

# Automated, Economical Sample Preparation: Bottle Liquid-Liquid Extraction

The extraction of organics from water is fundamental in environmental, pharmaceutical, process, food, forensic, and other laboratories. Nearly all laboratories that perform organic analyses are equipped with a battery of separatory funnel (SF) and/or continuous liquid-liquid extractors (CLLEs) to conduct liquid-liquid extraction. For environmental laboratories that conduct liquid-liquid extractions in high volume on a routine basis, this task can be a critical element, often a bottleneck of a laboratory operation. The U.S. EPA imposes a seven-day holding time on water sample preparations, imparting a significant burden on extraction technicians, especially when there are so often delays in getting the samples from the field to the laboratory. If holding times are not met, analysis results are invalid and the laboratories are commonly charged with the responsibility to resample.

Laboratories equipped to do either CLLE or SF liquid-liquid extractions (for the environmental laboratory, most commonly Method 3510C or Method 3520C<sup>1</sup>) choose one or the other by considering the advantages and disadvantages of each. An assessment is made of available labor and capacity to extract the number of samples on hand, meet holding time requirements and data quality objectives, as well as turnaround time commitments. SFs are used primarily because a few sample preparations can be completed within several hours. However, SF extraction is extremely labor intensive and often fraught with problems of precision and accuracy. Emulsions, rendering the phase separation difficult and sometimes impossible, are too frequently observed. Extraction recovery can be inherently low for some species. CLLEs are costly and slow, difficult to clean, readily broken, and subject to drip rate variation, but require much less labor. For the extraction of herbicides from water using a lighter-than-water solvent, the use of CLLE is precluded, leaving no choice. The especially cumbersome herbicide method, with its extra steps, was an

additional driving force behind the development of the technique described here, so-named bottle liquid-liquid extraction (BLLE, or "Billie").

A simple concept in which water, in original sample bottles received directly from the field, is mixed with solvent and turned at a slow rate was explored and found to be markedly effective, eliminating the many problems associated with both SF and CLLE. The advantages of this new method are readily recognized by organic analysts who perform high-volume liquid-liquid extractions on a routine basis. Most notable benefits are striking simplicity and economy; radical reduction of labor, solvent, and solvent waste; ability to prepare a large number of samples at once; as well as freedom from emulsions. Extraction times can be significantly reduced while precision and overall quality are improved. There is no glassware to clean, no elaborate equipment needed, and virtually no labor required. The use of chlorinated solvents and other expensive supplies is sharply curtailed (a "green" technique).

Laboratory control sample (fortified blank) efficiencies for nearly 200 of the most important environmentally regulated semivolatile organic analytes including herbicides, pesticides, Method 625<sup>2</sup> components, and Appendix IX<sup>3</sup> Method 8270C target analytes were examined and compared to those obtained using conventional SF or CLLE techniques. While the study focuses on species of environmental interest, extraction efficiencies for a host of related chemical species can be readily gleaned. Also presented, an outcome of hundreds of studies conducted to validate this procedure, are little known but distinct recovery patterns and trends observed among SF, CLLE, and BLLE, which will help analysts to improve data quality. The dramatic effects of starting the semivolatile extraction at an acidic pH as opposed to base first are elucidated.

## Experimental

Early experiments were conducted by rotating bottles on two ordinary barbecue rotisserie spaced a few inches apart mounted on a wooden substrate. Two-inch sections of rubber hose were cut and slid over square rotisserie rods to create a smooth, rotating surface. Clear, wide-mouth 1-L glass jars were filled approx. 90% full with tap water and fortified with several drops of a 0.1% solution of methyl yellow (p-dimethylaminoazobenzene) in methanol, followed by a few drops of 1:1 sulfuric acid. (Methyl yellow, an Appendix IX target analyte, yellow in color in basic water and bright red in acidic conditions, served as a visual indicator of extraction efficiency.) Forty milliliters of methylene chloride (DCM) was then added along with 10 g of rock salt. The jar was placed horizontally on the rotisserie rack and turned at approx. 3 rpm for 22 hr. After the 22-hr period, the water layer was completely clear and the DCM layer was bright yellow.

