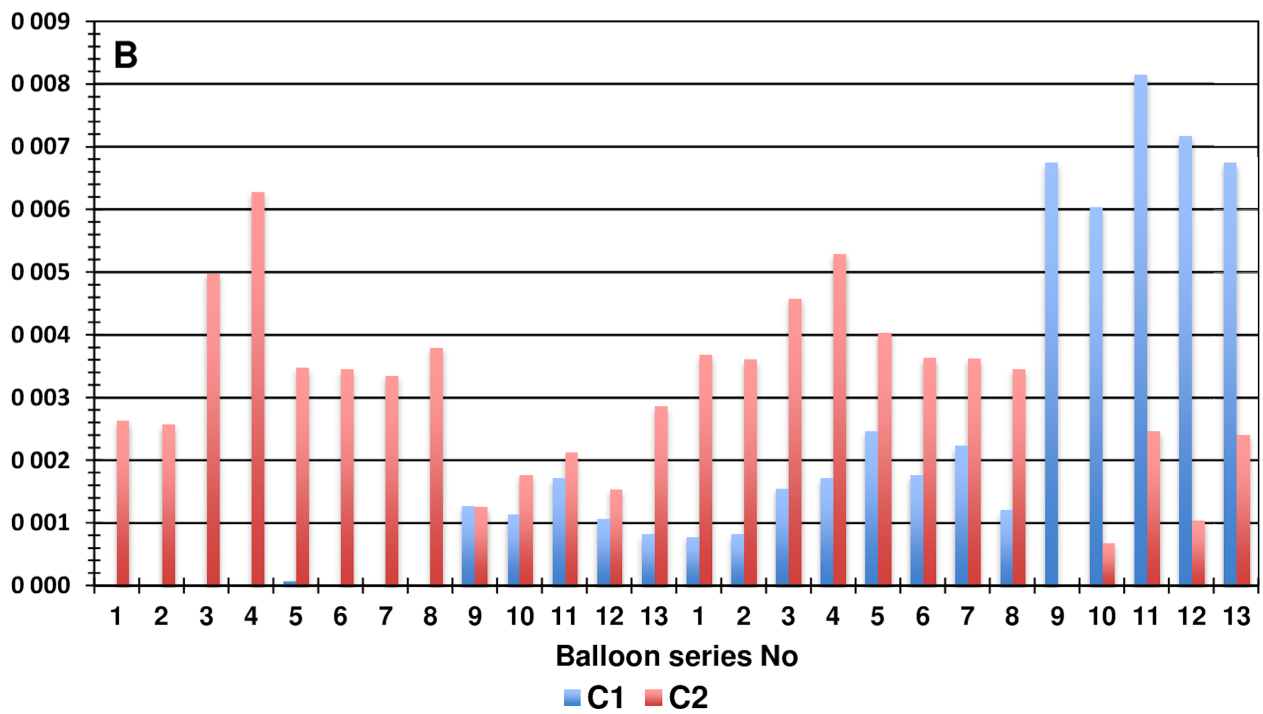
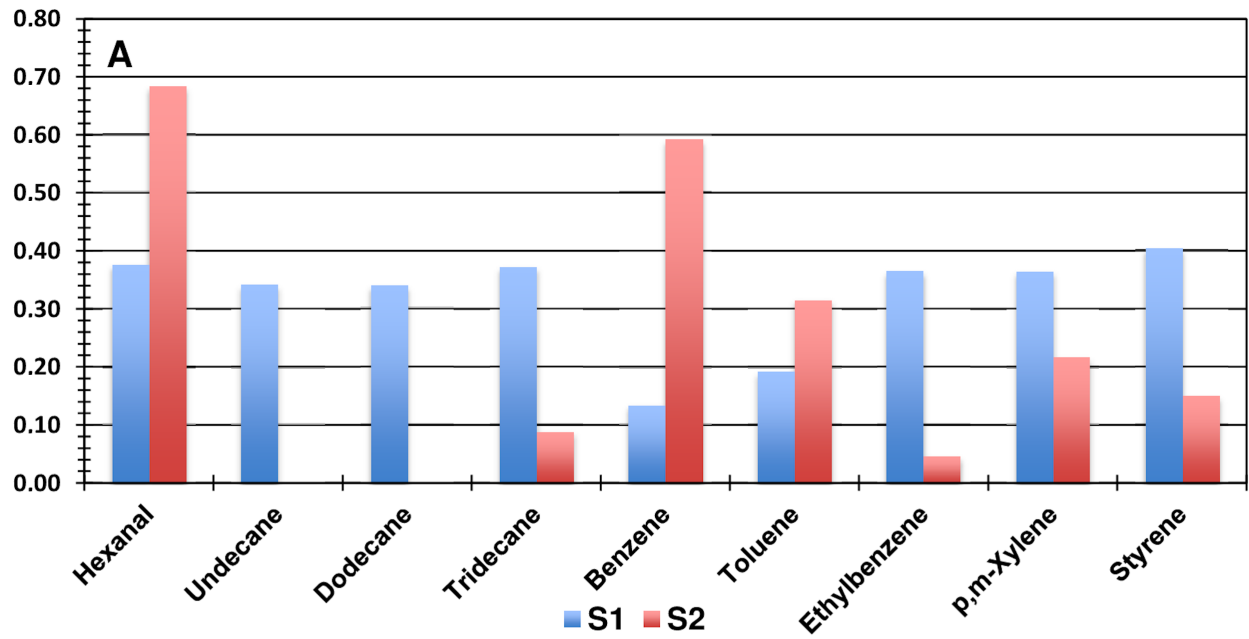
	Stand. Dev.	1.1	1.4	3.0	4.0	0.37	1.5	-	0.13	0.36	21
	Min	7.3	27.6	43.8	22.2	1.97	7.56	-	4.83	2.59	467
	Max	9.8	30.8	51.0	31.5	2.85	11.00	-	5.13	3.38	514
SMALL_GREEN_WG_4	Average	10.67	24.3	42.1	25.1	1.471	31.3	<LOD	4.94	2.26	472
	Stand. Dev.	0.92	2.7	4.2	3.4	0.074	3.3	-	0.62	0.53	56
	Min	9.35	22.5	38.9	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	30.5·10 ³
	Stand. Dev.	0.90	45	47	1.6	0.23	2.3	0.37	1.4	0.66	3.0·10 ³
	Min	6.37	346	279	40.4	0.38	5.75	0.63	3.73	3.76	28.1·10 ³
	Max	8.30	441	379	43.9	0.92	10.41	1.35	6.55	5.38	34.6·10 ³
