Compliance testing of phthalates in toys

Analytical chemical control of chemical substances and products

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Abstract: The content of phthalates in toys and other articles for children up to three years of age is regulated by the Statutory Order of Danish Ministry of Environment and Energy, No. 151 of 15th March 1999. In the present investigation, 15 products (toys and other articles for children up to 3 years of age) were analysed for the content of phthalates on the request of Danish Environmental Protection Agency (DEPA). The products received from DEPA were analysed for the contents of dimethyl-, diethyl-, dibutyl-, diisobutyl-, butylbenzyl-, dicyclohexyl-, diethylhexyl-, di-\textit{n}-octyl-, di-\textit{n}-nonyl-, di-\textit{iso}-nonyl- and di-\textit{iso}-decyl phthalate. The subsamples of the products were soxhlet extracted in dichloromethane, followed by analysis of the extracts by gas chromatography and mass spectrometry. The content of one or more phthalates in seven of the investigated products/part(s) of the products was found to be higher than the maximum authorised concentration, 0.05%.

Keywords: Toys, phthalates, gas chromatography, mass spectrometry, Statutory Order
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Summary

The content of phthalates in toys and other articles for children up to three years of age is regulated by the Statutory Order of Danish Ministry of Environment and Energy, No. 151 of 15th March 1999. In the present investigation, 15 products (toys and other articles for children up to three years of age) were analysed for the content of phthalates on the request of Danish Environmental Protection Agency (DEPA). The products received from DEPA were analysed for the contents of dimethyl-, diethyl-, dibutyl-, diisobutyl-, butylbenzyl-, dicyclohexyl-, diethylhexyl-, di-\(n\)-octyl-, di-\(n\)-nonyl-, di-\(iso\)-nonyl- and di-\(iso\)-decyl phthalate. The subsamples of the products were soxhlet extracted in dichloromethane, followed by analysis of the extracts by gas chromatography and mass spectrometry.

The content of one or more phthalates in seven of the investigated products/part(s) of the products was found to be higher than the maximum authorised concentration, 0.05%.

Present work has been performed as technical support to DEPA

Indholdet af en eller flere phthalater i syv af de undersøgte produkter/delprodukter var højere end 0,05%, den højest tilladte koncentration.

Arbejdet er udført som bistandsopgave for Miljøstyrelsen.
1 Introduction

The Statutory Order of Danish Ministry of Environment and Energy No. 151 of 15th March 1999 regulates the content of phthalates in toys and other children articles for the age group 0-3 years (1). The toys as well as other articles, which children may put in the mouth, should not contain > 0.05% phthalate according to the Statutory Order. In the Statutory Order, all diesters of o-phthalic acid have been considered as phthalates. This means that most of the commonly used phthalates in children’s products are covered by the Danish regulation. The European Commission (EC) has also implemented a restriction on phthalate content in toys and other articles for children in the age group 0-3 years (2). The EC regulation is, however, temporary and that concerns only six phthalates: dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), di-n-octyl phthalate (DnOP), diethylhexyl phthalate (DEHP), diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP). Furthermore, according to the EC regulation, the maximum authorised concentration of these phthalates (total phthalate content) in toys and other articles for children in the age group 0-3 years is ≤ 0.1% (w/w).

The Danish Environmental Protection Agency (DEPA) requested the National Environmental Research Institute (NERI) to determine contents of phthalates in toys and other articles for children in the age group 0-3 years, to check the compliance of these products with the Danish Statutory Order. In the present investigation, contents of some commonly used phthalates in consumer products, including those regulated by EU (in toys), have been determined in 15 products provided by DEPA.

Present work has been performed as technical support to DEPA.
2 Products

DEPA provided 15 products for the analysis of phthalate content (Table 1). The products were collected in December 2002 from Danish retail outlets. DEPA specified the part(s) of each product that should be analysed for the content of phthalates.

