

# Part 2: The Extraction and Determination of BPA and Phthalate Content in Imported Plastic Toys



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SPEX CertiPrep

- Everyone will receive a copy of the presentation slides
- The webinar is being recorded and will be posted to our YouTube account
- Questions will be answered at the end of the presentation
  - *Type any questions you may have into the question box and we will answer them during the Q&A session*
- One lucky attendee will win Theodore Gray's The Elements Card Deck!

# Phthalates Still A Topic of Concern

## Science News

... from universities, journals, and other research organizations

### Phthalates in PVC Floors Taken Up by the Body in Infants

*ScienceDaily (May 23, 2012)* — A new study at Karlstad University in Sweden shows that phthalates from PVC flooring materials is taken up by our bodies. Phthalates are substances suspected to cause asthma and allergies, as well as other chronic diseases in children. The study shows that children can ingest these softening agents with food but also by breathing and through the skin.



*Phthalates from PVC flooring materials is taken up by our bodies. Phthalates are substances suspected to cause asthma and allergies, as well as other chronic diseases in children. The study shows that children can ingest these softening agents with food but also by breathing and through the skin. (Credit: © burcucetin / Fotolia)*

<http://www.sciencedaily.com/releases/2012/05/120523102142.htm>

# Common Phthalates

Name	Acronym	Structural formula	CAS No.
Dimethyl phthalate	DMP	$C_6H_4(COOCH_3)_2$	131-11-3
Diethyl phthalate	DEP	$C_6H_4(COOC_2H_5)_2$	84-66-2
Diallyl phthalate	DAP	$C_6H_4(COOCH_2CH=CH_2)_2$	131-17-9
Di-n-propyl phthalate	DPP	$C_6H_4[COO(CH_2)_2CH_3]_2$	131-16-8
Di-n-butyl phthalate	DBP	$C_6H_4[COO(CH_2)_3CH_3]_2$	84-74-2
Diisobutyl phthalate	DIBP	$C_6H_4[COOCH_2CH(CH_3)_2]_2$	84-69-5
Butyl cyclohexyl phthalate	BCP	$CH_3(CH_2)_3OOC C_6H_4 COOC_6H_{11}$	84-64-0
Di-n-pentyl phthalate	DNPP	$C_6H_4[COO(CH_2)_4CH_3]_2$	131-18-0
Dicyclohexyl phthalate	DCP	$C_6H_4[COOC_6H_{11}]_2$	84-61-7
Butyl benzyl phthalate	BBP	$CH_3(CH_2)_3OOC C_6H_4 COOCH_2C_6H_5$	85-68-7
Di-n-hexyl phthalate	DNHP	$C_6H_4[COO(CH_2)_5CH_3]_2$	84-75-3
Butyl decyl phthalate	BDP	$CH_3(CH_2)_3OOC C_6H_4 COO(CH_2)_9CH_3$	89-19-0
Di(2-ethylhexyl) phthalate	DEHP	$C_6H_4[COOCH_2CH(C_2H_5)(CH_2)_3CH_3]_2$	117-81-7
Di(n-octyl) phthalate	DNOP	$C_6H_4[COO(CH_2)_7CH_3]_2$	117-84-0
Diisodecyl phthalate	DIDP	$C_6H_4[COO(CH_2)_7CH(CH_3)_2]_2$	26761-40-0
n-Octyl n-decyl phthalate	ODP	$CH_3(CH_2)_7OOC C_6H_4 COO(CH_2)_9CH_3$	119-07-3
Diisononyl phthalate	DINP	$C_6H_4[COO(CH_2)_6CH(CH_3)_2]_2$	28553-12-0

# Common Phthalates

Name	Acronym	Structural formula	CAS No.
Di-n-butyl phthalate	DBP	$C_6H_4[COO(CH_2)_3CH_3]_2$	84-74-2
Butyl benzyl phthalate	BBP	$CH_3(CH_2)_3OOC C_6H_4 COOCH_2C_6H_5$	85-68-7
Di(2-ethylhexyl) phthalate	DEHP	$C_6H_4[COOCH_2CH(C_2H_5)(CH_2)_3CH_3]_2$	117-81-7
Di(n-octyl) phthalate	DNOP	$C_6H_4[COO(CH_2)_7CH_3]_2$	117-84-0
Diisodecyl phthalate	DIDP	$C_6H_4[COO(CH_2)_7CH(CH_3)_2]_2$	26761-40-0
Diisononyl phthalate	DINP	$C_6H_4[COO(CH_2)_6CH(CH_3)_2]_2$	28553-12-0



# Common Phthalates

Compound	Uses
DMP	Insect repellent, plastic
DEP	Shampoo, scents, soap, lotion, cosmetics, industrial solvent, medications
DBP	Adhesives, caulk, cosmetics, industrial solvent, medications
DIBP	Adhesives, caulk, cosmetics, industrial solvent
BBP	Vinyl flooring, adhesives, sealants, industrial solvent
DCHP	Stabilizer in rubber, polymers
DEHP	Soft plastic, including tubing, toys, home products, food containers, food packaging
DOP	Soft plastic
DINP	Soft plastics, replacement for DEHP

**Phthalates and Cumulative Risk Assessment The Task Ahead (2008)**  
**Board on Environmental Studies and Toxicology (BEST)**

# Children & Exposure to Phthalates

- Medical Devices: may contain 20-40% DEHP by weight
- Medication: coatings
- Childcare Products
  - Ointments
  - Lotions
  - Shampoos
- Childcare Articles
  - Pacifiers
  - Bottles
  - Plates
  - Spoons
- Toys



