

DETERMINATION OF PHTHALATES AND BISPHENOL A IN BOTTLED DRINKING WATER

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INTRODUCTION

Phthalates and Bisphenol A (BPA) are chemicals widely used in manufacturing of plastics and epoxy resin. They are endocrine disrupters that can mimic human hormones. These chemicals are ubiquitous in our environment and can be found in 95% of humans. Recent studies have found human exposures to phthalates and BPA resulted in adverse health effects, such as altered hormone levels, reproductive effects, or increased incidence of diseases, including cancer [1].

EPA has regulated the maximum contaminant level (MCL) for Bis (2-ethylhexyl) phthalate to be 6 ppb [2] and Bis (2-ethylhexyl) adipate to be 400 ppb [3] in drinking water. EPA has not regulated BPA in drinking water but has set up current safety level of BPA exposure to be 50 μg/kg/day [1]. Bottled drinking water is often packed in plastic containers, thus it is important to determine phthalates and BPA levels in bottled drinking water. Eight bottled drinking water samples from different manufactures (Sample 1-8) and one water sample from a private well (Sample 9) were tested in this study.

Seven phthalates including Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Dibutyl phthalate (DBP), Benzyl butyl phthalate (BBP), Bis (2-ethylhexyl) adipate (DEHA), Bis (2-ethylhexyl) phthalate (DEHP), and Di-n-octyl phthalate (DNOP) were determined by solid phase extraction (SPE) with UCT's specially designed C18 cartridges followed by GC/MS detection. BPA was extracted into acetonitrile by QuEChERS (acronym for Quick, Easy, Cheap, Effective, Rugged and Safe) procedure. An aliquot of the extract was concentrated to dryness, derivatized by N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide with 1% tert-butyldimethylchlorosilane (MTBSTFA/1%TBDMCS), and detected by GC/MS in SIM mode.

Chemical structure

Dimethyl phthalate	O CH ₃	Bis (2-ethylhexyl) adipate	
Diethyl phthalate	CH ₃	Bis (2-ethylhexyl) phthalate	
Dibutyl phthalate		Di-n-octyl phthalate	
Benzyl butyl phthalate		Bisphenol A	HO \sim CH ₃ \sim OH CH ₃

EXPERIMENTAL

Standards and Reagents:

Phthalates and internal standards were purchased from Restek (Bellefonte, PA). BPA and BPA d16 were purchased from Sigma-Aldrich (St. Louis, MO). Triphenylphosphate was purchased from Cerilliant (Round Rock, TX). GC grade dichloromethane, ethyl acetate, toluene, and HPLC grade acetonitrile were purchased from Spectrum (New Brunswick, NJ).

Table 1: Nine water samples tested in this study

Water sample	From	Description			
Sample 1	CA	Natural spring water			
Sample 2	NE	100% Natural Spring Water			
Sample 3	PA	Purified water enhanced with minerals for taste			
Sample 4	GC	Natural Spring Water			
Sample 5	FL	N/A, label missing			
Sample 6	MN	Purified water, enhanced with minerals for a pure, fresh taste			
Sample 7	PA	Purified drinking water with flavor enhancing minerals			
Sample 8	TN	Purified water, enhanced with minerals for a pure, fresh taste			
Sample 9	PA	From a private well			

PHTHALATES TESTING PROCEDURES

Apparati

83 mL Universal 525 cartridge with 1500 mg special blend of C18 (UCT cat#: ECUNI525)
Vacuum pump (UCT cat#: ECROCKER400)

6-station manifold (UCT cat#: ECUCTVAC6)

Contribute a dente y / LCT and #1. ECUCTADD

Cartridge adaptor (UCT cat#: ECUCTADP)

20 L waste trap (UCT cat#: ECUCTTRAP20)

Fritted reservoirs with 50 µm Teflon frit (UCT cat#: ERTFT1FUNIP)

Sodium sulfate, anhydrous, ACS, Granular 60 Mesh (UCT cat#: ECSS05K)

SPE procedure:

- 1. Assemble the extraction system by attaching glass adaptors, C18 SPE cartridges to the 6-station manifold.
- 2. Wash the cartridges with 5 mL 1:1 EtOAc:MeCl2.
- 3. Condition the cartridges with 10 mL MeOH and 10 mL reagent water.
- 4. Load water samples, adjust the flow rate at a fast drop-wise fashion (about 10 mL/min).
- 5. Dry the cartridges under full vacuum for 10 min.
- 6. Insert 40 mL glass vials into the manifold to collect eluents.
- 7. Elute with 10 mL EtOAc, followed with 10 mL MeCl2.
- 8. Dry the extracts by passing through fritted reservoirs holding 10 g sodium sulfate, use new vials to collect the dried extracts, rinse the vials and salts with MeCl2, collect the rinse too.
- 9. Concentrate the dried extracts to 1 mL under a gentle N2 stream at 35 °C using TurboVap evaporator.