Table 1. Toys and other articles analysed

<table>
<thead>
<tr>
<th>NERI Reg No.</th>
<th>MST No.</th>
<th>Product identification</th>
<th>Product description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-0001</td>
<td>675</td>
<td>Building blocks</td>
<td>Soft Building blocks</td>
</tr>
<tr>
<td>3-0002</td>
<td>676</td>
<td>Santa Claus</td>
<td>Inflatable figure, to be blown up</td>
</tr>
<tr>
<td>3-0003</td>
<td>677</td>
<td>Book</td>
<td>Laminated cardboard book</td>
</tr>
<tr>
<td>3-0004</td>
<td>678</td>
<td>book</td>
<td>Laminated cardboard book</td>
</tr>
<tr>
<td>3-0005</td>
<td>679</td>
<td>Hippopotamus + 3 pups + 2 bathing rings</td>
<td>Hippopotamus shaped as a bath tub, pups and inflatable rings</td>
</tr>
<tr>
<td>3-0006</td>
<td>680</td>
<td>Tooth brush</td>
<td>Yellow shaft covered with soft blue material</td>
</tr>
<tr>
<td>3-0007</td>
<td>681</td>
<td>Tooth brush</td>
<td>Blue shaft covered with soft yellow material</td>
</tr>
<tr>
<td>3-0008</td>
<td>682</td>
<td>Book</td>
<td>Laminated cardboard book</td>
</tr>
<tr>
<td>3-0009</td>
<td>683</td>
<td>Book</td>
<td>Laminated cardboard book</td>
</tr>
<tr>
<td>3-0010</td>
<td>684</td>
<td>Book</td>
<td>Laminated cardboard book</td>
</tr>
<tr>
<td>3-0011</td>
<td>688</td>
<td>Bib</td>
<td>Cotton bib with soft plastic lining</td>
</tr>
<tr>
<td>3-0012</td>
<td>689</td>
<td>Bib</td>
<td>Cotton bib with soft plastic lining</td>
</tr>
<tr>
<td>3-0039</td>
<td>674</td>
<td>Cash register</td>
<td>A cash register with keyboard, calculator, etc.</td>
</tr>
<tr>
<td>3-0040</td>
<td>704</td>
<td>Bull</td>
<td>A solid figure made of plastic material</td>
</tr>
<tr>
<td>3-0041</td>
<td>705</td>
<td>A chicken on a boat</td>
<td>A soft chicken melted on a soft boat</td>
</tr>
</tbody>
</table>
3 Analysis

The products were analysed for the content of following phthalates: dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate, dibutyl phthalate (DBP), dicyclohexyl phthalate (DCHP), di-n-octyl phthalate (DnOP), diethylhexyl phthalate (DEHP), di-n-nononyl phthalate (DNP), diisononylphthalate (DINP), diisodecyl phthalate (DIDP) and butylbenzyl phthalate (BBP). Duplicate subsamples of each product were soxhlet extracted in dichloromethane followed by analysis using gas chromatography - mass spectrometry (GC-MS) and GC-flame ionisation detection (GC-FID), as described previously (3, 4).

3.1 Experimental

For qualitative analysis, 1 g sample was soxhlet extracted in 100 ml dichloromethane for 16 h at 66°C. 90 ml of the extract were concentrated to 10 ml using a rotary evaporator. 1µl of the concentrated as well as non-concentrated extract was analysed by GC-MS as described in 3.2.1. For quantification, fresh extracts of the samples were prepared so that concentration/dilution of the extracts was avoided, and subsequently analysed by GC-FID as described in 3.2.2. All samples were analysed in duplicate, both for qualitative and for quantitative analysis.

The recoveries of all phthalates at two concentration levels (600 mg/L and 6000 mg/L for DINP and DIDP, and 60 mg/L and 600 mg/L for all other phthalates) were determined by the extraction of known amounts of phthalates under the same conditions as the samples.