# Regulations & Banned Phthalates

		DEHP	DBP	BBP	DINP	DIDP	DNOP
<b>US</b>	CPSIA CPSC-CH-C1001-09.03	0.1% individual (All toys & Childcare)	0.1% individual (All toys & Childcare)	0.1% individual (All toys & Childcare)	0.1% individual (Oral Contact)	0.1% individual (Oral Contact)	0.1% individual (Oral Contact)
<b>EU</b>	EC Directive 2005/84/EC	0.1% combined (All toys)			0.1% combined (Toys with Oral Contact)		
<b>Japan</b>	ST Standard Part 3 / Food Sanitation Law	0.1% combined (All toys)			0.1% combined (Toys with Oral Contact)		



# Infant & Children's Exposure to BPA

- Food & Food Packaging
  - Can linings & Containers
  - Baby Bottles
    - up to 13  $\mu\text{g/kg}$  of body wt/day
  - Water Bottles
  - Liquid Baby Formula
    - 0.48 to 11 ng/g
- Paper: Receipts & Labels
- PVC Pipes
- Medical Devices
- Toys
- During Pregnancy
  - US study (2009): avg 2.8 ng/mL in 9/10 umbilical cord bloods



# Regulations

Area	Scope of BPA Ban	Requirement
US	Various childcare products	No National Ban; State by State
EU	PC baby bottles	Banned
Canada	PC baby bottles	Banned
	BPA deemed toxic	Action

## 26 Toys from Discount or Dollar Stores

### Items with Oral Contact

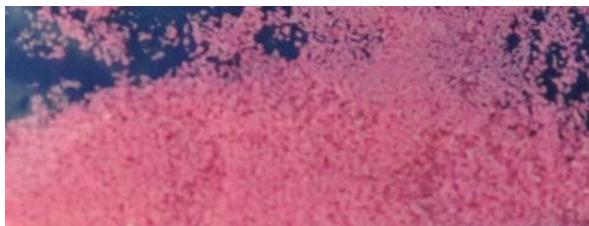


### Items with Possible Oral Contact



# Sample Preparation: Grinding

Cryogenic grinding allows for a fine analytical powder not possible with room temperature grinding





# Sample Identifications

Type	# of Samples
LDPE	22
PVC	17
HDPE	6
PC	7
PP	2
ABS	1
Silicone	1
Cloth	1



## CPSC-CH-C1001-09.03



- *Standard Operating Procedure for Determination of Phthalates (Children's Toys & Childcare Articles)*
- Measurement of 6 Restricted Phthalates
- Outlines:
  - Sample Preparation
  - Extraction
  - Analysis



# Sample Extraction: CPSC

Sample Preparation	Extraction Method	Analysis Method
CPSC-CH-C1001-09.3	CPSC-CH-C1001-09.3	CPSC-CH-C1001-09.3
	Health Canada Method C-34 <sup>2</sup> ( <a href="http://www.hc-sc.gc.ca/cps-spc/prod-test-essai/method-chem-chim/c-34-eng.php">http://www.hc-sc.gc.ca/cps-spc/prod-test-essai/method-chem-chim/c-34-eng.php</a> )	
	EN 14372:2004 <sup>3</sup>	Health Canada Method C-34
	EPA 3540C, Soxhlet Extraction ( <a href="http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3540c.pdf">http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3540c.pdf</a> )	
	EPA 3541, Automated Soxhlet Extraction ( <a href="http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3541.pdf">http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3541.pdf</a> )	EN 14372:2004
	EPA 3545A, Pressurized Fluid Extraction ( <a href="http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3545a.pdf">http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3545a.pdf</a> )	
	EPA 3546, Microwave Extraction ( <a href="http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3546.pdf">http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3546.pdf</a> )	EPA 8270D <sup>4</sup> (must be modified appropriately to include DINP and DIDP)
	EPA 3550C, Ultrasonic Extraction ( <a href="http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3550c.pdf">http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/3550c.pdf</a> )	California Dept. of Toxic Substances Control Method
	ASTM D 2124-99 (2004) <sup>5</sup>	
	California Dept. of Toxic Substances Control Method <sup>6</sup>	

# CPSC Wet Extraction Method: PVC

- Intended for PVC not other materials
- For 0.05 g = 15 mL solvent minimum
  - PVC Toy samples don't always precipitate with 15 mL
  - Increased solvent dilutes sample
- At the CPSC limit (0.1% or 1000 µg/g)
  - Straight GC injection = 3 ppm
  - Diluted per method = 0.7 ppm
    - SIM Mode
      - Miss other additives
      - Misidentify other additives as phthalates
      - Miss low level phthalates or BPA
- What is the extraction efficiency of the method?



# CPSC Wet Extraction Method: PVC

- SPEX CertiPrep CRM-PE001: Polyethylene Matrix
  - Recovery for PE material using PVC wet method = 50%
- New CRM developed for PVC
  - Recovery for CPSC Method = 83 – 94%
  - Poor Reproducibility
  - GC Contamination

Phthalate	CPSC Wet Method %RSD
Dimethyl phthalate	35.09
Diethyl phthalate	36.96
Di-n-butyl phthalate	48.42
Butyl benzyl phthalate	57.72
Bis(2-ethylhexyl)phthalate	58.05
Di-n-octyl phthalate	58.24
Diisononyl phthalate	50.97
Diisodecyl phthalate	60.69

# Microwave Method Optimization

- Methods Developed by CEM
  - HDPE method: Cyclohexane: Acetone (Recovery >95%)
  - LDPE method: IPA solvent
  - PVC method: Ether
    - Did not want to run ether
    - Possible dissolution of PVC with Acetone
- Goal was not to dissolve polymer

Temp °C	Cyclohexane	IPA	Acetone	Solubility	% Recovery
130	50	-	50	Dissolved	NA
130	80	-	20	Dissolved	NA
100	80	-	20	Partitioned/Slightly dissolved	91-101
100	80	20	-	Not dissolved	86-98
130	80	20	-	Not dissolved	93-100
150	80	20	-	Dissolved	NA
130	50	50	-	Not dissolved	95-105
150	50	50	-	Not dissolved	99-102