10. Add internal standards (IS) and inject 1 µL to GC/MS for analysis.

Instrumentation

Full scan: 45-500 amu

GC/MS: Agilent 6890N GC coupled with 5975C MSD, equipped with 7683 auto sampler. GC column: Restek Rxi®-5sil MS 30m*0.25mm*0.25um

Injector: 1 µL splitless injection at 250 °C, with a split vent of 30 mL/min at 1 minute.

Liner: 4 mm splitless gooseneck, 4mmID*6.5mmOD*78.5mm (UCT cat#: GCLGN4MM)

Oven temperature program: Initial oven temperature of 55 °C, hold for 1 minute, ramp at

10 °C/min to 200 °C, ramp at 7 °C/min to a final temperature of 320 °C and hold for 0.36 minute. **Carrier gas**: Ultra high purity Helium at a constant flow of 1.2 mL/min. **MSD condition**: Aux temperature: 280 °C, MS Source: 250 °C, MS Quad: 150 °C



BISPHENOL A TESTING PROCEDURES

Apparatus

50 mL QuEChERS centrifuge tubes and salts packed in Mylar pouch (4000 mg magnesium sulfate, 1000 mg sodium chloride, 500 mg sodium citrate dibasic sesquihydrate, and 1000 mg sodium citrate tribasic dehydrate) (UCT cat#: ECQUEU750CT-MP) Derivatizing agent: MTBSTFA w/1% TBDMCS (UCT cat#: SMTBSTFA-1-1)

Sodium culfato, anhydroug, ACS, Granular 60 Mach /LICT cat#: ECSSOEk

Sodium sulfate, anhydrous, ACS, Granular 60 Mesh (UCT cat#: ECSS05K)

QuEChERS Procedures:

- 1. Add 10 mL water sample into 50 mL QuEChERS centrifuge tube, spike with 5 ng/mL Bisphenol A d16 (BPA d16), let equilibrate for 15 minutes.
- 2. Add 10 mL MeCN, vortex 30 seconds, add the salts in Mylar pouch. Shake vigorously for 1 min, then centrifuge at 4000 rpm for 5 minutes.
- 3. Transfer 1 mL supernatant into 12*75 mm test tube, concentrate to dryness by N2 at 35 °C.
- 4. Add 50 μL pyridine and 50 μL MTBSTFA/1%TBDMCS, derivatize at 70 °C for 30 min.
- 5. Cool down, concentrate to dryness by N2 at 35 °C.
- 6. Reconstitute with 75 μ L toluene and 25 μ L of 2 ppm triphenyl phosphate (TPP) (IS), vortex.
- 7. Transfer to auto-sampler vial with 100 μ L insert, inject 1 μ L to GC/MS.

Instrumentat

GC/MS: Agilent 6890N GC coupled with 5975C MSD, equipped with 7683 auto sampler.

GC column: Restek Rxi®-5sil MS 30m*0.25mm*0.25um

Injector: 1 µL splitless injection at 250 °C, split vent of 30 mL/min at 1 min.

Liner: 4 mm splitless gooseneck, 4mmID*6.5mmOD*78.5mm (UCT cat#: GCLGN4MM)

Glass wool for liner: Restek Deactivated Wool

Oven temperature program: Initial oven temperature of 100 °C, hold for 1 min; ramp at 20 °C/min to 300 °C, hold for 1 min; ramp at 40 °C/min to 320 °C, hold for 2.5 min.

Carrier gas: Ultra high purity Helium at a constant flow of 1.2 mL/min.

MSD condition: Aux temperature: 280 °C, MS Source: 230 °C, MS Quad: 150 °C

Tune file: atune.u

Simultaneous Scan/SIM:

Scan range: 50-500

SIM: Dwell time: 100 ms for all ions

Group 1: 9.0 min: 326.1, 325.1 (TPP)

Group 2: 10.5 min: 441.3, 456.3, 442.3 (BPA-2TBDMS) 452.4, 470.4, 453.4 (BPA d16-2TBDMS)



