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App Note

The Effect of Heat Exposure on BPA and Phthalate Content in Commercial Bottled Water

Introduction

The goal of the present study was to examine the phthalate and bisphenol A (BPA) levels of several popular commercial bottled waters in comparison with municipal tap water. In addition, the study attempted to discover whether the phthalate and BPA levels increased after being heated one week at temperatures equivalent to those reached inside an automobile during the summer (60 °C). Samples were extracted and tested for phthalate and BPA levels by GC/MS. The concentration of phthalates and BPA found in all the commercially bottled water samples and the municipal water sources were either non-existent or well below established guidelines. In addition, the exposure of bottled water to heat did not significantly increase the concentration of phthalates. BPA was not detected in any of the bottled water or municipal water source.

Materials and Methods

Reagents

HPLC grade water, LC-MS grade water, dichloromethane (CH_2Cl_2 or DCM), and acetone were purchased from major chemical distributors. All of the solvents were contained in glass containers with plastic caps. The other reagent materials such as the sodium sulfate, sodium hydroxide, and hydrochloric acid were also purchased at major chemical distributors in ACS reagent grade. The solid reagent materials were contained in plastic containers with plastic cups.

Reagent Preparation

The solid chemicals for this experiment were contained original manufacturers' plastic containers. In order to produce a blank with the least amount of outside contaminants, the solid reagents were rinsed well with several milliliters of dichloromethane (DCM) per gram of solid material. After the DCM had drained, the solids were placed in a 210 °C oven for 10-30 minutes to evaporate any remaining solvent.

Two 60 mL aliquots of the DCM rinses were collected from each of the solids washed to determine if phthalates were eluting from the solid materials. At the end of the experiment, pre-cleaned solids were rinsed a second time with DCM. This DCM rinse was also collected into two 60 mL aliquots for each solid. The "pre-cleaned" and "post-cleaned" solid rinses were analyzed for BPA and phthalates

Standards

Spex CertiPrep standards were used in this experiment:

- Phthalate Ester Standard (1,000 µg/mL) in Hexane (Part # 8061-X)
- Bisphenol A Standard (1,000 µg/mL) in Acetone (Part # S-509)
- Deuterated Internal Standard Mix (2,000 µg/mL) in CH_2Cl_2 (Part # CLPS-I90)
- Surrogate Standard Mix (4,000 µg/mL) in CH_2Cl_2:Benzene (Part # CLPS-SC4)

Standard Preparation

Working standard solutions of the phthalate esters, bisphenol A and surrogate standard mixes were created at the 100 µg/mL level with DCM. A combined standard mix at the 20 µg/mL level prepared with DCM was created using the bisphenol A standard, the phthalate ester standard and the surrogate mix standard. All standards were stored at 4 °C.

Table 1. Target compounds observed in laboratory and consumer water supply.

Name	Abbreviation	Retention Time	Ions	Structural Formula	CAS #
Diethyl phthalate	DEP	8.43	149, 177, 150, 65	$C_{12}H_{14}O_4$	84-66-2
Diisobutyl phthalate	DIBP	10.28	149, 57, 41, 223	$C_{16}H_{22}O_4$	84-69-5
Di-n-butyl phthalate	DBP	10.8	149, 150, 29, 41, 57	$C_{16}H_{22}O_4$	84-74-2
Bisphenol A	BPA	11.83	213, 228, 119, 214, 91	$C_{15}H_{16}O_2$	80-05-7
Butyl benzyl phthalate	BBP	12.42	149, 91, 206, 65, 104	$C_{19}H_{20}O_4$	85-68-7
Di(2-ethylhexyl) phthalate	DEHP	12.95	149, 167, 279, 71	$C_{24}H_{38}O_4$	117-81-7

Sample Collection & Treatment

Identical sets of three commercial bottled water brands were purchased November, 2008 at a local retail store. The bottled water samples were in plastic containers with plastic screw caps. The plastic identification code on the bottles was "1", indicating the bottles were composed of PET. The bottled water sources as stated by the packaging were as follows: Brand A: purified public water sources, USA; Brand B: spring water, France; and Brand C: spring water, Maine, USA. One set of bottled water was left at ambient laboratory temperature for the entire experiment. A second set of identical bottled water was placed in an incubating oven set at 60 °C for one week to simulate exposure to temperatures reached inside vehicles during hot summer days in an effort to determine whether high temperatures cause an increase in phthalates or BPA. The heated bottles of water were allowed to cool for a day before the samples were measured out into 500 mL aliquots testing. There was no apparent loss of water volume found between the heated and room temperature bottles.