## HDPE

### Microwave Extraction

- 10 mL Cyclohexane: Acetone (30:70)
- 0.2 g sample
- Ramp to Temperature
  - 10 minutes to 140 °C
  - Hold 10 minutes
- Stirring used



## PVC

### Microwave Extraction

- 10 mL Cyclohexane: IPA (50:50)
- 0.2 g sample
- Ramp to Temperature
  - 10 minutes to 130 °C
  - Hold 10 minutes
- Stirring used



# CEM

## Application Note for Solvent Extraction

Additives  
from High Density  
Polyethylene

**Sample Type:** **High Density Polyethylene** (Ground to 1mm)

**Sample Category:** Polymers/Plastics

**Analyte:** Anti-oxidants, slip agents, stabilizers

### Sample Preparation Procedure

**Sample Weight:** 2 grams

**Reagents:** Acetone:Cyclohexane (7:3)

**Reagent Volume:** 25mL

### Recommended Equipment



**MARS**



**GreenChem**

*This method is appropriate for use with  
GreenChem, Xpress*

### Heating Program: Ramp to Temperature Control

Stage	Max. Power	% Power	Ramp (min.)	Pressure (psi)	Temperature (°C)	Hold (min.)
(1)	1600 W	100	10:00	200	140	10:00



# Comparison of CPSC Wet Method vs. Microwave Extraction for PVC

## THF Wet Method

- Large amounts of solvent
- Less concentration on GCMS system: miss some additives
- Interference of polymers with GCMS operation
- Poor reproducibility
- Time consuming



## Microwave Method

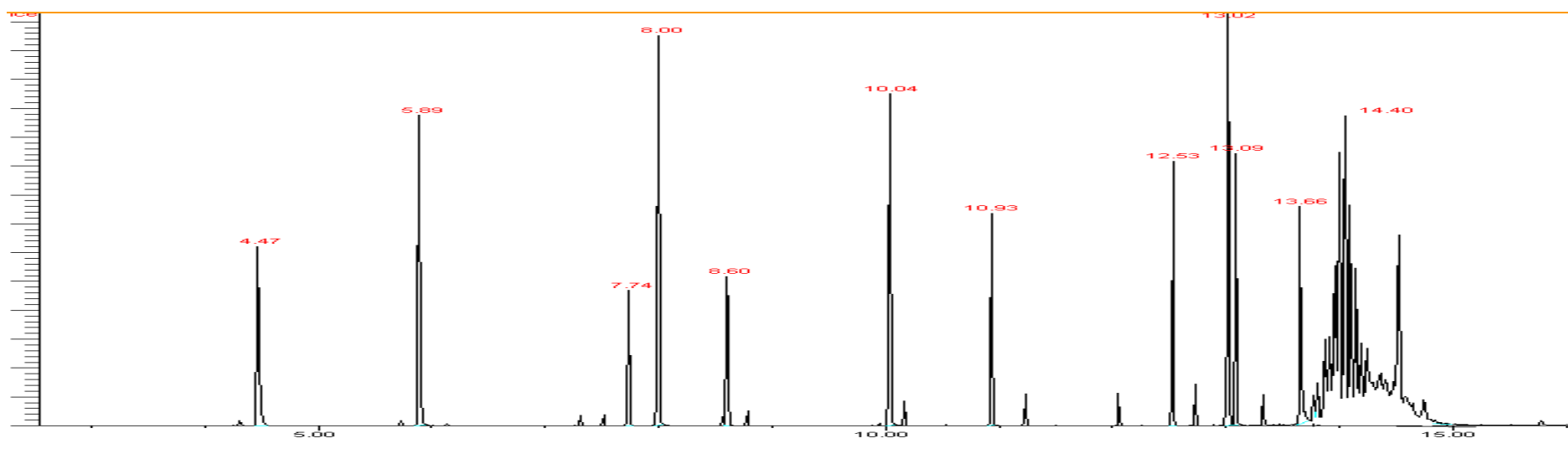
- 10 – 15 mL of solvent for up to 1 g of sample
- Allows high enough concentration of small phthalates to see on GCMS
- Dilution possible for higher concentration phthalates
- Little interference/carryover seen on GCMS
- Great reproducibility
- Fast, multiple samples processed at once

# Comparison of CPSC Wet Method vs. Microwave Extraction

Phthalate	Optimized Microwave Method %RSD	CPSC Wet Method %RSD
Dimethyl phthalate	2.48	35.09
Diethyl phthalate	0.72	36.96
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

# Methods & Materials: Instrument Conditions

- GC-MS in scan mode with EIC (35-450 m/z)
- CV-5 capillary column (30 m x 0.25 mm x 0.25  $\mu$ m)



Phthalate	Abbreviation	Ions
Di-n-butyl phthalate	DBP	149, 150, 29, 41, 57
Bisphenol A	BPA	213, 228, 119, 214, 91
Butyl benzyl phthalate	BBP	149, 91, 206, 65, 104
Di(2-ethylhexyl) phthalate	DEHP	149, 167, 279, 71
Di(n-octyl) phthalate	DNOP	149, 279, 43, 57
Dinonyl phthalate	DINP	149, 293, 71, 57, 43
Diisodecyl phthalate	DIDP	149, 307, 71, 141

