ANALYSIS OF HARMFUL COMPONENTS IN TOYS BY MODERN METHOD: REVIEW

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Abstract: At present, the demand for toy products is growing every day. Including a high level of consumption of plastic toys because of its strength, saturated colors, flexibility, etc. To improve these properties, various organic compounds such as phthalates, bromo-antipyrines, bisphenol A, phenol are added to the plastic, and heavy metals to create bright colors. This article was reviewed over the past 20 years of research, which are methods for identifying organic compounds in toys. These are gas chromatography-mass spectrometry, liquid chromatography-mass spectrometry, high-performance liquid chromatography, etc. At the same time, in determining heavy metals in a toy, such methods were considered: atomic absorption spectrometry, mass spectrometry-inductively coupled plasma, X-ray fluorescence methods.

Keywords: toys, high performance liquid chromatography, harmful substances, methods of analysis, sample preparation, safety, gas chromatography-mass spectrometry, atomic absorption spectrometry, extraction.
Introduction

Nowadays doing research on composition of toys is one of the actual topics. Children spend a lot of time playing toys, putting them in their mouths and even swallowing them. Small children may be exposed to environmental chemicals that are released from toys and baby products. The topic of low-quality and toxic toys containing toxic substances is of great concern to the public. Inspections in different countries have revealed that such toys contain lead, mercury, cadmium, phenols, brominated flame retardants, PVC, formaldehydes, phthalates and other toxic chemicals. With constant contact with such toys, children can develop skin-allergic reactions, headaches, cough, and reduced immunity. In the market of children’s goods are represented, first of all, goods of Chinese production. Imported children’s goods also come from Turkey, Korea, Ukraine, Germany, the USA and other countries. In Kazakhstan, the Children of the Rainbow Foundation produces three table games: «Golden Yurt», «Batyr» and «Cockpar». There are several other companies that produce games with a national flavor. However, all these products can be attributed to souvenir rather than goods for children. Since 2011, buyers can buy Kazakh-speaking and dancing toys, which are produced by the company “Bal Bala”. Toys are made in the Chinese cities of Hong Kong and Guangzhou. In Kazakhstan, unfortunately, factories do not produce toys. “Bal Bala” has opened in the country only a factory for assembling parts of toys. The quality of domestic and imported toys in the country is regulated by the EN-71-3 standard approved by the European Union and technical regulation TR TR 008/2011 “Toy Safety” approved by Custom Union. In 2008, Congress enacted the Consumer Product Safety Improvement Act to strengthen the authority of Commission for Safety of Consumer Goods (CPSC) to eliminate health hazards associated with lead and phthalates. The European Commission prohibits the placement of toys and childcare products on the market that contain bis(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP) or benzylbutyl phthalate (BBP) at concentrations greater than 0.1% by weight of the material. There is an equivalent level for diisonyl phthalate (DINP), diisodecyl phthalate (DIDP) or di-n-octyl phthalate (DNOP) in products that can be taken in the mouth by children [1, 2]. According to the statistics of recent years, in 2014 more than two hundred and fifty thousand cases related to toy were registered [3]. Unfortunately, this indicates that many toys do not comply with the standard. In order to save health of children and environment and define poisonous substance in compound of toys it is important to apply methods such as gas chromatography-mass spectrometry, liquid chromatography-mass spectrometry, high-performance liquid chromatography, atomic absorption spectrometry, X-ray fluorescence analysis.