The experiment was repeated, altering the initial pH to basic conditions. After 22 hr,



Figure 1 Photograph of prototype BLLE bottle rotation device.

the DCM layer was observed to be bright yellow, while the water layer retained a yellow tinge.

Encouraged by this crude initial study, more elaborate experiments were designed, fortifying deionized, charcoal-filtered water in 1-L bottles with 50  $\mu\text{g}$  of a 76-component mixture of semivolatile organics (Mega-Mix, catalog no. 31850, Restek Corp., Bellefonte, PA) containing acid, neutral, and basic extractables. Traditional 8270C surrogates were also added at levels customary for laboratories following environmental procedures. The pH was brought down to  $<2$  and 40 mL DCM was added. Following a 22-hr turn at 3 rpm, the bottle contents were transferred to a 2-L separatory funnel and the DCM was collected. The water layer was returned to the bottle, the pH readjusted to  $>12$ , and a second 22-hr turn was performed. The combined acid/neutral and basic extracts were concentrated to 1 mL using a Turbo-vap apparatus (Zymark Corp., Hopkinton, MA) prior to analysis by the conventional environmental 8270C method. All components were recovered, most with 75% or greater recovery. Phenol, pyridine, and N-nitrosodimethylamine were low, however, recovering only at about the 10% level.

Additional studies were undertaken to improve the recovery of the phenol and amines. The ionic strength of the water was increased by adding sodium chloride, and the effect of intermixing diethyl ether and other solvents with the DCM was explored. Extracting with a 60/40-mL mix of DCM/diethyl ether in place of pure DCM was found to markedly enhance the recovery for phenol. Adding sodium chloride to the water (250 g per 1000 mL) significantly improved the recovery for the pyridine and other amines.

A heavy-duty turning apparatus was constructed using five sets of 6-ft-long galvanized rods mounted on a rack driven by an electric motor, sprockets, and chain (Figure 1). The device was engineered to turn at triple the earlier experiment rate (12 rpm) as well as to enable 30 1-L bottles to be spun at once. With this apparatus, scores of additional experiments were conducted over years of time to examine the effects of the faster spin, varied durations of spin, alternate mixtures of salt, ether, as well as reversing the extractions by initializing

with base rather than acid (Method 625). A vented stopcock bottle cap adapter was designed (Figure 2) to allow the solvent to be removed directly from the bottle, thereby eliminating the need to transfer to a separatory funnel.

Using the new rotisserie, the following procedures were optimized and are offered here for use:

**Procedure A: DCM/ether**—Generally semivolatile acid and base-neutral extractables (Environmental Methods 8270 and 625, specifically)

Step 1: Remove the sample bottle from refrigerated storage and allow to equilibrate to room temperature.

Step 2: Shake the bottle briefly to homogenize the sample. Discard up to 250 mL and mark the water level meniscus on the bottle for subsequent accurate volume measurement.

Step 3: Fortify the sample with surrogates and quality control (QC) samples with appropriate solutions. Shake to mix.

Step 4: Adjust the pH of the sample with approx. 3 mL of 12N sulfuric acid. Check that pH is  $\leq 2$  with wide-range pH paper. (A lesser amount of a stronger acid solution may be substituted.)

Step 5: Add 100 mL of a 60/40 mix of DCM/diethyl ether (BHT-preserved ethyl ether used for this study; methanol-preserved likely as good).

Step 6: Cap bottle, place horizontally on rotation rack, and spin for 12 hr at 12 rpm. (Because the spinning is gentle, there is no pressure buildup, and venting is not necessary.)

Step 7: Attach an adapter and stopcock to the bottle or transfer the bottle contents to a conventional separatory funnel to effect phase separation. Discharge the DCM/ether layer (heavier than water) into a 200-mL bottle. Add approx. 10 g of sodium sulfate to the extract and mix.

Step 8: If using a separatory funnel, return the water to the original bottle and readjust the pH of the water to  $\geq 12$  (check with pH paper) using approx. 9 mL of 6N NaOH or a smaller quantity of 10N NaOH.