# HDPE Toys

- Plastic Figures

- Police
- Military
- Fireman



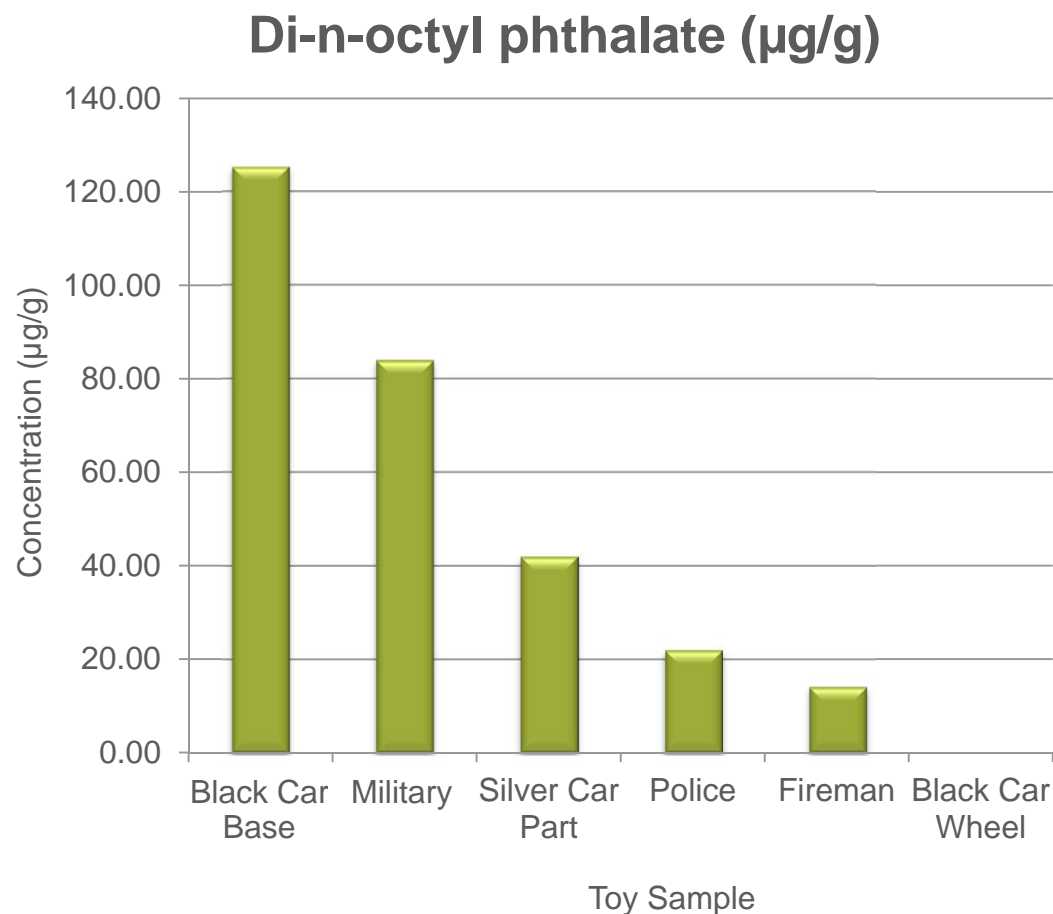
- Toy Car Parts

- Black Base
- Black Wheel
- Silver parts



# Results: HDPE Toys

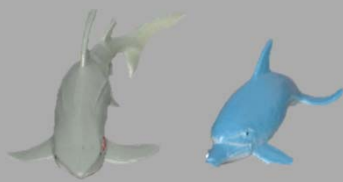
- One restricted phthalate
  - DNOP
  - < 0.1% (1000 µg/g)
- No BPA
- Wheel
  - Higher Alkanes





