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Phthalates in Toys Available in Indian Market

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Abstract Twenty four children's toys and child care articles available in the local market of India were analyzed for eight phthalates as children toys are plasticized with phthalates. All toy samples showed the presence of one or more phthalates including di-(2-ethylhexyl) phthalate (96% of the samples), di-iso-nonyl phthalate and di-iso-decyl phthalate (42% of the samples) at a concentration ranging from 0.1% to 16.2%. Soft toys contain higher levels of phthalates as compared to hard toys as primary function of phthalates is softening of hard plastic materiel.

Keywords Phthalates · Plasticizers · Toys · Gas chromatograph · Mass spectra

Phthalates or phthalate esters (Fig. 1) are esters of phthalic acid, mainly used as plasticizers (substances added to plastics to increase their flexibility, transparency and durability). They are used primarily to soften polyvinyl chloride (PVC). PVC is a widely used material, including extensive use in toys and other children's products such as chewy teethers, soft figures and inflatable toys. The most widely used phthalates are di(2-ethylhexyl)phthalate (DEHP), dibutyl phthalate (DBP), di-iso-nonylphthalate (DINP), di-iso-decyl phthalate (DIDP), benzyl butyl phthalate (BBP) and di-n-octyl phthalate (DNOP). Phthalates can be released from soft PVC plastic by surface contact, especially where mechanical pressure is applied (e.g. during chewing of a PVC teether) as they are not tightly bound to the plastic, but are present as mobile components of the plastic matrix. Phthalates, which make up 10%–40% of the total weight of a toy, have been under scrutiny because of their potential health effects, particularly on reproductive development (Duty et al. 2003). Children are more vulnerable to the potential adverse effects of phthalates given their increased dosage per unit body surface area, immature metabolic system capability and developing endocrine and reproductive system. Several studies across the world reported the presence of high levels of DINP, DEHP and even DIOP, DIDP, DBP and other phthalates in products intended for mouthing, or with a high potential for mouthing, by children of the age group 0.5–3 years and their migration into saliva (Stringer et al. 2000; Niinoa et al. 2001; Bouma and Schakel 2002; Schreder 2007; Hitchcock 2008).

There are recommendations which suggest removal of DINP and DEHP from children's toys because exposure may be high enough to cause concern (Fiala et al. 2000). In the United States of America and Canada, the uncertainty in predicting exposure levels, especially in very young children and infants, has led to the removal of all phthalates from infant bottle nipples, pacifiers, teethers, and infant toys intended for mouthing (Kavlock et al. 2002). The European Union (EU) has banned the use of DBP, DEHP, BBP from children's toys and childcare articles, and DINP, DIDP and DNOP from items that children are likely to put in their mouths. The toys as well as other articles, which children may put in the mouth, should not contain >0.1% phthalate mass percent of the plasticized part of the toy according to EU regulation (1999/815/EC). Other countries including USA,

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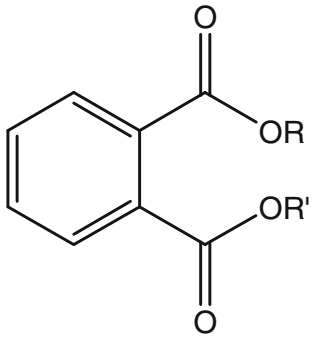

Fig. 1 General chemical structure of phthalates. R and R′ = C_nH_{2n+1}; n = 4–15

Japan, Denmark, Argentina, and Mexico, have also banned phthalates from children's toys. A safer alternative to PVC include toys made out of bio based plastics, polyethylenes, polypropylenes, thermoplastic elastomers, and ethylene vinyl acetate (EVA) that are free of phthalates. Two of the most common alternatives to phthalates are acetyl tributyl citrate (ATBC) and 1, 2-Cyclohexanedicarboxylic acid di-isononyl ester (DINCH), which is derived from DINP and has a similar chemical structure; however, existing data on their chronic toxicity on humans is insufficient (Schmidt 2008).

Toys sold in the Indian market have been shown to contain shockingly high levels of lead and cadmium (Kumar and Pastore 2007) but there is no report on phthalates in toys. With regard to safety guideline for toys, Bureau of Indian Standards (BIS) has published three standards, but none of them gives limit for phthalates in children's toys and childcare articles. Therefore it was considered imperative to undertake a study on phthalates in children's toys and other childcare articles available in the Indian market.