Ultra high performance liquid chromatography

Among modern methods also – ultra-high performance liquid chromatography- tandem mass spectrometry method is applied. Ultra high performance liquid chromatography is an important stage in the development of liquid chromatography [4]. This method is very sensitive to detect phthalate from UHPL-MS - PVC toys. The advantage of the method can be that the concentration of the substance in question is minimal in ng /l [5]. That is, it is possible to detect almost all the phthalate in the toy. According to the study, the separation and analysis of the bisphenol A (BFA) from toys was determined by the UHPLC. Two different extraction methods were used to detect the (30 g samples were obtained for each extraction) [6].
Atomic absorption spectrometry

A number of qualitative methods can be used to determine the toxic elements in the polymer material. These include: atomic absorption spectroscopy [7-13], fluorescence [13-16], inductively coupled plasma-optical emission analyzer, neutron activation analysis [17], mass spectrometry-inductively coupled plasma. With the help of AAS, the discovery of cadmium and lead in toy materials was considered. Samples were separated at 450 °C in a muffle furnace. The powder was dissolved in 1N hydrochloric acid and 0.2% nitric acid. Heavy metals were determined using a Perkin-Elmer atomic absorption spectrometer equipped with electrodeless discharge lamps at 228.8 nm for Cd and 283.3 nm for Pb. Ammonium dihydrogen phosphate and magnesium nitrate were used as a template modifier for Pb and Cd. The method was tested on analytical parameters. The average yield of lead and cadmium was 82.05% and 98.4%. Their analytical limit values were 0.001 and 0.0001 µg/g [18].

Laser-induced breakdown spectrometry (LIBS)

Laser-induced breakdown spectrometry (LIBS) is considered a very useful analytical tool for chemical analysis and industrial process. LIBS is a method based on the emission of excited atoms, ions and molecules in which a focusing lens and a pulsed laser are used to generate a microplasma that evaporates a small amount of a sample [19]. The advantages indicated for laser breakdown spectroscopy are minimal or do not require preparation of samples and reduction of preparation procedures, universal sampling for all media, both conducting and non-conductive materials, that are difficult to get into the solution [20]. The Nd: YAG laser was used at a wavelength of 1064 nm in studies of the metals Ba, Ca, Al, Cu, Na, Co, Cd, Cr, Hg, Zn, Ti and Pb in the methods discussed above [21, 22]. To study samples made of polyethylene, polyvinyl chloride, polyethylene terephthalate and polypropylene, the visible area and ultraviolet spectrum were chosen. Depending on the type of polymer, the accuracy showed an interval of 90% to 100%. However, there are some drawbacks to the original method: they cause pollution in the transport system, plasma torch, at a very high concentration [23].

High performance liquid chromatography

Methods for phthalic acids (PAE) determination at very low concentrations in various matrices are found in the literature. This methods was used for determine phthalates from water [24-27], food [28-30], toys [31, 32], etc. Various sample treatments, extraction and preconcentration steps such as liquid – liquid extraction (LLE), solid phase extraction (SPE) [33], solid phase micro extraction (SPME), stir bar sorptive extraction and thermal desorption have been used before the instrumental analysis to determine these compounds in these types of samples. In recent years, several authors have also focused their research to study the migration of phthalates from various matrices to body fluids. K. Bouma and D. J. Schakel applied a modern method to definition migration of bis (2-ethylhexyl) phthalate into saliva using high performance liquid chromatography (HPLC) [34]. A. O. Earls researched two methods for the definition of the migration of phthalates into saliva [35]. In their early research, the migration of some phthalates from toys to artificial saliva was determined by gas chromatography – mass spectrometry (GC/MS) after activated carbon enrichment [36]. Due to the solubility and hydrophobic properties of the phthalic acid ester, activated carbon is an effective adsorbent for separation from the liquid phase. Activated carbon was mainly used to enrich elements in different matrices after the addition of a complex constructor [37].

Liquid chromatography - ultra spectrometry and tandem mass spectrometry

Liquid chromatography - ultrasonic spectrometry and tandem mass spectrometry - is a complex analytical method based on the determination of sixteen carcinogenic and allergenic dyes from a toy. Various types of toys: plastic, textiles, wood, paper, hard toy material, clay mud, ball, etc. Toys were extracted with ethanol
in an ultrasonic bath. Quantitative analysis was carried out after chromatographic separation. Compatibility of dyes LC/Tandem was supplemented with mass spectrometry. This method is effectively used in the study of various components of the toy [38].

