

Sample Preparation, Extraction and Analysis of Imported Children's Toys for Bisphenol A and Phthalates

Introduction

The US has started to limit levels of some phthalates for use in children's products including DEHP, DBP, BBP, DINP, DIDP, and DIOP. The Consumer Product Safety Commission (CPSC) has published testing methods for these regulated phthalates. The regulation of bisphenol A (BPA) remains under debate. This study examined the levels of phthalates and BPA in 26 children's toys purchased from local discount or 'dollar' type stores. The toys were all reported as being made in China.

Microwave extraction methods were created and optimized against Spex CertiPrep certified solid reference materials to compare levels of phthalates and BPA found in toys. Samples were examined using GC/MS. High levels of phthalates and BPA were detected in the majority of the PVC toys. In many samples the concentration of phthalates far exceeded the limits set by the CPSC.

Materials and Methods

Sample Preparation

The 26 toys were separated by material type and coloration. Composite toys were subdivided into constituent parts and materials. The 26 toys became over 58 samples. Paint was not removed from painted surfaces but surface stickers were removed prior to further processing.

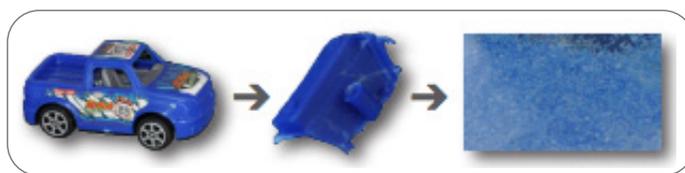


Figure 1. Original toy, subdivision and final ground powder.

The toys were cut up into 5 mm pieces and ground to a fine powder using Spex SamplePrep 6970 Freezer/Mill[®] with the Multi-Vial Adapter and 6571 Vials. Two to three grams of toy material were ground using the following cryogenic program: twenty minutes of precool followed by five cycles of grinding at 2 minutes per cycle. Each cycle was followed by 2 minutes of cooling. The impact rate for the grinding was 16 impacts per second.

In the absence of an IR system, the plastic toys were identified with density and chemical testing. The 58 samples were identified as follows: 22-LDPE samples, 18-PVC samples, 7-PC samples, 6-HDPE samples, 2-PP samples, 1-cloth textile sample, and 1-silicone sample. The majority of children's toys and products were composed of polyethylene (28 samples) and polyvinyl chloride (18 samples).

Sample Extraction

Two different extraction methods were employed against a corresponding plastic standard to determine extraction efficiency. The first method was a dissolution/precipitation method outlined in the CPSC method: CPSC-CH-C1001-09.03.

0.05 g of a PVC sample was dissolved into 5 mL THF and precipitated with 10 mL hexane. PVC and HDPE toy samples were extracted using this method with a matching PE and PVC certified reference material containing phthalates (CRM-PE001 & CRM-PVC001, respectively). For this method, recovery data showed that the extraction efficiency for the PE matrix was 50% and 83-94% for the PVC matrix. The PVC matrix had higher efficiency than the PE matrix but the relative standard deviation (RSD) for subsequent GC/MS ranged from 35-60%, showing a possible contamination issue of the GC/MS system by a polymer still in the solution.

Methods for extracting phthalates from polyethylene and polyvinyl chloride using microwave digestion were developed to maximize the recovery of phthalates from each type of plastic matrix. 0.2 g of sample was extracted using a CEM Mars Microwave system with XPress Vessels.

Polyethylene Extraction Method:

- 10 mL Cyclohexane:Acetone (30:70)
- Ramp to temperature
- 10 minutes to 140°C
- Hold for 10 minutes
- Stirring: On

Polyvinyl Chloride Extraction Method:

- 10 mL Cyclohexane:IPA (50:50)
- Ramp to temperature
- 10 minutes to 130°C
- Hold for 10 minutes
- Stirring: On

Comparisons of the CPSC Wet Method and the Optimized Microwave Extraction Method showed increased recovery and reduced % RSD results. The recovery of PVC increased from 85-94% to > 95% by using the optimized microwave extraction method. The % RSD for the microwave method was less than 2.5% for all of the targeted phthalates.

Table 1. Comparison of % RSD between CPSC Wet Method for PVC and Optimized Microwave Method for PVC.