# PVC Toys

## Without Oral Contact



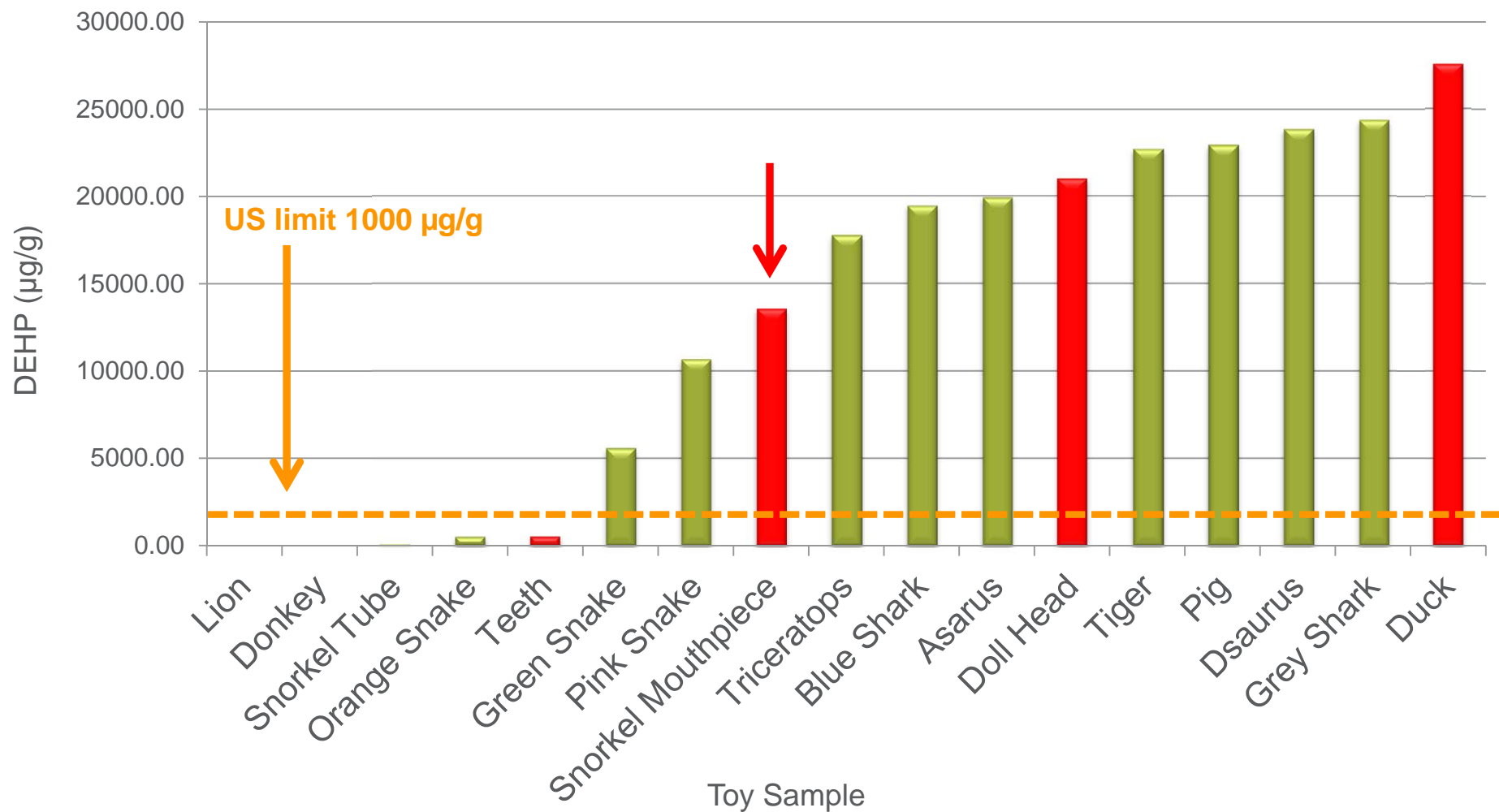
## Possible Oral Contact



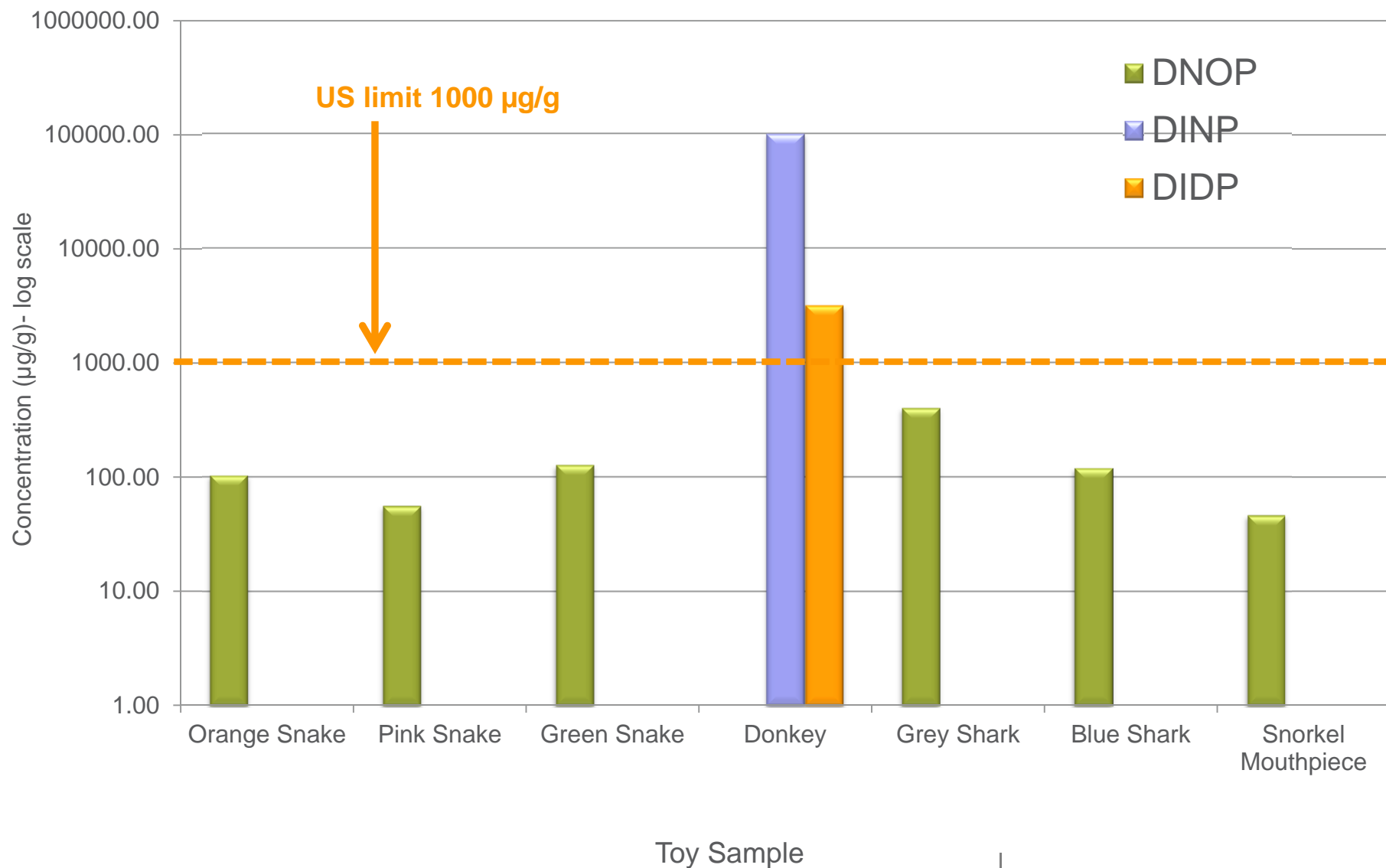