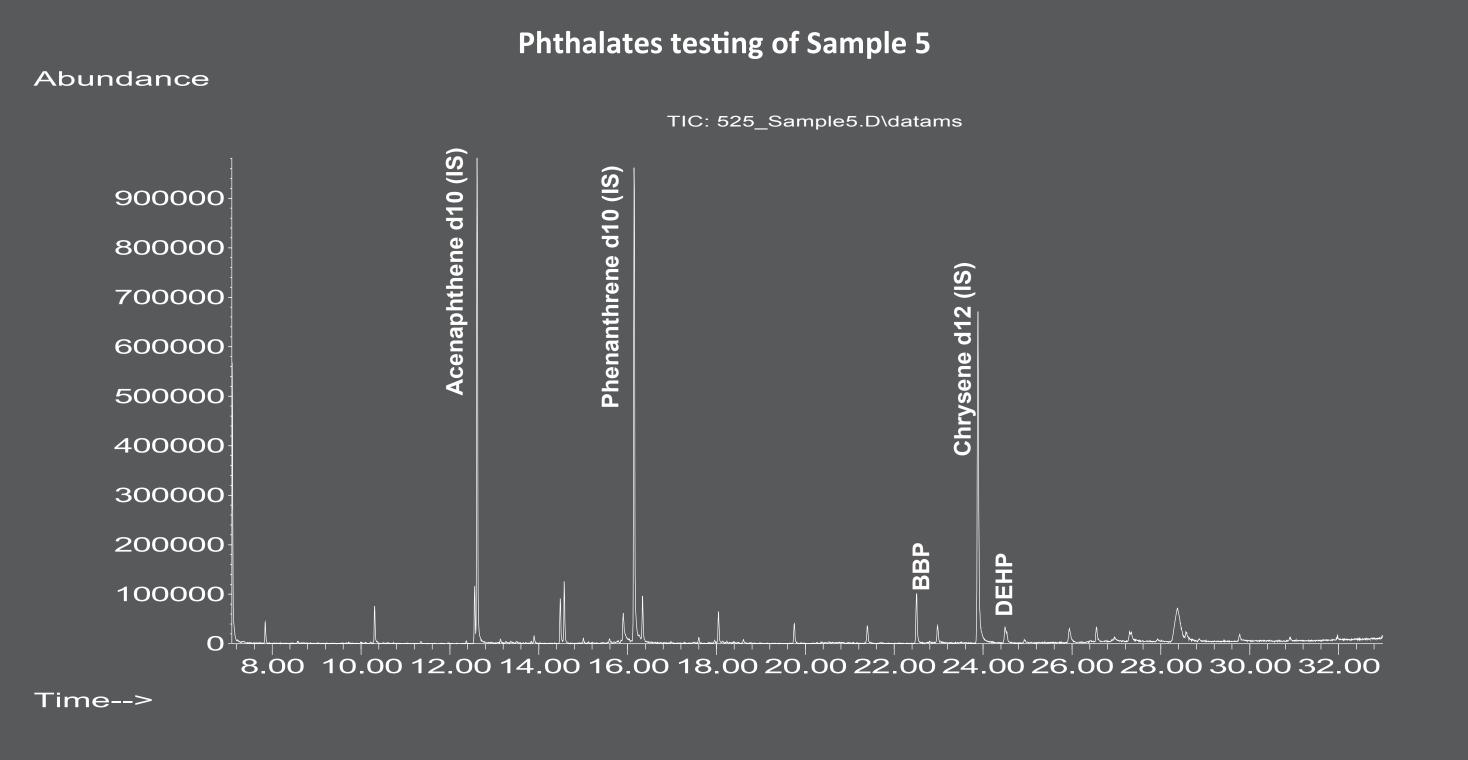
RESULTS

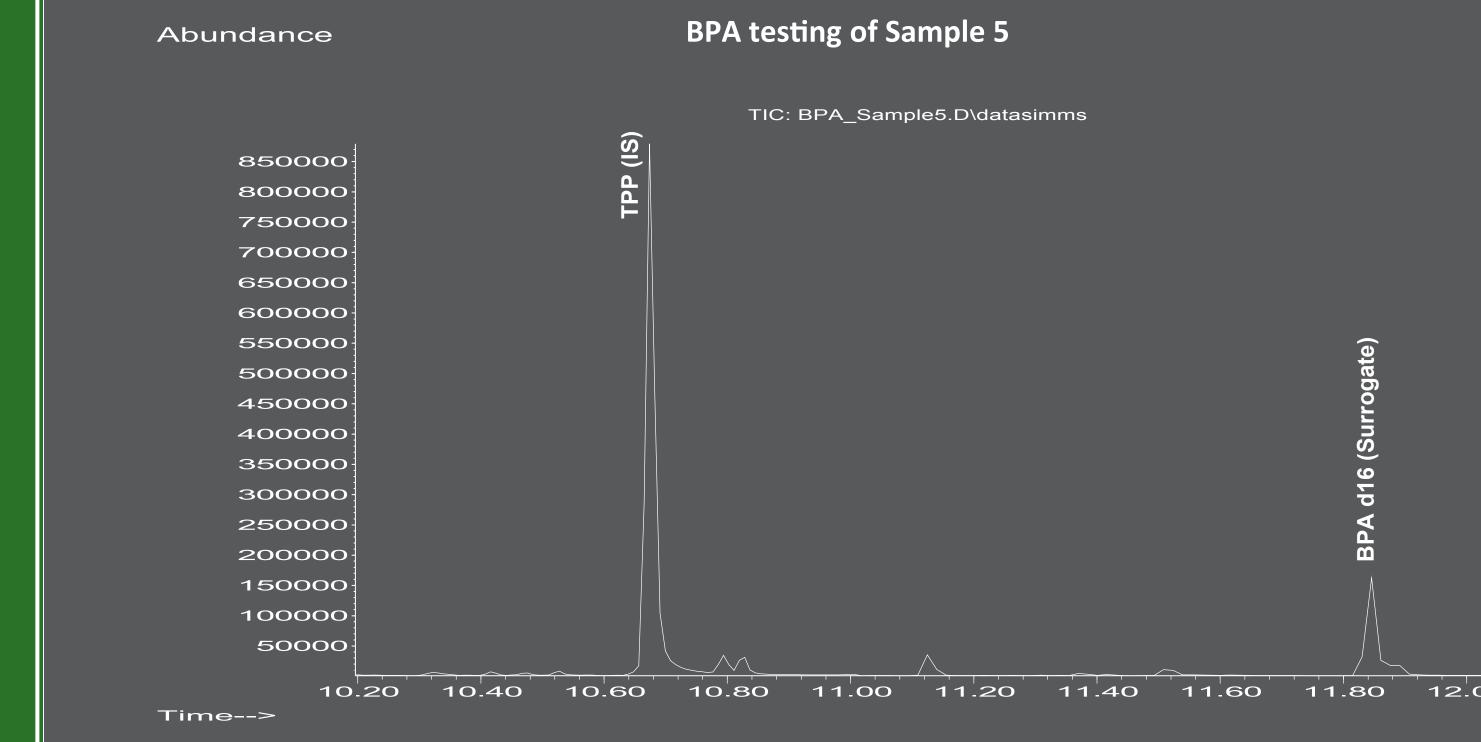
The minimal reporting levels of phthalates are 0.33 ppb for Sample 1 to 8, and 0.56 ppb for Sample 9 due to insufficient sample volume.
The minimal reporting level for BPA is 1.0 ppb for all the nine samples. Table 2 listed the detected concentrations.

Table 2: Detected phthalates and BPA levels in the blank and nine water samples (unit: ppb)

Compound	Blank	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9
Dimethyl phthalate	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.56
Diethyl Phthalate	< 0.33	1.29	0.43	0.69	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.56
Dibutyl phthalate	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.56
Benzyl butyl phthalate	0.40	0.53	0.59	0.50	0.43	2.48	0.43	< 0.33	0.36	1.62
Bis(2-ethylhexyl)adipate	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	26.71
Bis(2-ethylhexyl) phthalate	< 0.33	0.36	< 0.33	3.50	< 0.33	0.36	< 0.33	< 0.33	< 0.33	0.67
Di-n-octyl phthalate	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.33	< 0.56
Bisphenol A	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0

CHROMATOGRAMS:





CONCLUSIONS

In this study, eight bottled drinking water samples from different manufacturers and states, and one sample from a private well were tested for phthalates and BPA levels. Phthalates were determined by SPE using UCT's Universal 525 cartridge packed with proprietary C18. Four phthalates: DEP (up to 1.29 ppb), BBP (up to 2.48 ppb), DEHA (up to 26.71 ppb), and DEHP (up to 3.5 ppb) were detected, with the concentrations lower than the EPA regulated levels. The other three phthalates (DMP, DBP, and DNOP) were not found. BPA was determined by the QuEChERS procedure. An aliquot of the extract was concentrated to dryness and derivatized by MTBSTF/1%TBDMCS to form the more volatile TBDMS derivatives that can be detected by GC/MS. BPA was not found in the nine samples tested in this study.

REFERENCES

[1] http://www.umaryland.edu/bin/y/h/Phthalates_and_BPA_FINAL.pdf
[2] http://water.epa.gov/drink/contaminants/basicinformation/di_2-ethylhexyl_phthalate.cfm
[3] http://water.epa.gov/drink/contaminants/basicinformation/di-2-ethylhexyl-adipate.cfm