

## Identification of unknown plasticizers in polyvinyl chloride toys

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### Abstract

In our previous study, three unknown plasticizers were detected in five polyvinyl chloride (PVC) toys on the Japanese market. In this study, we isolated these three plasticizers (**1–3**), and their structures were determined using accurate mass and nuclear magnetic resonance (NMR) spectral data. One of the plasticizers was identified as bis(2-propylheptyl) phthalate (DPHP). The others were assumed to be (4-methyl-2-propylhexyl)(2-propylheptyl) phthalate and bis(4-methyl-2-propylhexyl) phthalate. This is the first study to detect these phthalic acid esters in PVC toys in Japan. Isolated DPHP was subjected to quantitative NMR (qNMR). Using the NMR solution with the absolute concentration as a calibrant, the DPHP concentration in five PVC toys was then determined by GC/MS. The amount of DPHP ranged from 14.5–21.9wt%, whereas the DPHP level in one of the PVC toys was below the quantification limit (0.05wt%).

Keywords : polyvinyl chloride (PVC), toy, plasticizer, phthalate, bis(2-propylheptyl) phthalate (DPHP)

## I Introduction

Polyvinyl chlorides (PVCs) are polymeric organic compounds derived from the polymerization of vinyl chlorides, and the resulting polymers are a type of plastic. Originally forming a hard structure (rigid PVCs), the plastics become more flexible (flexible PVCs) after being mixed with plasticizers. Rigid PVCs are often used in pipe products, whereas flexible PVCs are utilized in hose products, food wrapping materials, and toys for infants.

Phthalic acid esters (PAEs) are plasticizers that were commonly used in PVC products until the 1990s. However, in the early 2000s, it was found that some PAEs exhibit endocrine-disrupting activity and reproductive toxicity<sup>1)</sup>, and the use of PAEs for PVC toys was banned worldwide, especially the use of PAEs in toys for infants. In Japan, the use of six PAEs (regulated PAEs) as plasticizers for “Designated Toys” was prohibited<sup>2)</sup>.

As the concentrations of plasticizers in PVC toys are relatively high (sometimes up to 50wt%), the type and amount of a plasticizer directly affects infants’ safety. To focus on this concern, we surveyed plasticizers in PVC toys on the Japanese

market<sup>3–5)</sup>. Our analysis revealed that (1) regulated PAEs were not used for Designated Toys; (2) regulated PAEs were used for non-Designated Toys; (3) PAEs were gradually replaced with non-PAEs, such as bis(2-ethylhexyl) terephthalate (DEHTP) and 1,2-cyclohexane dicarboxylic acid diisononyl ester (DINCH); and (4) the amount of plasticizers was less than in the past<sup>4, 5)</sup>.

However, three unknown plasticizers were recently detected in five PVC toys purchased on the Japanese market in 2019<sup>5)</sup>. These plasticizers could not be identified because the experimental GC/MS data did not match our in-house GC/MS data. In this study, therefore, we determined the structures of the three unknown plasticizers (**1–3**) and the amounts of **1–3** present in five PVC toys.

## II Materials and Methods

### 1. Toys

Five PVC toys purchased on the Japanese market in 2019<sup>5)</sup> were analyzed. The toys included two swim rings (toys 1 and 2), two soft rugby balls (toys 3 and 4), and one balloon toy for bathtub use (toy 5).