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Assessment of ecotoxicity and total volatile organic compound (TVOC) emissions from food and children's toy products

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ABSTRACT

The development of new methods for identifying a broad spectrum of analytes, as well as highly selective tools to provide the most accurate information regarding the processes and relationships in the world, has been an area of interest for researchers for many years. The information obtained with these tools provides valuable data to complement existing knowledge but, above all, to identify and determine previously unknown hazards. Recently, attention has been paid to the migration of xenobiotics from the surfaces of various everyday objects and the resulting impacts on human health. Since children are among those most vulnerable to health consequences, one of the main subjects of interest is the migration of low-molecular-weight compounds from toys and products intended for children. This migration has become a stimulus for research aimed at determining the degree of release of compounds from popular commercially available chocolate/toy sets. One of main objectives of this research was to determine the impact of time on the ecotoxicity (with *Vibrio fischeri* bioluminescent bacteria) of extracts of products intended for children and to assess the correlation with total volatile organic compound emissions using basic chemometric methods. The studies on endocrine potential (with XenoScreen YES/YAS) of the extracts and showed that compounds released from the studied objects (including packaging foils, plastic capsules storing toys, most of toys studied and all chocolate samples) exhibit mostly androgenic antagonistic behavior while using artificial saliva as extraction medium increased the impact observed. The impact of time in most cases was positive one and increased with prolonging extraction time.

The small-scale stationary environmental test chambers – μ-CTE™ 250 system was employed to perform the studies aimed at determining the profile of total volatile organic compounds (TVOCs) emissions. Due to this it was possible to state that objects from which the greatest amounts of contaminants are released are plastic containers (with emission rate falling down from 3273 to 2280 ng/g of material at 6 h of conditioning in elevated temperature).

1. Introduction

For parents around the world, the health and wellbeing of their children is an issue of paramount importance. Still, despite numerous legislative and procedural difficulties for producers of substandard toy and food producers, several accidents occurred that forced the scientific community to search for new ways to respond to this threat. Promisingly, research is being conducted to combine biological, instrumental and chemometric studies to assure holistic assessment of the quality of products intended for children and determine the impact on human well-being.

To rapidly obtain screening data about the estimated amount of volatile organic compounds (VOCs) released from the surfaces of various types of products into indoor air, research is carried out to assess the values of total volatile organic compounds (TVOCs) in a defined medium. According to published information, TVOC parameter is determine as the sum (total amount) of wide spectrum of organic compounds eluting between the defined analytical window – retention times from n-hexane to n-hexadecane on an appropriate gas chromatography capillary column (non-polar or slightly polar stationary phases) employing flame ionization detection (GC-FID) and quantified as toluene equivalents (ECA, 1997; Formela et al., 2017, 2016; Ghaffar et al., 2014; Hakkarainen, 2010; Kaykhaii and Linford, 2017; Liu et al., 2012; Massold et al., 2005). Chemical compounds such as aromatic

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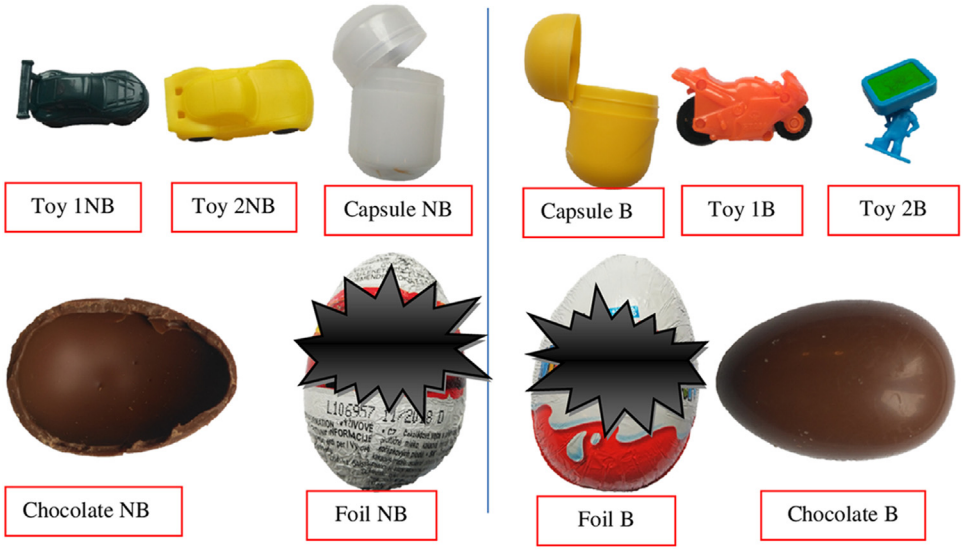