# PVC Toys: DEHP

**Total DEHP in each toy sample**

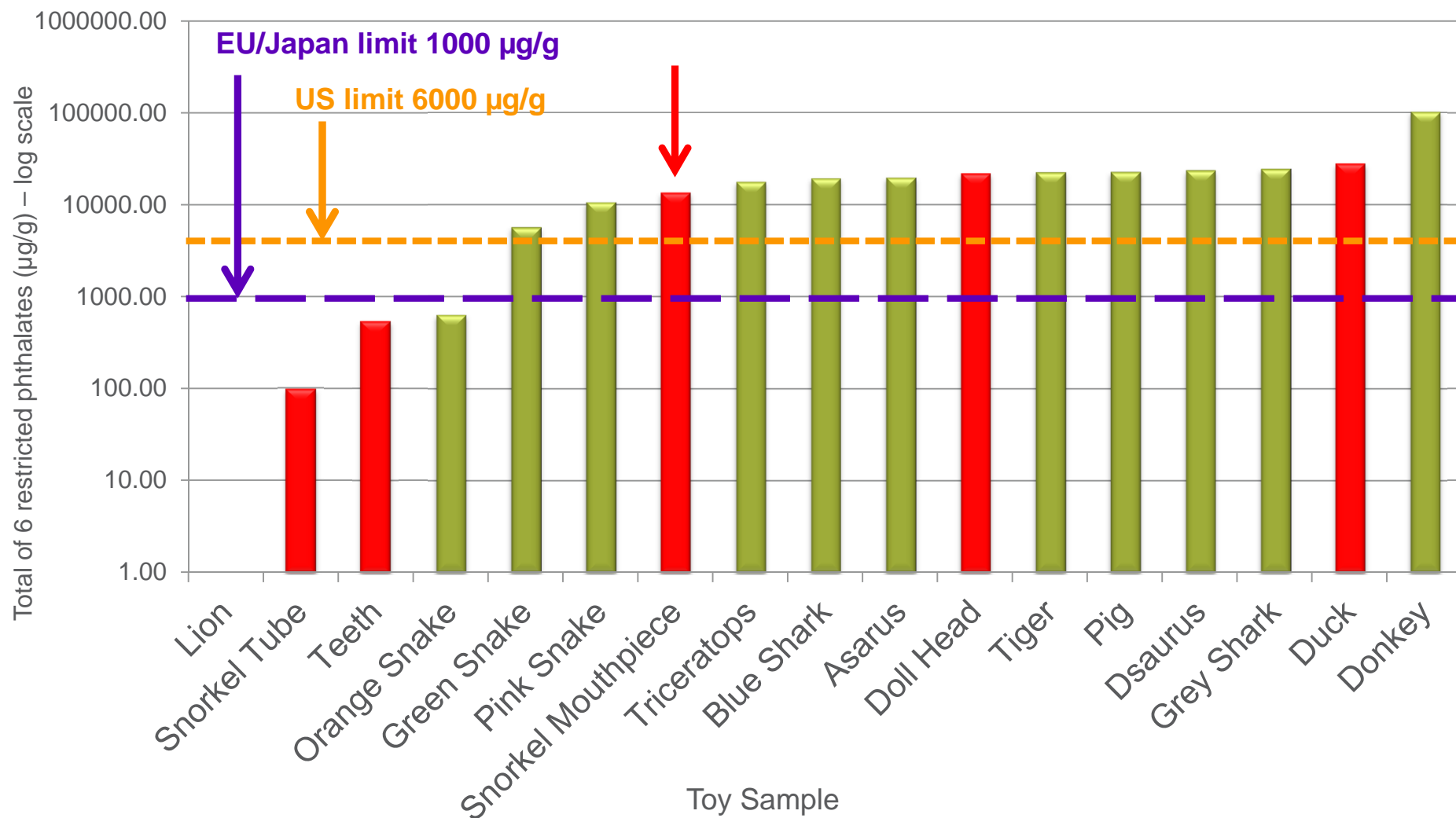


# PVC Toys: DINP, DIDP, DNOP



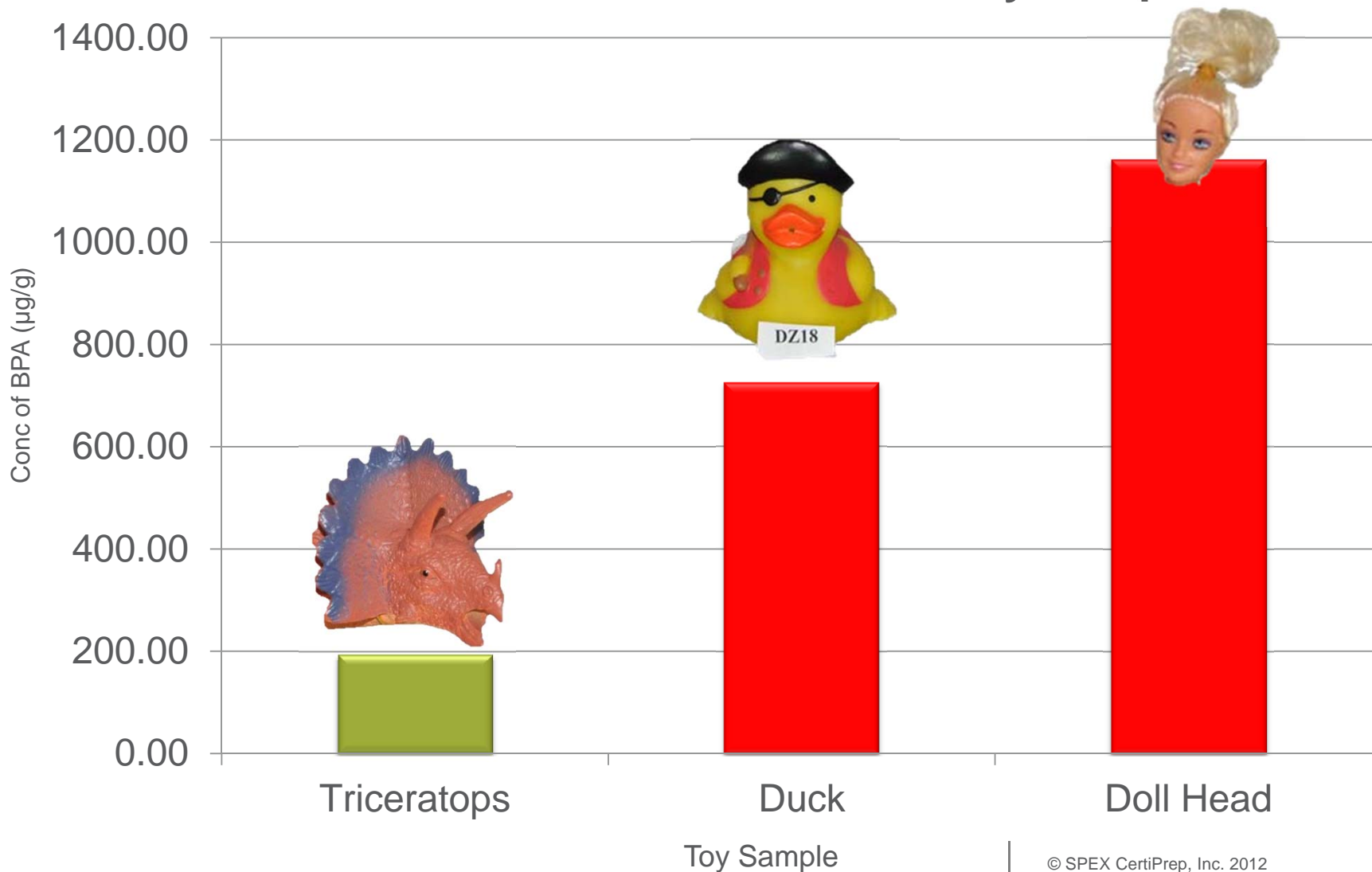