Water samples were taken from municipal water to compare the composition of consumer municipal water sources to the bottled water sources. Several sources of laboratory water were also tested for phthalates (see our previous application note on laboratory water). In addition to the bottled water, several blanks and recovery samples were created using LC-MS water. BPA and separate phthalate recovery samples were created by spiking 1 mL of the 100 µg/mL working standards into 500 mL of LC-MS water.

Instrumentation and Analytical Conditions

Samples were analyzed by GC/MS on a 5% diphenyl (CV-5) capillary column (3.0 m x 0.25 mm x 0.25 µm). The GC oven temperature program was an initial temperature of 55 °C for one minute, temperature ramped to 200 °C (20 °C/min) and held for one minute then raised to 310 °C at 30 °C/min and held for a final six minutes. The GC/MS interface and MS source were both 280 °C. The injected volume of sample extract was 1 µL.

The MS was operated in EI scan mode with a scan range of 35-450 m/z. The list of targeted ions for each analyte is summarized in Table 1. The presence of at least two predominant ions and a corresponding retention time was considered a confirmation of identity.

Extraction Procedure

A modified liquid-liquid acidified extraction method based on BPA extraction by del Olmo et al. was done, followed by an added base extraction.

500 mL of each water sample were measured into a cleaned and dried separation funnel. 15 g of cleaned NaCl were added to each water sample and shaken until dissolved. Hydrochloric acid (37% ACS grade) was added drop-wise until the resulting pH was below pH 3.

The samples were extracted using two 30 mL aliquots of DCM. To each 30 mL aliquots of DCM was added 0.5 mL of surrogate standard (100 µg/mL). The first 30 mL aliquot of DCM was added to the separator funnel and shaken for 30 seconds to one minute. The organic phase was collected into a 60 mL VOA vial. The second aliquot of 30 mL of DCM was added to the funnel and the process repeated. The organic phase was dehydrated using "cleaned" Na_2SO_4.

For the base extraction, NaOH solution was added until the pH of the water was measured from 9-10. The extraction procedure for the base phase of the samples was the same as the acid phase extraction. The acid and base phase extracts of each sample were combined and concentrated to 1 mL. All concentrated extracts were spiked with CLPS-I90 internal standard mix (2,000 µg/mL) prior to GC/MS analysis.

Blanks and recovery standard samples were extracted in the same manner as all of the water samples.

Results

Each of the commercial bottled water brands had less than 10 ppb total phthalates at room temperature. None of the bottled water samples contained detectable amounts of BPA. The total number of phthalates found in the bottled water ranged from two to six different phthalates. In comparison, the municipal tap water had less than 4 ppb total concentration of phthalates and two different detectable phthalates. The municipal water did not contain detectable amounts of BPA. See table 1 for target compounds detected in consumer water sources. Duplicate samples of the commercial bottled water were held at 60 °C temperatures for one week. The samples were then analyzed to determine if the heat exposure increased the BPA and phthalate levels in the heated temperature samples (see Figure 1). All of the bottled water samples had total concentrations of target compounds of less than 12 ppb. The heated samples had a small increase in the total number of target compounds as compared with the corresponding room temperature samples. The largest change was an increase from two identified phthalates to five identified phthalates for brand A (see Figure 2).