Materials and Methods

Twenty four toy samples of major brands from organized and unorganized sectors (manufactured in India, Taiwan, China and Thailand) were purchased randomly from various markets in Delhi in the month of October 2008 and analyzed for the following phthalates. Phthalate reference standards -dimethyl phthalate (99.9%), diethyl phthalate (99.5%), di-n-butyl phthalate (99.9%), benzyl butyl phthalate (99.2%), di-2-ethylhexyl phthalate (99.9%), di-*n*-octyl phthalate (99.2%), di-iso-nonyl phthalate (99.0%), di-iso-decyl phthalate (99.0%) were obtained from Sigma Chemicals, USA.

All solvents used were purchased from E-Merck. Each lot of reagents was checked for phthalate contamination. Phthalate reference standards were obtained from Sigma Chemicals, USA. Other chemicals were purchased from s. d. Fine Chem Ltd.

Samples were extracted according to the method of Rastogi (1998). Five grams of each sample was extracted in Soxhlet Apparatus using 100 mL of dichloromethane for 16 h at 40°C. The extract was concentrated under vacuum to 10 mL using a rotary evaporator at 30°C.

The samples were analyzed for Phthalates by using a Gas Chromatograph (Thermoquest-Trace GC) equipped with ^{63}Ni selective electron-capture detector (ECD). A DB- 5 (5%-phenyl-methylpolysiloxane) capillary column (30 m × 0.25 mm × 0.25 μm) was used for the analysis and nitrogen was used as carrier and makeup gas with a flow rate of 0.5 and 30 mL/min, respectively. Employing split less mode, 2.0 μL of the final extract was injected at a temperature of 250°C. The detector was maintained at 300°C. Calibration curves for all the phthalates were prepared at the concentrations range from 0.1 to 5 μg/mL. The curves were linear (R2 ≥ 0.999) over the range of 1.0–5.0 μg/mL for DINP and DIDP and for other phthalates it was 0.1–1.0 μg/mL. Identification of phthalates was performed by comparing the retention time (Rt) of the samples' peaks with the Rt of the phthalate standards. The detection limit was 5 ng/g (w/w) for DINP and DIDP and 1 ng/g for other phthalates. No phthalates were detected in reagent blanks. The phthalates present in high concentrations were analyzed after appropriate dilution of the sample extracts with hexane. The determinations were performed in triplicate samples using external standard technique with a calibration standard close to the estimated concentrations of phthalates in the sample extract. The recovery of all of the investigated phthalates under the experimental conditions was 85%–105%. The relative standard deviation (RSD) for the determination of most of the phthalates was within 10%.

GC chromatograms of DINP and DIDP overlap partly. Therefore, when a product contained DINP as well as DIDP, the content of both of these phthalates in the product was determined together as DINP (DINP is currently the most common plasticizer used in children toys). 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. The GC separation of the phthalates under study as well as chromatographic pattern of DINP and DIDP is shown in Fig. 2a and chromatogram of toy sample no. 22 is shown in Fig. 2b.

The identity of phthalates detected in the samples by GC–ECD was confirmed by GC–MS, Model Finnigan Polaris Q Ion trap GC/MS^n with EI ionization (70 eV), in Full Scan mode. The samples were injected using a programmable temperature injector (PTV). The carrier gas was helium with a 0.5 mL/min flow rate employing the split less mode. 1.0 μL of the final extract was injected at a temperature of 250°C keeping the ion source at 230°C, Mass Range: 50–650 m/z. The limit of detection ranged from 0.1 to 3.0 ng/g.