Step 9: Add 80 mL of a 50/30 DCM/ethyl ether mix and return to rotisserie for a second 12-hr period.

Step 10: Reattach an adapter and stopcock to the bottle or transfer the bottle contents to a separatory funnel to effect phase separation. Combine the DCM/ether layer with the initial DCM/ether extract.



Figure 2 Photograph of bottle cap attachment enabling phase separations to be conducted directly in bottles.

Step 11: Allow the extract to remain in contact with sodium sulfate for at least 2 hr, mixing periodically. If the sodium sulfate forms clumps, add additional sodium sulfate until it remains free-flowing. (Adding sodium sulfate directly to the extract in place of a common practice of pouring the extract through a funnel or column of sodium sulfate serves several purposes. The sodium sulfate remains in contact with the extract for longer periods of time, the successful removal of water is visibly indicated by an absence of clumps, and much less sodium sulfate is required.)

Step 12: Drain the extract through a glass fiber filter and concentrate the extract using conventional evaporative techniques. Submit for analysis.

Step 13: Recharge the original bottle with tap water to the original mark and pour into a 1000-mL volumetric flask to record the exact volume extracted.

**Procedure B: Hybrid**—Generally semivolatile acid and base-neutral extractables (Environmental Methods 8270 and 625, specifically)

Steps 1–7: Identical to Procedure A

Step 8: Returning the water to the original bottle, add 190 g of sodium chloride and shake to dissolve.

Step 9: Readjust the pH of the water to  $\geq 12$  (check with pH paper) using approx. 9 mL of 6N NaOH or a smaller quantity of 10N NaOH.

Step 10: Add 80 mL of DCM and return to rotisserie for a second 12-hr period.

Steps 11–14: Identical to steps 10–13 of Procedure A.

Procedure C: Herbicides (Environmental Methods 8151 and 615 including hydrolysis step)

Step 1: Remove the sample bottle from refrigerated storage and allow to equilibrate to room temperature.

Step 2: Shake the bottle briefly to homogenize the sample. Discard approx. 250 mL and mark the water level for later measurement.

Step 3: Fortify the sample with surrogate and batch QC samples with appropriate solutions.

Step 4: Add 190 g of sodium chloride and shake to dissolve.

Step 5: Adjust the pH of the sample with 14 mL of 6N NaOH. (Check that pH is  $\geq 12$  with wide-range pH paper.)

Step 6: Cap bottle, place on rotation rack, and spin for 2 hr at 12 rpm.

Step 7: Add 100 mL DCM to the water in the bottle and turn for an additional 4 hr.

Step 8: Attach an adapter and stopcock to the bottle or transfer the bottle contents to a separatory funnel to effect phase separation. Discard the DCM layer and return the water layer to the original bottle. Readjust the pH of the water to  $\leq 2$  (check with pH paper) using approx. 14 mL of 12N sulfuric acid.

Step 9: Add 140 mL of diethyl ether (BHT-preserved required as opposed to methanol-preserved to avoid quenching subsequent methylation) and return to the rotisserie for a 12-hr turn.

Step 10: Reattach an adapter and stopcock to the bottle or transfer the bottle contents to a separatory funnel to effect phase separation. Collect the ether layer (top layer) in an acid-washed 250-mL bottle containing approx. 10 g of acidified sodium sulfate.

Step 11: Returning the water to the original bottle, add an additional 100 mL of diethyl ether and spin for an additional 12-hr period.

Step 12: Reattach an adapter and stopcock to the bottle or transfer the bottle contents to a conventional separatory funnel to effect phase separation. Add the ether layer to the original ether extract in the 250-mL bottle containing sodium sulfate.

Step 13: Allow the extract to remain in contact with sodium sulfate for at least 2 hr, mixing periodically. If the sodium sulfate forms clumps, add additional sodium sulfate until it remains free-flowing.

Step 14: Concentrate and derivatize the extract conventionally and submit for analysis.