The levels of DEP and BBP increased slightly in the heated samples of all three brands while the level of DEHP decreased in brands B and C but remained virtually unchanged in brand A. Several researchers, including Jie et al,; Casajuana & Lacorte; and Leivandara et al. found higher concentrations of DEHP in water samples exposed to temperatures below 20 °C than water samples exposed to higher temperatures. These results suggest that DEHP may degrade at higher temperatures (see Figure 3).

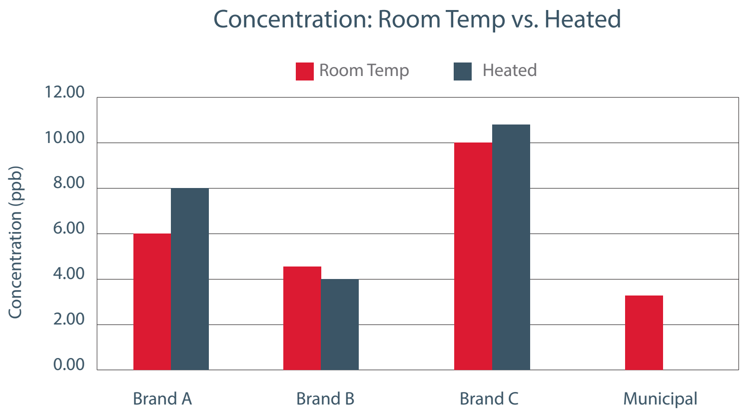

Figure 1. Comparison of total concentration compounds in consumer water sources in ppb.

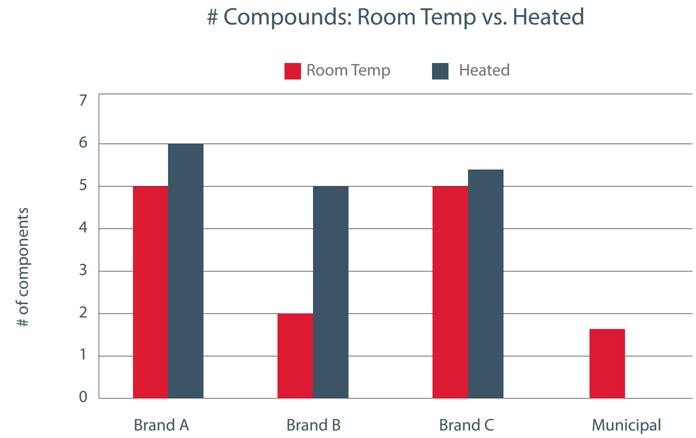

Figure 2. Comparison of number of compounds in room temperature vs. heated commercial water.