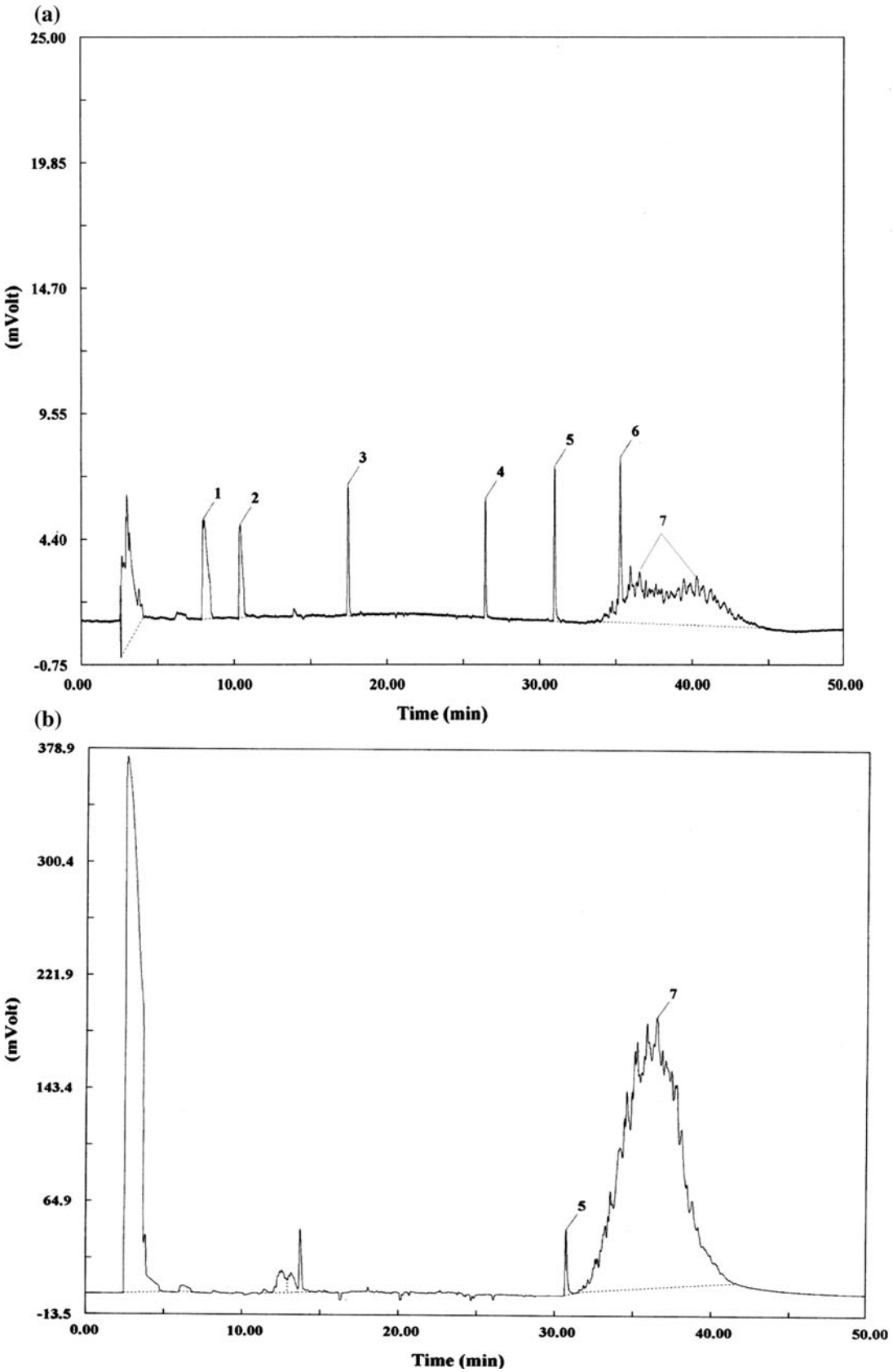

Fig. 2 **a** Chromatogram of the standard mixture of phthalates. Peak identity: 1. DMP; 2. DEP; 3. DBP; 4. BBP; 5. DEHP; 6. DNOP; 7. DINP + DIDP. **b** Chromatogram of sample extract from Toy No. 22. Peak identity: 5. DEHP; 7. DINP + DIDP

Results and Discussion

All 24 toy samples showed the presence of at-least one or more phthalates (Table 1). DEHP was detected in 96% of the samples at low concentrations, ranging from <0.1%–2.6%. DINP and DIDP were detected in 42% of the samples ranging from <0.1%–16.2%. DBP and BBP were detected in 5 and 3 toys out of 24 toys analysed, respectively and concentrations were <0.1%–0.2%; too low to have plasticizing function and could be present as a contaminant of another phthalate; constituent of ink or paint used in toys.DEHP, DBP, BBP and DINP + DIDP have been found to reduce testosterone production by the fetus which can result in off target reproductive development and abnormal genitals. DINP may be a risk for young children who routinely mouth DINP plasticized toys for 75 min per day or more (Bogen et al. 2001). The total amount of phthalates exceeded the EU limit (0.1% of the plasticized part of the toy) in more than 50%t of the samples analyzed. Total phthalate concentration in 24 samples ranged <0.1%–16.22%. Maximum value is 162 times higher than the EU limit of 0.1% of the plasticized

Table 1 Phthalates detected in baby toy samples (percent mass basis)