Fig. 1. Schematic representation of samples studied (legend for results description: foil B, foil NB – aluminum foil package for brand and non-brand product, respectively; capsule B, capsule NB – plastic capsule/package inside chocolate to cover toy, for brand and non-brand product, respectively; toy 1B, toy 2B – toys inside plastic package of brand original product; toy 1NB, toy 2NB – toys inside plastic package of non-brand (fake) product; chocolate B, chocolate NB – brand (original) and non-brand (fake), respectively, chocolate sample being in contact with aluminum foil).

hydrocarbons, aliphatic hydrocarbons, monoterpenes, alcohols, aldehydes and ketones (excluding formaldehyde) have a significant impact on the final value of the TVOC parameter. Depending on the object investigated, the intensity of the impact of a selected group of organic compounds on the final TVOC value varies. Preliminary determination of TVOC values allows researchers to obtain screening information on the quality of studied materials and make preliminary comparisons. In addition, the TVOC parameter consists of chemical compounds defined by the International Agency for Research on Cancer (IARC) as carcinogenic such as benzene (Group 1A), probably carcinogenic (Group 2A), or possibly carcinogenic like styrene or ethylbenzene (Group 2B) (IARC, 2016). Therefore, assessing TVOC values enables researchers to perform preliminary evaluations of the impact of studied objects on human health or the environment.

Without doubt, biological tests are becoming increasingly important in analytical practice. The main advantage of diagnostic tools is their capacity to specify the actual influence of compounds in tested samples on living organisms, taking into account all interactions between them (Wieczerzak et al., 2016). In the literature, there are many examples of studies showing that the coexistence of several pollutants leads to more severe adverse effects than predicted based on the toxicity of individual components (Backhaus and Faust, 2012; Pose-Juan et al., 2016; Sexton and Hattis, 2007; Silva et al., 2002). In most cases, such interactions were found in compounds such as bisphenol A and related compounds, phthalates, primary aromatic amines, and heavy metals (Abdul-Ghani et al., 2012; Fic et al., 2014; Michałowicz, 2014; Ramirez et al., 2014; Xu et al., 2014). In a study on the individual and combined effects of bisphenol A, dibutyl phthalate, and cadmium on oxidative stress and genotoxicity in HepG 2 cells, synergistic interactions were noted (Li et al., 2017). In another study, a similar harmful effect was observed between nonylphenol and di-n-butyl phthalate (Hu et al., 2014). These compounds are plasticizers, additives and printing inks also commonly used in the production of toys and other products intended for children (Lv et al., 2015; Szczepańska et al., 2016). Considering these findings, it seems necessary to intensify efforts to accurately estimate the degree of compound mobility and the effects of compound interactions on living organisms, particularly for children who are most vulnerable to the threat. Their tendency to get to know the world with their mouths in the early stages of life combined with weaker detoxicating abilities makes contact with xenobiotics a potential contributing factor to serious health consequences (Damstra, 2002; Mercan et al., 2015).

Therefore, the use of bioanalytical methods has become particularly important in research aimed to estimate the degree of xenobiotic migration from object surfaces. It might be observed that there is no information in the literature on the use of such a joint approach in research aimed at estimating the degree of xenobiotic migration from the surface of toys to liquid and gaseous phase. Therefore, the current research will make a significant contribution to knowledge about the degree of compound mobility and the resulting impacts on healthy children.

The main aim of the present study was to determine the impact of time on the ecotoxicity of samples extracted from products intended for children and to evaluate the correlation with TVOC emissions using basic mathematical methods performed on appropriate statistical software. The ecotoxicological tests used were Microtox® and XenoScreen YES/YAS, while TVOC emission rates were evaluated using a small-scale stationary emission chamber system at the samples seasoning stage. The thermal desorption technique (TD) combined with gas chromatography technique (GC) equipped with flame ionization detection (FID) was employed at the stage of liberation and final determination of VOCs. This mathematical approach is based on best-fit function modeling, with ecotoxicity or TVOC concentration as dependent variable Y and time as independent variable X. As in previous studies on ecotoxicity modeling, the most appropriate model seems to be the polynomial fit of the '$Y = a_1X^2 + a_2X + b$' type, which accurately describes the experimental data. The weight coefficient $\boldsymbol{a_1}$ (by value and by sign) can be used to interpret the impact of time. Model validation was performed using R^2 values (multiple correlation coefficients). The research protocol presented in the following paper is an important example of interdisciplinary studies, combining aspects of analytical chemistry, environmental chemistry, ecotoxicology and mathematical/chemometric methods. All of these elements should be considered in seeking novel approaches to evaluating the quality of polymer children's toys and assessing the potential impacts on human health.

2. Materials and methods

2.1. Objects studied

The objects studied were all elements of popular commercially available chocolate/toy sets, presented in Fig. 1 for easier visualization. All elements (sealing aluminum foil package, chocolate, plastic package for toy, toy itself) of both the original product and its cheaper equivalent were subjected to both toxicological and TVOC studies in duplicate.