



ANALYSIS OF LABORATORY WATER SOURCES FOR BPA AND PHTHALATES

INTRODUCTION

Phthalate and bisphenol A (BPA) levels were studied in municipal water straight from the tap and processed through drinking water treatment systems as well as various samples of laboratory water from commercial sources and from deionized (DI) filtration systems. Samples were extracted and tested by GC/MS. The water samples taken directly from municipal tap water had relatively small concentrations of phthalates and BPA but, when decanted through consumer Point-of-Use (POU) drinking water filtration systems, the level of phthalates and BPA varied greatly depending on the type of system and the amount of water flushed from the system prior to the sample being taken. Laboratory water sources appeared to have the greatest variability on phthalate concentration with LC-MS grade water having the lowest phthalate and BPA concentrations of all the laboratory water.

1. SAMPLE AND ANALYTICAL METHOD

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 from major chemical distributors in ACS reagent grade. The solid reagent materials were contained in plastic containers with plastic caps.

Reagent Preparation

The solid chemicals for this experiment were contained in 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 DCM per gram of solid material. After the DCM had drained, the solids were placed in a 210 °C oven for 10 to 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 CH₂Cl₂ (Part # CLPS-I90)
- Surrogate Standard Mix (4,000 µg/mL) in CH₂Cl₂:Benzene (Part # CLPS-SC4)

Standard Preparation

Working standard solutions of the phthalate esters, BPA 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 BPA standard, the phthalate ester standard and the surrogate mix standard. All standards were stored at 4 °C.

Instrumentation and Analytical Conditions

Samples were analyzed by GC/MS on a 5% diphenyl (CV-5) capillary column (3 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.

Sample Collection & Treatment

Water samples were taken from municipal tap water, and two point-of-use (POU) drinking water systems supplied by municipal tap water lines. POU system A was a dispensing unit for municipal water and has no filtration or sanitization functions. POU system B utilized a UV sanitation system and a compressed carbon filter. The POU drinking water systems were sampled at the start of the day when the systems had not been in use for over twelve hours (i.e. stationary systems) and then sampled again after more than 2 L of water had been flushed through the system and dispensing apparatus.

Laboratory water samples were taken from a laboratory DI water storage bottle, a DI tap connected to a DI filtration source, a bottle of HPLC grade water, and a bottle of LC-MS grade water. Two samples of the DI laboratory water from the source tap were taken: first after standing without use for more than twelve hours and again after more than 2 L of water were flushed through the system.

In addition to the bottled water, municipal water and laboratory water samples, 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.

Extraction Procedure

A modified liquid-liquid acidified extraction method based on BPA extraction by del Olmo et al.¹ was followed. This acid extraction was followed by an added base extraction.

500 mL of each water sample was measured into a cleaned and dried separation funnel. 15 g of cleaned NaCl was 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 30 mL aliquots of DCM. 0.5 mL of surrogate standard (100 µg/mL) was added to each extract. The first extract 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 extract was added to the funnel and the process repeated. The organic phase was dehydrated using “cleaned” Na₂SO₄.

For the base extraction, NaOH solution was added until the pH of the water measured between 9 and 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.

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

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
Dicyclohexyl phthalate	DCP	12.96	149, 167, 55, 150, 249	C ₂₀ H ₂₆ O ₄	84-61-7

2. RESULTS

The solid reagents obtained for this study were packed in plastic containers and subject to phthalate contamination. In an effort to reduce phthalate contamination, the solid reagents were rinsed with DCM and dried in a 210 °C oven.

The initial DCM rinses of the NaCl and Na₂SO₄ samples showed a difference in amount of phthalates recovered between rinses. The first rinse of Na₂SO₄ contained fourteen phthalates. Subsequent rinses showed decreasing numbers and amounts of phthalates. The initial NaCl rinses had fewer types of phthalates present but an increased concentration of those phthalates when compared to the Na₂SO₄ rinses (Figure 1 & 2). By the third and fourth rinses, the levels of phthalates and BPA in the NaCl samples were not detectable. The most prevalent phthalates found in both the Na₂SO₄ and NaCl washes were diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di(2-n-butoxyethyl) phthalate (DBEP), and di(2-ethylhexyl) phthalate (DEHP).

The analysis of the DCM solvent blank and the DCM rinses of the NaOH solid showed that there were no detectable phthalates in either set of samples. The DCM extraction blanks contained no detectable BPA or phthalates.

Compounds such as the sodium chloride and the sodium sulfate appeared to be highly contaminated with a wide range of different types of organic contaminants. The level of these contaminants could alter the ability of a researcher to obtain accurate phthalate and BPA levels.