Calibration curves of all phthalates, except DINP and DIDP, were prepared by analysing solutions of respective standard chemicals at seven concentrations (40 mg/L-2000 mg/L). The DINP calibration curve was prepared by analysing 200 mg/L-10000 mg/L solutions of this chemical. DIDP was determined as DINP because some of the GC peaks of isomers of these substances overlapped. Thus, it was not necessary to prepare calibration curve of DIDP. In each GC run, 3 calibration standard solutions of the phthalates concerned were analysed after every 2-3 samples (4-6 extracts). These calibration curves were used for the quantification. Each standard solution as well as sample extract was analysed two times by GC-FID. The contents of phthalates in a sample extract was calculated using the calibration standards analysed closest (in GC-sequence) to the sample extract.

Repeatability of the determination (precision) was calculated by 10 consecutive GC analysis of phthalate standard solutions at two concentration levels: 2000 mg/L and 6000 mg/L for DINP; 4000 mg/L and 10000 mg/L for DIDP; and 200 mg/L and 1000 mg/L for all other phthalates.
The identification of phthalates was performed by comparing the GC retention times and mass spectra of the sample peaks with the retention times and mass spectra of phthalate standards. Moreover, the chromatographic pattern of isomeric DINP and DIDP was considered for the identification of these phthalates. From the results of qualitative analysis, approximate concentrations of the phthalates present in the respective samples were calculated. On the basis of these results, fresh extracts of the samples were prepared, where the amount of the sample and the volume of extraction solvent were adjusted so that no concentration/dilution of the extract was necessary for the quantification (in most cases). In every second set of soxhlet extraction (eight extractions per set), a blank was included.

3.2 Chromatographic conditions for phthalate analysis

3.2.1 GC-MS

Instrument: Perkin Elmer Turbomass mass spectrometer coupled to AutoSystem XL gas chromatograph with split/splitless injector

Transfer line: Direct to ion source, 310°C

GC column: Chrompack fused silica column CP-Sil-5CB, 50 m x 32 mm, d, 0.12 µm

Temperature program: Start temperature 150°C, 5°C to 280°C, 5 min at 280°C

Carrier gas: He, 55 ml/min, column head pressure 19.5 psi

Injector: Split, 300°C, injection volume 1 µl

Ion source: 7 eV, 175°C, +ve ion mode, scan m/z 33-300 in 1 sec

MS Library: NBS and Wiley

3.2.2 GC-FID


GC column: Chrompack fused silica column CP-Sil-5CB, 50 m x 0.32 mm, d, 0.12 µm

Temperature program: Start temperature 150°C, 5°C to 280°C, 5 min at 280°C

Carrier gas: He, 55 ml/min, column head pressure 19.5 psi

Injector: Split, 300°C, injection volume 1 µl

Detector: Flame ionisation, 300°C, make-up gas N₂, 30 ml/min
4 Results and Discussion

The analyses of phthalate contents in the products were performed in two steps. In the first step, a screening analysis for the identification of phthalates as well as an estimation of their concentration in the sample extracts was performed. This was followed by quantitative determination of the identified phthalates in fresh sample extracts, where relevant calibration standards were analysed together with the extracts. The qualitative analysis of phthalates was performed using GC-MS. GC-FID was used for the quantification of the identified phthalates. The GC-MS method used in the present investigation is an extension of the GC-FID method (3, 4), that has previously been proved to be suitable for the identification and determination of phthalates in toys. As described below, the important characteristics of the method (stability of the GC-retention time, calibration range, recovery, repeatability of determination, etc.) were checked in the present investigation, and they were found satisfactory for the analysis of phthalate content in toys.