**Gas chromatography – mass spectrometry**

According to the EU Directive 2009/48 on the safety of toys, toys are forbidden to have aromatic allergens [39]. The aim of this study is to investigate allergens having 13 restricted aromatic allergens and 11 limiting states exceeding 1 g / 100 g [40-42]. Ethyl acetate and toluene were used as an extractant for extraction of solid liquids before quantitative analysis of toys for scattering. In addition, an easier method for detecting aromatic allergens was developed at temperatures of 23°, 40°. With it, you can learn about the dangers of aromatic allergens emanating from a child while playing a toy. For this purpose, samples obtained from solid-phase microextraction were analyzed in gas chromatography-mass spectrometry (GC/MS). Solid-state microextraction (SPME) is one of the most advanced pre-treatment methods for analyzing volatile and semi-volatile matter. SPME does not require the use of reagents and combines the extraction and purification steps. As a result, the running time is reduced. The main thing is that when working with the SPME method, you should be able to choose the right adsorbent, analyze the appropriate solvent for cleaning and elution. Flavored allergens were extracted from the gas phase on a polycrystalline fiber of 85 microns in a sealed container of 23° and 40°. The quantitative analysis of the compounds was made after calibrating. Aromatized allergens in the toy are dangerous to the health of the child, they can swallow or put them in your mouth [43]. Scientific articles are given in Table 1 in the definition of compounds in children’s toys.

<table>
<thead>
<tr>
<th>№</th>
<th>Analyte</th>
<th>Sample preparation</th>
<th>Method</th>
<th>Link</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzyl butyl phthalate, Di-n-butyl phthalate, Bis (2-ethyl hexyl) phthalate, Di-isononyl phthalate</td>
<td>Samples were extracted with 100 ml of methane chloride and they were mixed for 24 hours in a sealed conical flask. 1 ml of solution was filtered using a PTFE filter (0.45 mm)</td>
<td>LC/MS</td>
<td>[44]</td>
</tr>
<tr>
<td>2</td>
<td>Di (n-octyl) phthalate DNOP</td>
<td>The extract were filtered, the filters were dried in 70°C for 15 min. The filters were sonicated with chloroform using an ultrasonic bath for 15 min, 20.0 ml of benzoic acid-benzyl ester</td>
<td>GC/MS</td>
<td>[45]</td>
</tr>
<tr>
<td>3</td>
<td>Di(2-ethylhexyl phthalate) Di-n-butyl phthalate Butyl benzyl phthalate Di-isononyl phthalate</td>
<td>1 g sample was sonicated for 15 min in methylene chloride (10 ml) at 40°C in a sealed vial. 1 ml extract was filtered through a 0.45 mm glass fiber filter</td>
<td>GC/MS</td>
<td>[46]</td>
</tr>
<tr>
<td>4</td>
<td>As, Pb, Cd</td>
<td>Samples were digested with concentrated HNO₃. Extract was filtered with Whatman 43</td>
<td>Atomic absorption Varian AA240FS flame atomic absorption spectrometer</td>
<td>[47]</td>
</tr>
<tr>
<td>5</td>
<td>6 toxic metals (As, Cd, Cr, Ni, Pb and Sb)</td>
<td>0.5 g of simple was added into 50 ml 0.07 M HCl, shaken 37°C for 1 h, then sit for 1 h</td>
<td>MS/ISP Nex ION – 300</td>
<td>[48]</td>
</tr>
<tr>
<td>6</td>
<td>Cd, Cr, Ni, Cu and Pb</td>
<td>1 g Sample was digested in 20 ml HNO₃, H₂SO₄, HClO₄, than was filtered with 0.45 mm filter</td>
<td>Atomic absorption spectrometry Perkin Elmer AA analytics 400</td>
<td>[49]</td>
</tr>
<tr>
<td>7</td>
<td>Brominated flame retardants (BFR) Decabromodiphenyl ethane (DBDPE)</td>
<td>Samples were cleaned with distilled water.1 g sample was extracted in Soxhlet with a mixture of acetone and hexane (1:1 v/v) for 24 h</td>
<td>GC/MS</td>
<td>[50]</td>
</tr>
</tbody>
</table>
**Discussion**

Most information in this article has reviewed «Science Direct» website on scientific publications. This article provides an overview of research over the past 20 years, where about 70 scientific studies were examined. The GC/MS method was used more often in research work than other methods for determining organic components, such as: phthalate, brominated ethane, aromatic allergens, phosphine, three phenyl phosphate and azo dyes in toys. According to the data, most of the samples were dissolved in methyl chloride.