# PVC Toys: Total Phthalates

Total Concentration of Six Restricted Phthalates in Each Toy Sample

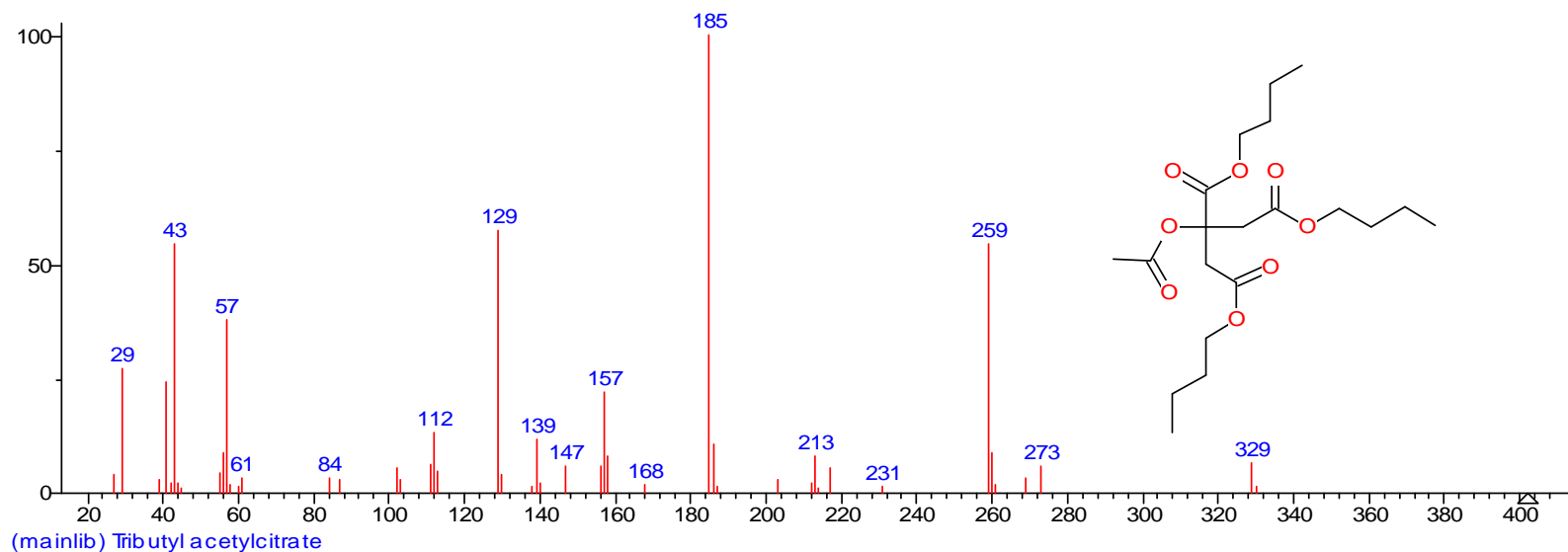
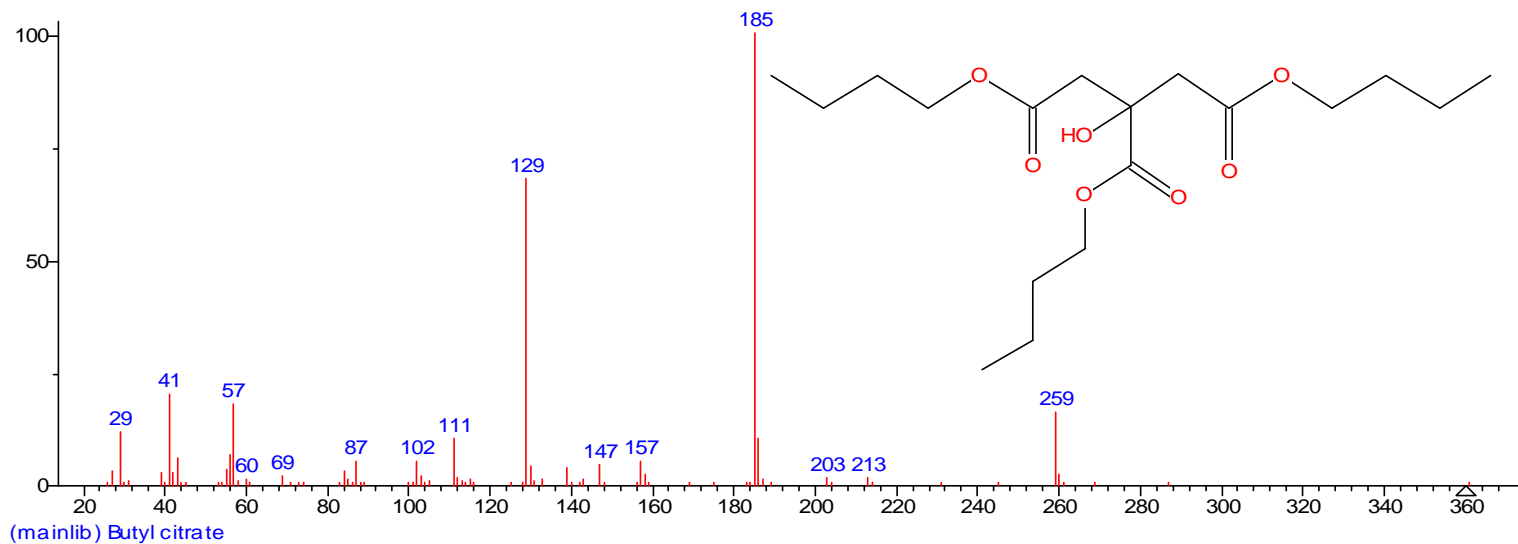