Toy No.	Type	Country	Soft/hard	DBP	BBP	DEHP	DINP + DIDP	Total phthalates (%)	No. of times of the EU limit (0.1% by mass)
1	Teether-1	India	Soft	<0.1	ND	<0.1	ND	<0.1	Within limit
2	Gum Soother-1	India	Soft	<0.1	ND	<0.1	ND	<0.1	Within limit
3	Gum Soother-2	India	Soft	ND	ND	<0.1	ND	<0.1	Within limit
4	Animal Figurine	India	Soft	ND	ND	0.1	ND	0.1	1
5	Pip Squeaks Toy	India	Soft	ND	ND	<0.1	16.2	16.2	162
6	Squeeze Toy-1	China	Soft	ND	ND	<0.1	6.0	6.0	60
7	Teether-2	Taiwan	Soft	<0.1	ND	0.3	ND	0.3	3
8	Soft & Hard Biter	Taiwan	Hard	0.2	ND	<0.1	<0.1	0.2	2
9	Toy-ball	China	Soft	ND	ND	<0.1	ND	<0.1	Within limit
10	Baby Rattle-1	Thailand	Hard	ND	<0.1	<0.1	ND	<0.1	Within limit
11	Softy-Soft Keys	China	Hard	ND	ND	<0.1	ND	<0.1	Within limit
12	Bath Fish	China	Soft	ND	ND	0.1	ND	0.1	1
13	Baby Rattle-2	India	Hard	ND	ND	<0.1	ND	<0.1	Within limit
14	Baby Rattle-3	China	Hard	ND	ND	<0.1	ND	<0.1	Within limit
15	Rattle & Teether	China	Hard	ND	ND	<0.1	ND	<0.1	Within limit
16	Squeeze Toy-2	China	Soft	ND	ND	<0.1	7.1	7.1	71
17	Inflatable-1	China	Soft	ND	ND	<0.1	4.4	4.4	44
18	Doll	China	Hard	<0.1	ND	ND	4.5	4.5	45
19	Barbie Doll	India	Hard	ND	<0.1	<0.1	0.2	0.2	2
20	Toy -My Little Pony	China	Hard	ND	<0.1	<0.1	0.2	0.2	2
21	Squeeze Toy-3	China	Soft	ND	ND	<0.1	6.2	6.2	62
22	Squeeze Toy-4	China	Soft	ND	ND	<0.1	8.0	8.0	80
23	Inflatable-2	China	Soft	ND	ND	2.6	ND	2.6	26
24	Bath Duck	China	Soft	ND	ND	0.2	ND	0.2	2

DMP, DEP and DNOP were not detected in any of the samples

Values are average of triplicate

ND = Not detected

Table 2 Characteristic ions for major phthalates detected in toy samples

S. No.	Phthalate	CAS	Retention time (min)	Molecular weight	Primary ion	Secondary ions
1	di-n-butyl phthalate	84-74-2	13.99	278.34	149	205, 223
2	Benzyl butyl phthalate	85-68-7	22.19	312.35	149	91, 206
3	di(2-ethylhexyl) phthalate	117-81-7	26.37	390.54	149	167, 279
4	di-iso-nonyl phthalate	68515-48-0	31.97	418.60	149	167, 293