<table>
<thead>
<tr>
<th>Step</th>
<th>Compound/Method</th>
<th>Description</th>
<th>Equipment/Conditions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Bisphenol A</td>
<td>1) 1000 ml HCl at 0.07 M at 37°C for 2 hours, 2) Leave on 40°C in 24 hours for 1000 ml of distilled water and then filtered</td>
<td>LC fluorescence Nd : YAG</td>
<td>[51]</td>
</tr>
<tr>
<td>9</td>
<td>Di-n-butyl phthalate, Di-isononyl phthalate, Dibutyl phthalate, Benzyl butyl phthalate</td>
<td>1 g pieces were Soxlet extracted in 120 ml of dichloromethane 6 h at 60-80°C</td>
<td>GC/MS DB-5 ms Ultra Inert column (30m × 0.25 mm, 0.25 mm)</td>
<td>[52]</td>
</tr>
<tr>
<td>10</td>
<td>2-ethylhexyl phthalate</td>
<td>The samples were extracted through 15 minutes of sonication in 10 ml of methylene chloride, in a sealed vial</td>
<td>GC/MS Elite – 5 ms DB-5 column (15 m × 0.25 mm, 0.10μm)</td>
<td>[53]</td>
</tr>
<tr>
<td>11</td>
<td>Triphenyl phosphate, di-octyl phthalate, (2,4,6-trimethoxyphenyl)phosphine</td>
<td>The sample was mixed, ultrasonication (15 min) with 4-6 ml hexane and ethanol (1:4). The extracts were divided in two and for one part a clean-up step on acid silica (44% H2SO4) was employed</td>
<td>GC/MS Agilent J &amp;W DB-5 column (15 m × 0.25 mm, 0.10μm)</td>
<td>[54]</td>
</tr>
<tr>
<td>12</td>
<td>Bisphenol A (BPA)</td>
<td>The first extraction method immersed the sample in 11 of water, at 40°C for 24. The second immersed the sample with 11 HCl (0.07 M) at 37°C for 2h</td>
<td>UHPLC C8 Brownlee column (τ = 5.43 min)</td>
<td>[55]</td>
</tr>
<tr>
<td>13</td>
<td>Carcinogenic and allergenic dyestuff</td>
<td>0.5 g of different samples were transferred into a 50 ml conical flask+15 ml of ethanol, vortex-mixed for 1 min. Then extracted in an ultrasonic bath at 42 kHz for 15 min. Then filtered through a 0.20 μm membrane filter</td>
<td>LC /MS Agilent 5 lm Zorbax Extend C 18 column (250 mm× 4.6 mm)</td>
<td>[26]</td>
</tr>
<tr>
<td>14</td>
<td>48 aromatic allergen</td>
<td>1 g sample was added into a 50 ml conical flask, dissolved with 10 ml + acetone or dichloromethane. Treated in an ultrasonic bath for 15 min+10 ml of slowly dripped methanol</td>
<td>GC/MS Agilent HP-1MS column (50μm × 0.2 mm, 0.5 mm)</td>
<td>[57]</td>
</tr>
<tr>
<td>15</td>
<td>Aromatic allergenic, PA, CAR/ PDMS</td>
<td>The samples were mixed in liquid nitrogen and extracted with toluene / ethyl acetate (1: 1) and 30 minutes</td>
<td>GC /MS DB-17 MS Column (30 m ×0.25 mm, 0.25 mm)</td>
<td>[58]</td>
</tr>
<tr>
<td>16</td>
<td>Diethyl phthalate</td>
<td>Add 1-2 ml of ethyl acetate in 10 ml of sample, then 1 minute of shaking. Centrifuged at 5000 rpm for 5 minutes. Transfer 1 ml of solution to a 2 ml bottle with an automatic sampler</td>
<td>GC /MS Agilent HP-1MS column (50μm × 0.2 mm, 0.5 mm)</td>
<td>[59]</td>
</tr>
<tr>
<td>17</td>
<td>Pb, Ni, Cr, Cu and Cd</td>
<td>1.0 g of the sample was digested with 20 ml ternary acid (HClO4, H2SO4 and HNO3 in the ratio of 2:1:1 respectively) mixture for 2 hrs, then were filtered</td>