Step 15: Recharge the bottle with tap water to the original mark and measure the sample volume using a 1000-mL volumetric flask.

## Results and discussion

Tables 1–3 summarize dozens of laboratory control sample and method blank analyses. Control matrices of purified water were fortified with a methanolic mix of compounds prior to pH change and solvent addition. Under the column header “List,” analytes associated with Method 625, the Appendix IX Groundwater Monitoring List, or the Toxicity Characteristic Leaching Procedure (TCLP) are encoded with the character 6, A, or T, respectively. In each table, applicable QC limits obtained from Method 625 are provided as a frame of reference. Recovery limits for those compounds not associated with Method 625 are arbitrarily set to 40–120. Surrogate recovery limits are those established by the U.S. EPA Contract Laboratory Program (CLP) for semivolatile organics. A composite of the results for a number of associated method blanks is provided. The pound sign (#) is used to call attention to analytes of special interest.

Table 1 provides recoveries and a measure of precision (relative percent difference, RPD) for 145 semivolatile components constituting a superset of Method 625, Appendix IX, TCLP, and other species of environmental concern. Due to chemical incompatibility, they were extracted and analyzed in three separate mixtures (the bulk in Mix A, 20 compounds in Mix B, and one in Mix C). Extraction efficiencies for three different solvent and solvent mixes using the BLLE technique are compared. The header “DCM/Et<sub>2</sub>O” reflects a set of duplicate bottle extractions performed using Procedure A explicitly as described above. The header “DCM Only” reflects a set of extractions utilizing Procedure A, substituting the mix of DCM and diethyl ether for 100 mL of DCM only for both the acid/neutral and base steps of the extraction (the extraction solvent used

primarily with SF or CLLE methods). The column labeled “DCM/Salt” shows results obtained with Procedure A again replacing the mix of DCM and diethyl ether with 100 mL of DCM following the addition of 190 g of sodium chloride. Finally, the column labeled “HYBRID” provides results obtained using the optimized Procedure B. The bulk of the analytes were extracted for a 12-hr period first at an acid pH followed by a second extraction also for 12 hr at a basic pH. The entire dual pH extraction process was thus completed in 24 hr.

Table 2 presents results for a set of duplicate extractions for herbicides using the steps of Procedure C.

Table 3 compares extractions of the Mega-Mix (Mix D) cited above using the solvent configuration of BLLE Procedures A and B with traditional CLLE and SF techniques. In Table 3, extractions conducted first at a basic pH (Method 625 convention) are compared to those extracted at an initially acidic pH (often Method 8270C convention). Compiling available data, results reflect an average of two or more replicates in most cases.

The extraction recoveries obtained using the BLLE technique are highly favorable in comparison to SF and CLLE. All of the methods have problems with low recovery for one or more given analyte or another. BLLE, having fewer variables, will produce more consistent data of better-known quality.

To better understand the differences among SF, CLLE, and BLLE, the following components (designated “#” in the tables) warrant special attention. To make an informed decision regarding which extraction process to use, careful consideration must be given to these compounds or those similar in chemical class.

- 2,4-Dimethylphenol: This compound is consistently poorly recovered using CLLE (base first appears better than acid first), but is good with either SF or BLLE.
- 2-Chloronaphthalene: This compound is marked for special attention because it is frequently the first to fail the recovery requirement of Method 625 (lower limit of 60%) using current technology. As indicated by the examples provided in this paper, acid-