# Results: BPA

## Concentration of BPA in Selected Toy Samples



# Results: Other Compounds



# Results: Other Compounds

- Alternative Plasticizers
  - Butyl Citrate
  - Tributyl Acetyl Citrate
- Measurable levels in 9 of 17 toys
  - Large % amounts of either one or both = 7 toys
  - Highest amounts of BC & ATBC = Lion





# Conclusions: PVC Toys

- DBP & BBP:  $<50 \mu\text{g/g}$
- DEHP: Most detected phthalate
  - 15/17 Contained DEHP
  - 12/17  $>$  CPSC limit of 0.1% DEHP

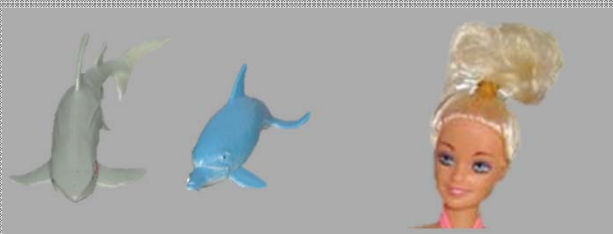


# Conclusions: PVC Toys

## Highest Amounts of DEHP



28000 µg/g



25000 µg/g

21000 µg/g



14000 µg/g

## Lowest Amounts of DEHP



- No phthalates but % of alternate plasticizers
  - Tributyl Acetyl Citrate
  - Butyl Citrate

# Conclusions: PVC Toys

- Total Phthalates
  - Highest total
    - Donkey (DIDP & DINP)
  - Oral Contact Toys
    - Snorkel mouthpiece (> limit)
  - Possible Oral Contact Toys
    - Duck (DEHP & BPA)
- Bisphenol A
  - Detected in 3 of 17 toys
  - Up to 1200 µg/g (Doll Head)



# Conclusions

- HDPE Toys contained low amounts of phthalates
  - Only DNOP detected (< limit)
  - Higher alkanes seen for one toy part
- PVC toys
  - Most of the toys contained large amounts of DEHP > all limits
  - Some PVC toys also contained DINP, DIDP and DNOP
  - BPA detected possible oral contact toys: Duck & Doll Head
  - 50% of PVC toys contained % quantities of alternate plasticizers
- Further studies planned on the other polymer toys





# Standards Used in This Study

## Phthalate & BPA Standards from SPEX CertiPrep:

- S-509: Bisphenol A Standard
- CRM-PE001: PE QC Standard
- CRM-PEBLK: PE Blank
- **CRM-PVC001: PVC QC Standard**
- **CRM-PVCBLK: PVC Blank**
- CLPS-1: Internal Standards





# Thanks

- SPEX CertiPrep Chemists
- CEM Corporation



# CEM Applications Support

- For Applications Support
  - Email: [analytical.support@cem.com](mailto:analytical.support@cem.com)
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# Questions?

**Additional questions can be sent to  
[CRMSales@spex.com](mailto:CRMSales@spex.com)**

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- 
- A close-up photograph of a clear glass bottle pouring white wine into a stemmed glass. The wine is a pale yellow color and is captured mid-pour, creating a dynamic splash and bubbles within the glass. The background is a plain, light color.

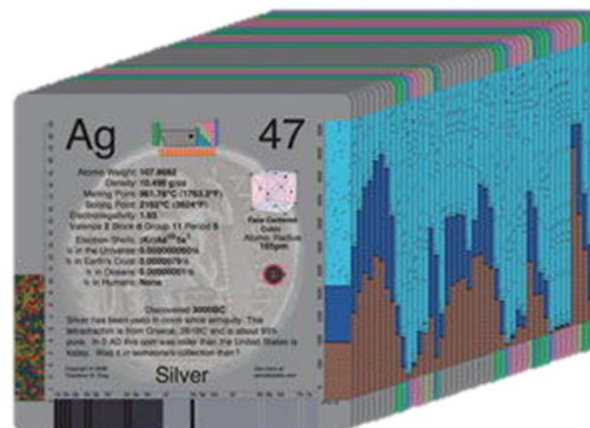
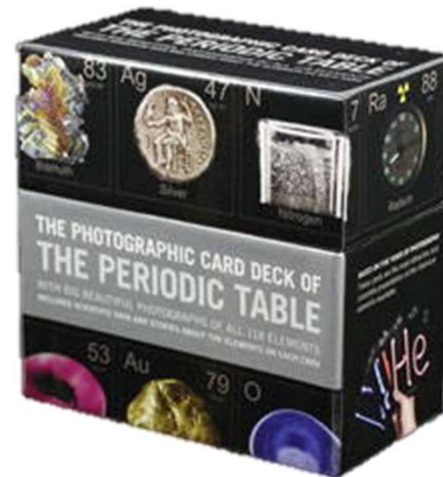
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