The GC retention times ($t_R$) of the investigated phthalates were stable throughout the study, with a maximum variation <1%. The $t_R$ of standard phthalates as well as their mass spectra were used for the identification of all phthalates. Moreover, the chromatographic pattern of DINP and DIDP were considered for the presence of these substances in the sample extracts. The GC separation of the phthalates under study (as well as chromatographic pattern of DINP and DIDP) is shown in Figure 1. The detection limit considered as the concentration of a phthalate in a solution showing a visible GC-peak, without any noise at the base line, was 0,05% (w/w) for DINP and DIDP and ≤0.005% (w/w) for other phthalates. The identification was performed both by analysing the sample extracts (approximately 1 g sample/100 ml dichloromethane) extracts as well as by analysing concentrated (9:1) sample extracts, so that phthalates present in low concentration (<0.05%) could also be identified. The sample extracts containing high concentration of phthalates were reanalysed after appropriate dilution. All of the samples were analysed in duplicate. The phthalates identified in some selected samples are shown in Figures 2-5. The analysis of blank extracts by GC revealed only the signal of the extraction solvent.

The calibration curves for all of the phthalates were linear ($R^2 \geq 0.999$) in the investigated concentration range: 200-10000 mg/L for DINP and 40-2000 mg/L for all other phthalates. The recovery of all of the investigated phthalates under the experimental conditions was 93-105%. The DINP recovery was determined at concentration levels 600 mg/L and 6000 mg/L, and the recoveries of all other phthalates were determined at concentration levels 60 mg/L and 600 mg/L. The repeatability of determination was calculated by 10 consecutive GC injections of the phthalate standard solutions at two concentration levels: 2000 mg/L and 6000 mg/L for DINP, 4000 mg/L and 10000 mg/L for DIDP, and 200 mg/L and 1000 mg/L for all other
phthalates. The relative standard deviation (RSD) for the
determination of all phthalates was within 5%.

For the determination of the phthalate content in the products, fresh
sample extracts were prepared so that concentration/dilution of the
extracts before GC analyses was avoided in most cases. The
determination was performed in duplicate samples using 3-point
calibration curves prepared by the analysis of the relevant standard
solutions run in the same sequence as the samples. The GC-sequence
was designed so that appropriate standard solutions were analysed
before and after each set of 2-3 samples (in duplicate). The calibration
standards were selected to match the estimated concentrations of
phthalates in the sample extract. The regression line equation was
used for the quantification. The determination revealed that the
content of phthalates in a product was similar or very close to the
estimated concentrations derived from the screening analysis. When
a product contained DINP as well as DIDP, GC chromatograms of
which overlap partly (Figure 1), the content of both of these
phthalates in the product was determined together as DINP.

The results of the analysis of phthalate contents in the investigated
products/part(s) of the products are described in Table 2. Of the 15
products (toys and other articles for children) investigated in the
present study, one or more of the phthalates were found in 10
products. Among the investigated phthalates, BBP (<0.005-0.019%)
was present in three samples, DIBP (<0.005-0.226%) in three samples,
DBP (<0.005-0.463%) in six samples, DEHP (0.037-28.976%) in four
samples, DINP+DIDP (1.200-37.290%) was present in three samples
(of which DIDP was present in only one sample). None of the other
investigated phthalates were identified in any of the products. When
a product contains both DnOP and DINP, DnOP in such a product
could not be determined by the present method because of
interference by isomeric GC peak(s) of DINP (Figure 1).

Among the 10 samples containing phthalates, three products (3-0005,
3-0012, 3-0041) contained 16-37% phthalates (mainly
DEHP/DINP/DINP), while total phthalate contents in seven of the
products were rather low (<0.60%). Five of the products with low
phthalate contents, laminated cardboard books (DMU No. 3-0003, 3-
0004, 3-0008, 3-0009, 3-0010), contained DBP/DIBP/BBP. Considering
that the laminates were phthalate-plasticised PVC materials, a higher
phthalate content in these products should be expected. The source of
phthalates in these products may thus either be the contaminated
cardboard or the material used for gluing the lamination on the
cardboard. The other two samples with low amounts of phthalates
are plastic material on a bib (3-0011), and keys on the keyboard of a
cash register (3-0039). The low content in these products may also be
a phthalate contamination during manufacturing process or the use
of phthalate contaminated plasticiser in the manufacture of the
products.