ORANGE_BLACK_IMPRINT_10	Average	7.67	483	459	52.1	1.24	8.9	0.513	4.06	2.69	34.5·10 ³
	Stand. Dev.	0.78	45	93	9.5	0.49	1.5	0.091	0.35	0.37	6.3·10 ³
	Min	6.97	459	325	41.0	0.70	7.47	0.44	3.68	2.28	26.1·10 ³
	Max	8.70	551	527	63.9	1.80	10.38	0.64	4.38	3.16	41.4·10 ³
ORANGE_BLACK_IMPRINT_11	Average	17.9	416	667	93	1.16	10.06	0.712	4.76	4.15	36.1·10 ³
	Stand. Dev.	1.2	35	76	11	0.10	0.82	0.081	0.38	0.68	3.3·10 ³
	Min	16.8	394	592	82.4	1.02	9.34	0.61	4.33	3.34	33.0·10 ³

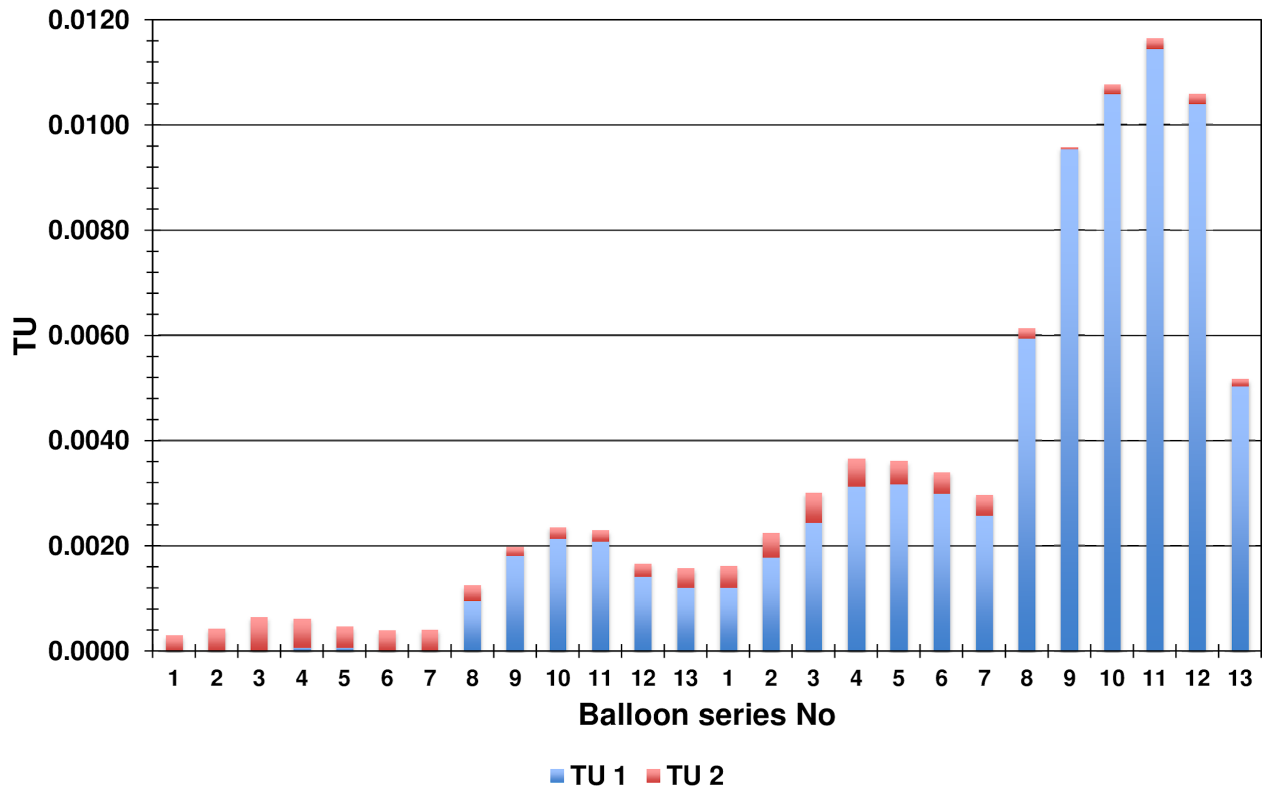


	Max	19.3	468	773	107.6	1.27	10.80	0.80	5.24	4.96	$40.4 \cdot 10^3$
BLACK_WHITE_IMPRINT_12	Average	9.3	319	343	52	0.96	15.0	1.22	7.4	3.87	$23.6 \cdot 10^3$
	Stand. Dev.	1.8	161	127	17	0.18	4.3	0.40	1.4	0.21	$10.1 \cdot 10^3$
	Min	7.5	148	188	31.9	0.76	11.05	0.85	6.10	3.68	$12.4 \cdot 10^3$
	Max	11.2	488	482	71.0	1.13	19.43	1.67	9.03	4.16	$34.6 \cdot 10^3$
BLACK_WHITE_POWDER_13	Average	10.10	348	372	52.5	1.67	20.82	0.96	7.2	4.24	$23.5 \cdot 10^3$
	Stand. Dev.	0.91	86	41	6.5	0.17	0.83	0.22	1.4	0.25	$1.9 \cdot 10^3$
	Min	9.05	290	319	44.5	1.49	19.95	0.75	6.03	4.08	$21.6 \cdot 10^3$
	Max	11.05	475	418	60.5	1.87	21.85	1.16	8.43	4.60	$25.6 \cdot 10^3$









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