Compound	Optimized Microwave Method for PVC (% RSD)	CPSC Wet Method for PVC (% RSD)
Di-n-butyl phthalate	0.70	48.42
Butyl benzyl phthalate	2.26	57.72
Bis(2-ethylhexyl) phthalate	1.02	58.05
Di-n-octyl phthalate	1.29	58.24
Diisononyl phthalate	0.36	50.97
Diisodecyl phthalate	0.94	60.69

Analytical Conditions

- Instrument: GC/MS in scan mode with EIC (35-450 m/z)
- Column: CA-5 capillary column (30 m x 0.25 mm x 0.25 µm)
- Run program:
 - 55 °C x 1 minute; 20 °C/minute to 200 °C, hold for 1 minute; 30 °C/minute to 310 °C, hold for 3 minutes
 - Detector: 280 °C & injector 150 °C
- MS Ions: The primary ion monitored for four of the six phthalates was 149 m/z. Since DINP and DIDP partially coeluted, secondary ions of 293 m/z (DINP) and 307 m/z (DIDP) were used. Bisphenol-A was quantitated using 213 m/z.

All samples were spiked with an internal standard (Spex CertiPrep CLPS-I90) as well as compared to an external standard phthalate mix standard (SS-CRM-PVC001) prepared at multiple levels to obtain a calibration curve. A BPA standard (S-509) was also run at multiple levels to create a BPA calibration curve.

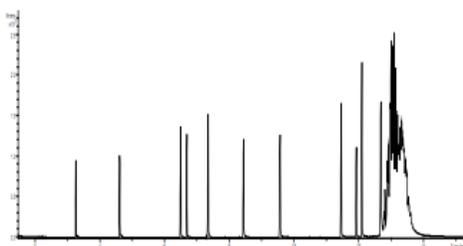


Figure 2. Chromatogram of analysis for BPA and Phthalates.

Results

HDPE Toys

Of the two types of plastic toys discussed here, PCV and HDPE, the HDPE toys showed the lowest levels of phthalates. DNOP was detected in low levels in 5 of the 6 HDPE toys at levels below 130 µg/g. This level is well below the CPSC limit of 0.1% of DNOP. Bisphenol A was not detected in any of the HDPE toys.

PVC Toys

The PVC toys contained high levels of several different phthalates. The predominant phthalate in these toys was DEHP. Fifteen of the seventeen PVC toys contained DEHP. Twelve toys exceeded the CPSC limit of 0.1%. The highest amount of DEHP was detected in a rubber duck toy with 28,000 µg/g of DEHP. Eleven toys contained over 10,000 µg/g of DEHP.

Three other phthalates were found in the PVC toys; DIDP, DINP, and DNOP. The average DNOP level in toys was found to be about 100 µg/g. DIDP and DINP were detected predominantly in one donkey toy where the highest overall phthalate level was detected, with 100 mg/g of DINP.

Bisphenol A was detected in four toys. The highest levels of BPA were 1,200 µg/g in the fashion doll's head and 700 µg/g in the rubber duck toy.

Conclusions

The PVC toys contained the highest levels of phthalates and bisphenol A of all the types of plastic tested. The PVC predominantly contained DEHP at levels over the current CPSC limits of 0.1%. BPA was found in four of the PVC toys, two of which approached or exceeded 1,000 µg/g.

Proper sample preparation and extraction is critical to ensuring an accurate recovery of phthalates from the different plastic polymers. Each polymer type requires a different method to achieve an optimized recovery rate. The failure to recognize that one extraction method (primarily the CPSC PVC method) does not suit for different types of polymer could alter the recovery rate and analysis for these restricted phthalates.

References

1. Consumer Product Safety Commission, Test Method: CPSC-CH-C1001-09.3. Standard Operating Procedure for Determination of Phthalates (http://www.cpsc.gov/s3fs-public/pdfs/blk_media_CPSC-CH-C1001-09.3.pdf)
2. CEM Corporation, Application Note for Solvent Extraction: HDPE (<http://cem.com/downloads457.html>)
3. CEM Corporation, Application Note for Solvent Extraction: PVC (<http://cem.com/downloads465.html>)
4. Spex SamplePrep, Application Note SP007, Grinding Polymers for Qualitative and Quantitative Analysis (http://www.spexsampleprep.com/knowledge-base/resources/application_notes/sp007.pdf)

Additional Resources

To watch our webinar on BPA and Phthalates in Plastic Toys, or BPA and Phthalates in Consumer Water Sources, visit our YouTube channel at www.youtube.com/spexcertiprep.

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