<td>Atomic absorption spectrometry Perkin Elmer AA analytics 400 Lamp current between 5-12 mA, fuel flow between 2.0-3.0 L/ min and air flow of 10L/min</td>
<td>[60]</td>
</tr>
<tr>
<td>18</td>
<td>Bisphenol A, bisphenol F, Bisphenol C, cyclohexane</td>
<td>1.6 ml of 5 g phosphate buffer pH-11 and 4.0 ml 1.4 ml 25% sodium chloride were added. The mixture was mixed with 30 ml of carbon tetrachloride and held in a 15-minute ultrasonic bath. Centrifuged at 2000 rpm at 3000 rpm</td>
<td>GC /MS Agilent 6890/5973 HP-1 MS and HP- 5 MS (30m × 0.25 mm, 0.25 mm)</td>
<td>[61]</td>
</tr>
<tr>
<td>19</td>
<td>Bisphenol A</td>
<td>The baby bottles were boiled in a water bath at different temperatures (24°, 40°, 100°) for 1 hour. After 1 day it was transferred to solid phase extraction</td>
<td>GC/MS DB 5- MS column (30 μm × 0.2 mm, 0.25μm)</td>
<td>[62]</td>
</tr>
<tr>
<td>20</td>
<td>8 kind of phthalate</td>
<td>The samples were extracted by 5 ml of chloroform with the liquid-liquid extraction method</td>
<td>GC/MS Agilent 6890/5973 DB 5- MS column (30μm × 0.25 mm, 0.25μm)</td>
<td>[63]</td>
</tr>
</tbody>
</table>
and in various columns. And when determining the heavy metals present in the toy, methods like atomic absorption spectroscopy and laser inductively coupled plasma were widely used. In Kazakhstan, in 2007, Law № 306 III “On Toy Safety” was introduced to monitor the quality of toys from domestic and foreign countries (introduced and amended on October 29, 2015) and has been effective from 2008. The most interesting point is that according to the law, types like electronic toys and control of baby’s nipples are not considered. Although the law is adopted in the country, but it must be strengthened for the safety of our children and our society. In Kazakhstan, there is almost no own methodology or methods for analyzing the composition of toys. In the articles reviewed, China and the United States are at the forefront of toy analysis.

**Conclusion**

In the course of work, chromatographic and other methods of detecting harmful components in toys were analyzed, their advantages and disadvantages were compared. To analyze the composition of the toy, according to the table, studies were conducted in the US, China, Brazil, Germany, Belgium, Spain, Canada and Turkey. Based on the data, it has become clear that the most widely used and optimal method of analyzing the composition of toys is the GHI-MS method. In addition, the most important step in development of liquid chromatography is a highly efficient liquid chromatography method with the ability to detect very small concentrations of compounds in a toy. Thus, in order to increase toy safety in Kazakhstan, we must focus on the quality and consumption of toys. In addition, it is necessary to establish domestic production of toys, so that the toy industry should operate on their own. The materials used in this article can be used to control the quality of toys and products for childcare produced in Kazakhstan and imported from other countries, as well as to protect children’s health and environmental safety.

**REFERENCES**