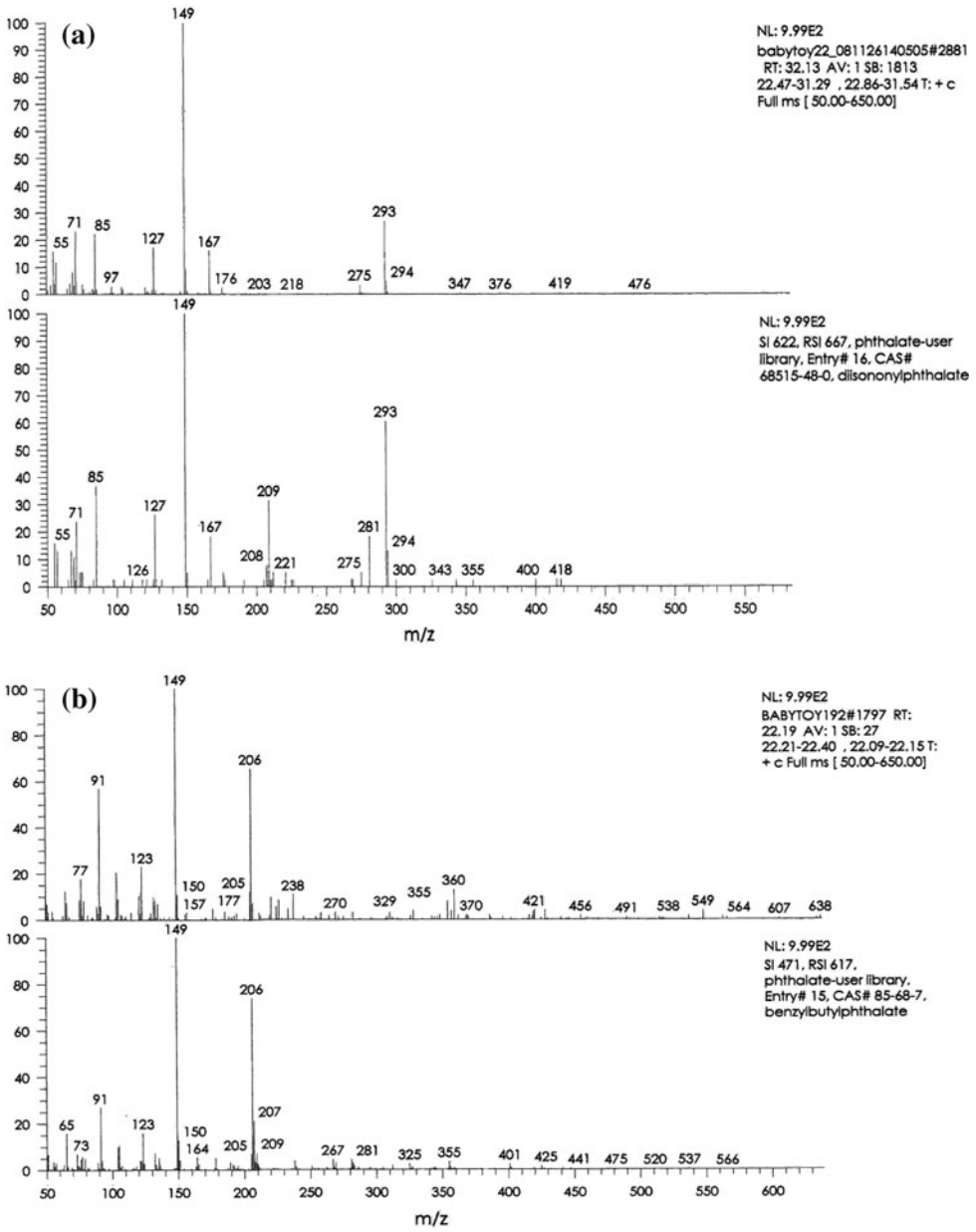

Fig. 3 **a** Mass spectra of sample extract from Toy No. 22 (DINP). **b** Mass spectra of sample extract from Toy No. 22 (DEHP)

part of the toy. Squeeze toys (Toy No. 6, 16, 17, 18, 21, 22, 23), manufactured in China, contained 2%–8% of total phthalates and pip squeak toy (Toy No. 5) from India contained more than 16% of total phthalates. Majority of the toys which contained high levels of phthalates were manufactured in China.

DINP was found in very high concentration in many samples, especially in Chinese toys; which reflects a marked shift away from DEHP towards the use of the poorly characterized isomeric phthalates. The samples containing higher quantities of DINP + DIDP contained smaller quantities of DEHP, perhaps as a contaminant in the manufacturing process. Phthalates were also detected in baby teethers and soothers made from non-toxic food grade silicone rubber in very low concentrations (<0.1%).

The phthalates-BBP, DBP, DEHP and DINP detected in toy samples were confirmed by GC–MS. The dominant fragment of all phthalates measured in electron impact ionization MS is at m/z149 this is a result of the loss of the alkyl ester groups and the formation of protonated phthalic anhydride moiety. Characteristic ions – primary and secondary ions and the retention time for major phthalates detected in toy samples are given in Table 2. Mass Spectra for sample no. 22 are given in Fig. 3a, b.

The soft toys contained higher levels of phthalates as compared to hard toys like rattles. Young children

(below 3 years) suck and chew on toys containing phthalates may be at a higher risk of adverse effects of phthalates because of anticipated higher exposures during a time of developmental and physiologic immaturity as they may extract and ingest certain quantities of it. Some manufacturers have removed phthalates from toys and other products intended for very young children or those intended to be mouthed (like teethers) and others have shifted to safer alternatives for phthalates but there is no law regulating phthalates in toys and other articles for children up to 3 years of age in India. There is a need of regulations for phthalates in toys in India to ensure the safety of children (below 3 years).

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