**Table 1 Bottle extraction: Replicate results of four techniques**

SEMIVOLATILES	UG/L <sup>(1)</sup>	BLANK VALUE µg/L	SPIKE LEVEL µg/L	DCM/Et <sub>2</sub> O			DCM Only			DCM/Salt			HYBRID			QC LIMITS (%) <sup>(2)</sup>
				RECOVERY (%)		R.D.	RECOVERY (%)		R.D.	RECOVERY (%)		R.D.	RECOVERY (%)		R.D.	
				EXT 1	EXT 2		EXT 1	EXT 2		EXT 1	EXT 2		EXT 1	EXT 2		
<b>MIX A (EXPERIMENT 19/29) ALL ACID/NEUTRAL THEN BASE EXTRACTION</b>																
1,2,4-Trichlorobenzene	6.A	<1	38-50	76	76	1	63	68	8	63	54	16	81	84	4	44 -142
1,2-Dichlorobenzene	6.A	<1	38-50	76	77	2	60	66	9	66	54	20	81	83	3	32 -129
1,3-Dichlorobenzene	6.A	<1	38-50	70	75	6	55	62	11	60	50	18	80	83	3	1 -172
1,4-Dichlorobenzene	6.A	<1	38-50	74	76	3	57	64	10	60	50	18	81	83	2	20 -124
2,4,6-Trichlorophenol	6.A,T	<1	38-50	81	81	0	72	72	1	70	65	8	85	86	1	37 -144
2,4-Dichlorophenol	6.A	<1	38-50	80	78	2	64	65	1	68	56	20	80	82	2	39 -135
2,4-Dimethylphenol	6.A	<1	38-50	82	75	8	62	66	6	66	56	16	83	85	2	32 -119
2,4-Dinitrophenol	6.A	<1	38-50	92	82	12	66	57	13	81	87	7	89	95	6	1 -191
2,4-Dinitrotoluene	6.A,T	<1	38-50	92	88	4	83	82	2	81	87	7	93	89	4	39 -139
2,6-Dinitrotoluene	6.A	<1	38-50	86	84	2	80	79	2	79	79	0	89	89	0	50 -158
2-Chloronaphthalene	6.A	<1	38-50	80	81	1	75	75	0	70	60	14	86	86	0	60 -118
2-Chlorophenol	6.A	<1	38-50	73	76	4	52	57	10	64	53	19	76	79	3	23 -134
2-Nitrophenol	6.A	<1	38-50	77	78	1	67	71	5	67	55	21	78	81	4	29 -182
4,6-Dinitro-2-methylphenol	6.A	<1	38-50	74	67	9	68	67	1	68	72	7	88	87	1	1 -181
4-Bromophenyl phenyl ether	6.A	<1	38-50	85	81	6	80	79	2	72	76	6	85	85	0	53 -127
4-Chloro-3-methylphenol	6.A	<1	38-50	85	83	3	73	69	5	78	77	1	83	82	1	22 -147
4-Chlorophenyl phenyl ether	6.A	<1	38-50	87	85	3	80	79	2	70	72	2	91	90	1	25 -158
4-Nitrophenol	6.A	<1	38-50	69	97	34	49	44	9	69	72	4	69	68	2	1 -132
Acenaphthene	6.A	<1	38-50	60	61	1	78	79	1	71	67	6	60	63	4	47 -145
Acenaphthylene	6.A	<1	38-50	87	85	2	79	78	1	72	67	7	90	89	1	33 -145