Laboratory Water Samples

Five sources of laboratory water were tested for BPA and phthalates. Three of these samples came from a laboratory deionization water system and two came from reagent grade bottled waters. The water from the deionized source was tested after sitting in the lines overnight and after flushing over 2 L of water (as described for the consumer POU systems). In addition to the flowing DI water, samples were taken from a laboratory carboy made of HDPE (High Density Polyethylene) containing DI water from the same source. The DI water in the carboy had been exposed to the carboy for an indeterminate amount of time, no less than three weeks. A sample of municipal tap water was taken directly from the laboratory sink faucet to compare to the laboratory water samples.

The highest levels of total concentration of phthalates and total number of phthalates were found in the HPLC grade water. The lowest total concentration of phthalates was found in the LC-MS grade water. The lowest total number of separate phthalates was found in the municipal tap water. DEHP and BBP had the highest concentration of all the phthalates in the laboratory water samples. The HPLC grade water was the only sample with a detectable amount of BPA (Table 2).

The laboratory water sources showed widespread contamination by a large number of phthalates as well as BPA. All water samples had a total concentration of target compounds of over 1 ppb.

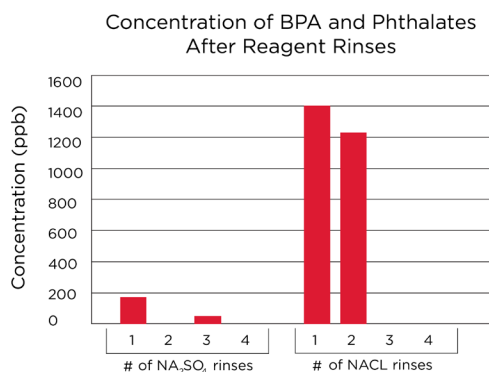


Figure 1. Comparison of total concentration (ppb) of BPA & phthalates detected in solid reagent rinses.

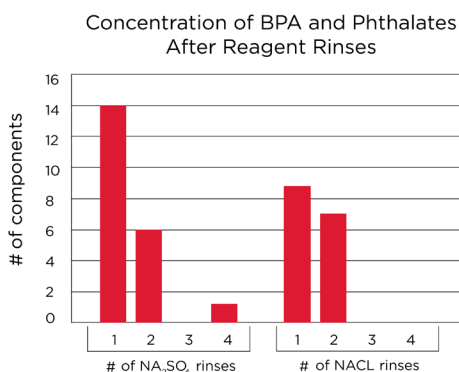


Figure 2. Comparison of total number of BPA & phthalates detected in solid reagent rinses.

Table 2. Phthalates and BPA concentrations found in laboratory water sources (ppb).

Compound	HPLC	LCMS	DI Source Flushed	DI Source	DI Bottle	Municipal Tap
DEP	6.28	0.18	0.00	0.30	0.50	0.00
DIBP	3.52	0.16	0.88	1.36	0.52	0.00
DBP	16.72	0.00	0.00	0.00	0.54	0.00
BPA	3.16	0.00	0.00	0.00	0.00	0.00
BBP	44.74	0.20	2.32	0.63	0.47	1.29
DCP	1.00	0.00	0.00	0.00	0.00	0.00
DEHP	15.60	0.63	5.92	26.41	2.44	1.94
Total c (ppb)	91.02	1.17	9.12	28.70	4.47	3.23
Total # of compounds	7	4	3	4	5	2

3. CONCLUSIONS

The innate problem associated with the study of phthalates and BPA in water was found to be the numerous potential sources of contamination. It was necessary to limit analyte contamination by attempting to remove phthalate and BPA residue from as many experimental components as possible. The cleaning of reagent solids with DCM and subsequent heating appeared to dramatically reduce the amount of phthalate and BPA contamination coming from the solid reagents.

The choice of laboratory water was critical to the analytes being measured. Common laboratory water sources, such as HPLC grade water or house DI water, may be within specifications for their intended and designated use, but were shown to be unsuitable for low level phthalate or BPA analysis.

Levels and numbers of phthalates in municipal tap water were generally low in phthalate concentrations (3 ppb). POU filtration, sanitization and dispensing systems had a wide range of variability in the number and concentration of phthalates depending on the system and the amount of flow through that system. In general, with regard to POU systems, it appeared allowing the system to void several liters of water prior to collection was effective in lowering the amount of phthalates and BPA dispensed.

The only consumer water source that was found to have BPA was the POU-A. Both the initial stationary samples and the subsequent flushed samples contained similar amounts of BPA (0.04 to 0.09 ppb).

The lowest amount of phthalates among the water sources was the LC-MS grade water with just over 1 ppb of phthalates and no detectable BPA.

4. REFERENCES

1. Analytica Chimica Acta 346 (1997) 87-92. "Determination of bisphenol A (BPA) in water by gas chromatography-massspectrometry." M. del Olmo, A. Gonzalez-Casado, N.A. Navas, J.L. Vilchez *
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5. ADDITIONAL RESOURCES

To watch our webinar on BPA and Phthalates in Consumer Products, including water bottles, cosmetics, and perfumes, visit our YouTube channel at www.youtube.com/spexcertiprep.