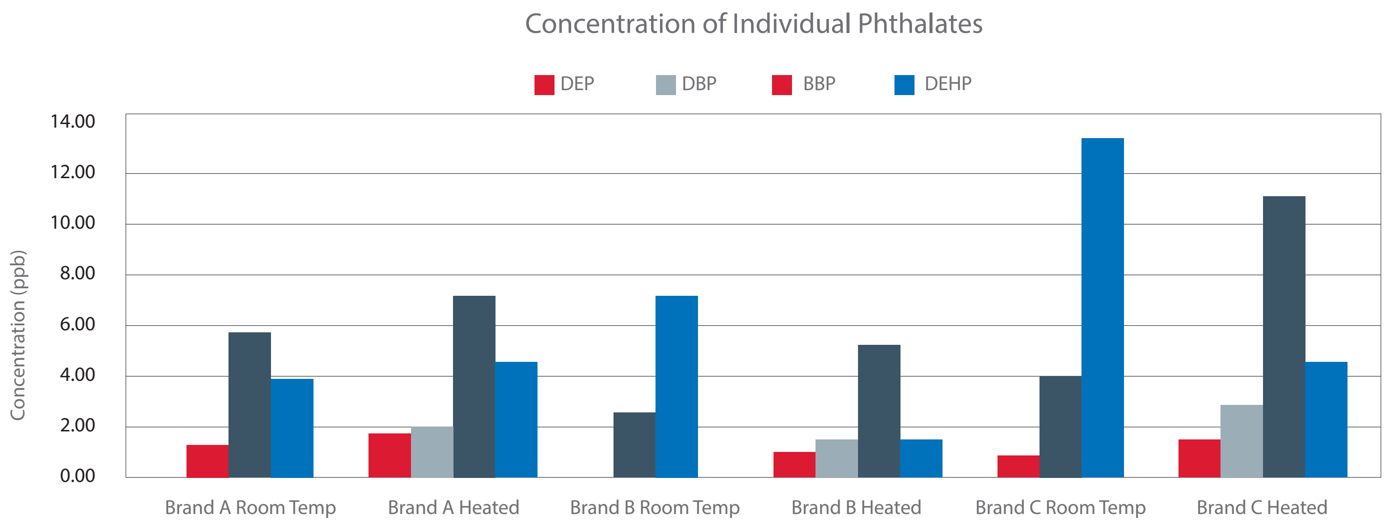

Figure 3. Changes in individual phthalate levels in bottled water after exposure to heat (in ppb).

All of the consumer water sources had less than 11 ppb of total targeted compounds. The most prevalent phthalates found in the consumer water sources were BBP and DEHP. In the bottled water industry the common phthalate (2-ethylhexyl) phthalate (DEHP) is often used as a gasket for inside the plastic cap of the bottles. BPA was not found in any of the bottled water sources or municipal water samples. The water samples from the municipal tap sources had the overall lowest amount of phthalates of all the consumer and laboratory sources.

Conclusions

The first part of our study looked at the phthalate and BPA levels in bottled water. We compared these samples to each other and to samples of other consumer and laboratory waters maintained at room temperature. Looking at the number of compounds of interest and their concentration, it was found that there was no significant difference in levels between the brands of bottled water studied.

The second part of our study was to determine whether our data supported the commonly debated theory that heating bottled water increases the level of phthalates and BPA in the water. Our results did not find any significant increase in the concentration of phthalates in the commercial bottled water after being heated, however, there was a slight increase in the number of phthalates detected. One phthalate, DEHP, appeared to decrease in two of the water brands after heating. Studies cited previously seem to suggest there is a possibility that some phthalates, DEHP in particular, are subject to degradation at temperatures above 20 °C.

There was little to no statistical difference between phthalate levels in the different brands of bottled water and the municipal water sources. In comparing the other consumer water sources we found that the levels and numbers of phthalates in municipal tap water were generally slightly lower than the amount and concentration of phthalates found in bottled water.

Additional Resources

To watch our webinar on Toxic Metals in Gourmet Foods, an analysis of trace metals in common gourmet foods including salt, chocolate and fish, visit our YouTube channel at www.youtube.com/spexcertiprep.

References

- M. del Olmo, A. Gonzalez-Casado, N.A. Navas, J.L. Vilchez. Determination of bisphenol A (BPA) in water by gas chromatography-mass spectrometry. *Analytica Chimica Acta* (1997), 346: 7-92.
- Jie, C., Guo-Lan, H., Xin, L., De-Gang, M., & Yuan, W. DEHP enrichment in the surface microlayer of a small eutrophic lake. *Water Research* (2003), 37: 4657-4662.
- Casajuana, N., and Laborte, S. "New Methodology for the Determination of Phthalate Esters, Bisphenol A, Bisphenol A Diglycidyl Ether, and Nonylphenol in Commercial Whole Milk Samples." *Journal of Agricultural and Food Chemistry* (2004), 52: 3702-3707.
- Casajuana, N., and Lacorte, S. "Presence and Release of Phthalic Esters and Other Endocrine Disrupting Compounds in Drinking Water." *Chromatographia* (2003), 57: 649-655.
- Leivadara, S.V., Nikolaou, A.D., and Lekkas, T.D. "Determination of organic compounds in bottled waters." *Food Chemistry* (2008), 108: 277-286.

For additional product information, please contact us at 1.800.LAB.SPEX or CRMSales@spex.com.

Phone: +1.732.549.7144 • +1.800.LAB.SPEX
Fax: +1.732.603.9647
spexsales@antylia.com