Anthracene	6.A	<1	38-50	89	87	3	85	85	0	79	85	7	90	86	4	27 -133
Benzo(a)anthracene	6.A	<1	38-50	90	87	4	87	88	0	79	84	6	88	85	4	33 -143
Benzo(a)pyrene	6.A	<1	38-50	101	89	13	90	91	1	82	88	6	87	84	4	17 -163
Benzo(b)fluoranthene	6.A	<1	38-50	96	90	6	85	88	4	76	86	12	89	87	3	24 -159
Benzo(ghi)perylene	6.A	<1	38-50	102	97	6	97	99	2	89	89	0	100	103	3	1 -219
Benzo(k)fluoranthene	6.A	<1	38-50	94	87	7	92	92	1	86	83	4	86	82	5	11 -162
bis(2-Chloroethoxy)methane	6.A	<1	38-50	80	82	2	71	75	5	71	60	16	83	85	1	33 -184
bis(2-Chloroethyl)ether	6.A	<1	38-50	84	89	6	66	74	13	71	60	17	78	80	2	12 -158
bis(2-Chloroisopropyl)ether	6.A	<1	38-50	79	81	3	64	72	11	68	57	19	82	84	1	36 -166
bis(2-ethylhexyl)phthalate	6.A	<1	38-50	95	90	6	90	91	1	83	89	7	87	84	3	8 -158
Butyl benzyl phthalate	6.A	<1	38-50	92	88	4	88	90	2	81	85	5	89	86	4	1 -152
Chrysene	6.A	<1	38-50	92	88	4	88	89	1	81	85	5	89	84	6	17 -168
Dibenz(ah)anthracene	6.A	<1	38-50	96	90	6	93	94	1	84	85	1	93	96	2	1 -227
Diethylphthalate	6.A	<1	38-50	93	86	8	84	82	2	78	84	7	94	90	4	1 -114
Dimethylphthalate	6.A	<1	38-50	84	81	4	81	79	3	77	79	1	91	87	4	1 -112
Di-n-butylphthalate	6.A	<1	38-50	96	90	6	88	88	1	80	87	8	92	87	6	1 -118
Di-n-octylphthalate	6.A	<1	38-50	94	89	5	89	91	2	81	87	7	91	87	4	4 -146
Fluoranthene	6.A	<1	38-50	92	87	5	88	86	2	77	82	6	90	87	4	26 -137
Fluorene	6.A	<1	38-50	84	82	3	79	76	3	70	71	3	92	90	2	59 -121
Hexachlorobenzene	6.A,T	<1	38-50	86	79	8	78	79	1	72	76	6	87	87	1	1 -152
Hexachloroethane	6.A,T	<1	38-50	67	71	5	53	58	9	56	45	20	80	82	2	40 -113
Hexachlorobutadiene	6.A,T	<1	38-50	68	71	4	56	60	7	55	47	15	81	82	1	24 -116
Indeno(1,2,3-cd)pyrene	6.A	<1	38-50	97	91	6	93	95	2	85	84	0	95	98	3	1 -171
Isophorone	6.A	<1	38-50	80	79	1	72	73	2	72	59	21	83	84	1	21 -196
Naphthalene	6.A	<1	38-50	80	82	2	70	74	6	69	58	17	84	86	2	21 -133
Nitrobenzene	6.A,T	<1	38-50	81	82	2	70	74	6	71	60	17	82	83	1	35 -180
N-Nitroso-di-n-propylamine	6.A	<1	38-50	80	82	3	71	77	8	72	59	20	82	82	0	1 -230