According to Statutory Order of the Ministry of Environment, toys
and other articles for children in the age group 0-3 years should not
contain >0.05% phthalate, defined as diester of o-phthalic acid. In the
present investigation, the content of phthalates in seven of the
investigated products was higher than the maximum allowed concentration.

**Table 2: Phthalate content in the investigated toys.**

<table>
<thead>
<tr>
<th>NERI Reg. No.</th>
<th>DEPA No.</th>
<th>The part/piece of the toy analysed</th>
<th>Phthalate content (% w/w)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3-0001</td>
<td>675</td>
<td>Building blocks</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Green</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yellow</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blue</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-0002</td>
<td>676</td>
<td>Plastic material from the head</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-0003</td>
<td>677</td>
<td>Book, subsamples of page 3/4</td>
<td>DBP 0.153</td>
<td>BBP 0.010</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-0004</td>
<td>678</td>
<td>Book, subsamples of pages 7/8 and 9/10</td>
<td>DBP 0.004</td>
<td>DIBP 0.226</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-0005</td>
<td>679</td>
<td>Bathing ring</td>
<td>DEHP 28.976</td>
<td>DINP+DIDP 1.666</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hippopotamus tub</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-0006</td>
<td>680</td>
<td>Blue material on the shaft</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-0007</td>
<td>681</td>
<td>Yellow material on the shaft</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-0008</td>
<td>682</td>
<td>Book, subsamples of pages 3/4</td>
<td>DBP 0.463</td>
<td>BBP 0.019</td>
</tr>
<tr>
<td>3-0009</td>
<td>683</td>
<td>Book, subsamples of pages 3/4</td>
<td>DBP &lt; 0.005</td>
<td></td>
</tr>
<tr>
<td>3-0010</td>
<td>684</td>
<td>Book, subsamples of back pages</td>
<td>DBP &lt; 0.005</td>
<td>DIBP 0.032</td>
</tr>
<tr>
<td>3-0011</td>
<td>688</td>
<td>Soft lining material</td>
<td>DBP &lt; 0.005</td>
<td>DEHP 0.189</td>
</tr>
<tr>
<td>3-0012</td>
<td>689</td>
<td>Soft lining material</td>
<td>BBP &lt; 0.005</td>
<td>DEHP 14.800</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>DINP 1.202</td>
<td></td>
</tr>
<tr>
<td>3-0039</td>
<td>674</td>
<td>Keys 0 and 1 of the keyboard</td>
<td>DIBP &lt; 0.005</td>
<td>DEHP 0.0365</td>
</tr>
<tr>
<td>3-0040</td>
<td>704</td>
<td>Solid material from the back side of the figure</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3-0041</td>
<td>705</td>
<td>Boat material</td>
<td>DINP 37.290</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1: GC-separation of investigated phthalates. DINP and DIDP approximately 0.6% and other phthalates approximately 0.04%.
Figure 2: GC chromatogram of the extracts of laminated cardboard books 3-0003 (A) 3-0004 (B).
Figure 3: GC chromatogram of the extracts of bathing ring 3-0005 (A) and laminated cardboard book 3-0008 (B).
Figure 4: GC-chromatogram of the extracts of bib samples 3-0011 (A) and 3-0012 (B).
Figure 5: GC-chromatogram of the extract of chicken on the boat (3-0041)
5 References

1. Miljø- og Energiministeriets bekendtgørelse nr. 151 af 15. marts 1999Bekendtgørelse om forbud mod phthalater i legetøj til børn i alderen 0-3 år samt i visse småbørnsartikler m.v.


National Environmental Research Institute

The National Environmental Research Institute, NERI, is a research institute of the Ministry of the Environment. In Danish, NERI is called Danmarks Miljøundersøgelser (DMU). NERI's tasks are primarily to conduct research, collect data, and give advice on problems related to the environment and nature.

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Publications:
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