Pentachlorophenol	6.A,T	<1	38-50	81	76	7	71	64	10	73	82	12	93	92	1	14 -176
Phenanthrene	6.A	<1	38-50	91	86	6	85	83	2	77	84	8	88	87	1	54 -120
Phenol	6.A	<1	38-50	65	69	5	27	28	4	55	46	18	62	63	2	5 -112
Pyrene	6.A	<1	38-50	92	88	4	88	88	0	81	86	5	89	86	4	52 -115
β-BHC	6.A	<1	38-50	86	82	5	82	83	0	78	86	9	87	86	2	24 -149
γ-BHC	6.A,T	<1	38-50	86	81	6	84	81	4	77	83	7	89	86	3	1 -110
Heptachlor	6.A,T	<1	38-50	89	84	6	84	84	0	74	80	8	88	86	3	1 -192
Aldrin	6.A	<1	38-50	87	83	4	82	82	0	65	67	4	71	66	7	1 -166
Heptachlor epoxide	6.A,T	<1	38-50	91	82	10	83	78	6	73	79	9	87	83	4	26 -155
p,p'-DDE	6.A	<1	38-50	90	86	4	86	83	3	78	84	7	88	85	3	4 -136
p,p'-DDD	6.A	<1	38-50	89	86	4	87	87	0	79	84	7	88	84	4	1 -145
Endosulfan Sulfate	6.A	<1	38-50	92	87	6	90	92	2	85	91	7	89	87	1	1 -107
p,p'-DDT	6.A	<1	38-50	93	88	6	91	90	1	77	81	5	87	84	3	1 -203
Endrin aldehyde	6.A	<1	38-50	91	91	0	89	90	1	81	85	5	114	88	26	1 -209
Dieldrin	6.A	<1	38-50	76	76	0	76	84	10	76	84	10	86	85	1	29 -136
N-Nitrosodimethylamine	6.A	<1	38-50	17	19	9	23	26	12	40	33	20	40	42	5	40 -120
Hexachlorocyclopentadiene	6.A	<1	38-50	73	75	3	74	74	0	72	71	2	80	84	6	40 -120
α-BHC	6.A	<1	38-50	87	84	4	83	82	1	74	80	8	94	89	5	40 -120
δ-BHC	6.A	<1	38-50	89	85	5	82	83	2	81	85	5	90	87	4	40 -120
Endosulfan I	6.A	<1	38-50	93	89	5	83	84	0	77	88	13	95	89	7	40 -120
Endrin	6.A,T	<1	38-50	88	86	3	87	86	1	75	81	9	86	84	2	40 -120
Endosulfan II	6.A	<1	38-50	88	79	11	85	81	5	75	79	6	87	81	7	40 -120
Pyridine	A,T	<1	38-50	22	22	0	24	26	9	41	35	16	50	54	8	40 -120
Aniline	A	<1	38-50	65	67	3	46	49	7	63	54	16	76	70	9	40 -120
Benzyl alcohol	A	<1	38-50	58	60	4	45	46	1	63	52	20	79	80	2	40 -120
2-Methylphenol	A,T	<1	38-50	75	77	4	46	50	8	65	56	15	74	76	2	40 -120
3-& 4-Methylphenol	A,T	<1	38-50	79	76	3	45	45	1	64	51	23	77	78	1	40 -120
4-Chloroaniline	A	<1	38-50	78	75	5	71	76	7	78	66	16	81	68	17	40 -120
2-Methylnaphthalene	A	<1	38-50	81	81	1	72	74	2	68	58	16	83	85	2	40 -120

continued

Table 1 Bottle extraction: Replicate results of four techniques *continued*

SEMIVOLATILES	LIST <sup>(V)</sup>	BLANK VALUE µg/L	SPIKE LEVEL µg/L	DCM/Et <sub>2</sub> O			DCM Only			DCM/Salt			HYBRID			QC LIMITS (%) <sup>(V)</sup>
				RECOVERY (%)		R.D.	RECOVERY (%)		R.D.	RECOVERY (%)		R.D.	RECOVERY (%)		R.D.	
				EXT 1	EXT 2		EXT 1	EXT 2		EXT 1	EXT 2		EXT 1	EXT 2		
2-Nitroaniline	A	< 1	38-50	85	83	3	83	78	6	77	77	1	89	88	1	40 -120
3-Nitroaniline	A	< 1	38-50	75	74	0	84	82	2	86	87	1	80	78	2	40 -120
Dibenzofuran	A	< 1	38-50	87	86	2	80	79	2	72	70	3	90	89	1	40 -120
2,3,4,6-Tetrachlorophenol	A	< 1	38-50	90	92	2	82	79	4	79	89	11	95	88	7	40 -120
4-Nitroaniline	A	< 1	38-50	102	102	0	96	92	5	99	99	1	104	110	5	40 -120
Methyl methanesulfonate	A	< 1	38-50	27	29	4	36	35	2	31	25	20	42	43	3	40 -120
Ethyl methanesulfonate	A	< 1	38-50	55	55	1	57	62	8	61	53	14	72	73	2	40 -120
Pentachloroethane	A	< 1	38-50	72	76	5	55	61	11	60	51	16	78	80	2	40 -120
Acetophenone	A	< 1	38-50	85	87	2	70	78	10	74	59	23	86	85	0	40 -120
O,O,O-Triethylphosphorothioate	A	< 1	38-50	80	78	2	69	72	4	67	53	23	84	85	1	40 -120
Hexachloropropene	A	< 1	38-50	61	64	5	51	55	7	55	43	23	81	82	2	40 -120
Isosafrole	A	< 1	38-50	80	79	2	70	72	2	70	58	19	82	83	1	40 -120
1,2,4,5-Tetrachlorobenzene	A	< 1	38-50	77	78	2	69	70	1	62	52	17	85	88	3	40 -120
Safrole	A	< 1	38-50	81	79	2	77	74	3	67	61	10	87	87	1	40 -120
1,4-Naphthoquinone	A	< 1	38-50	83	82	1	79	77	2	69	68	1	87	86	1	40 -120
Pentachlorobenzene	A	< 1	38-50	86	84	2	77	76	1	68	64	6	90	91	1	40 -120
Thionazide	A	< 1	38-50	112	107	5	104	102	1	97	102	6	94	91	4	40 -120
Sulfotep	A	< 1	38-50	90	84	7	82	82	0	74	81	9	93	90	3	40 -120
Diallate	A	< 1	38-50	90	86	4	84	84	1	75	81	8	89	86	3	40 -120
Phorate	A	< 1	38-50	90	87	4	85	85	0	77	83	8	93	88	6	40 -120
1,3,5-Trinitrobenzene	A	< 1	38-50	86	83	3	88	86	2	81	90	11	90	86	5	40 -120
Phenacetin	A	< 1	38-50	88	85	4	86	86	0	87	91	5	89	86	3	40 -120
Dimethoate	A	< 1	38-50	58	57	2	72	71	1	85	89	4	73	70	3	40 -120
Pronamide	A	< 1	38-50	92	86	6	88	87	2	85	89	5	88	84	5	40 -120
Pentachloronitrobenzene	A	< 1	38-50	83	81	3	83	79	5	73	77	6	87	86	2	40 -120
Dinoseb	A	< 1	38-50	84	79	6	78	78	0	70	77	10	88	87	1	40 -120
Disulfoton	A	< 1	38-50	88	84	4	84	83	1	76	82	8	90	86	4	40 -120
Methylparathion	A	< 1	38-50	96	89	8	92	89	3	84	90	7	90	87	4	40 -120
4-Nitroquinoline-1-oxide	A	< 1	38-50	66	62	6	76	73	4	24	28	13	61	60	0	40 -120
Parathion	A	< 1	38-50	95	90	5	93	90	3	82	88	7	90	87	3	40 -120
Isodrin	A	< 1	38-50	90	83	8	82	82	0	62	63	2	71	67	6	40 -120
cis-Chlordane	A,T	< 1	38-50	89	81	9	86	80	6	77	81	6	88	87	2	40 -120
Aramite	A	< 1	38-50	95	90	6	88	87	1	80	83	4	86	83	4	40 -120
Chlorobenzilate	A	< 1	38-50	92	87	5	88	87	1	80	84	4	87	84	3	40 -120
Famphur	A	< 1	38-50	105	101	4	102	103	1	94	98	5	93	90	4	40 -120
Kepone	A	< 1	38-50	96	87	10	95	88	7	82	87	6	91	85	7	40 -120
Methoxychlor	A,T	< 1	38-50	94	89	5	90	92	1	78	83	7	90	84	7	40 -120
7,12-Dimethylbenz(a)anthracene	A	< 1	38-50	101	96	5	85	85	0	79	80	1	84	82	3	40 -120
3-Methylcholanthrene	A	< 1	38-50	82	78	4	78	79	0	66	71	7	84	85	1	40 -120
trans-Chlordane	A,T	< 1	38-50	89	86	3	89	86	3	89	86	3	89	86	3	40 -120
2,6-Dichlorophenol	A	< 1	38-50	80	77	4	80	77	4	80	77	4	81	81	0	40 -120
1,3-Dinitrobenzene	A	< 1	38-50	86	81	6	86	81	6	86	81	6	87	81	7	40 -120
Diphenylamine	A	< 1	38-50	88	83	6	88	83	6	88	83	6	88	87	1	40 -120
N-Nitrosodiphenylamine	A	< 1	38-50	88	83	6	88	83	6	88	83	6	88	87	1	40 -120
1-Methylnaphthalene	A	< 1	38-50	81	82	0	74	76	2	71	61	15	88	91	3	40 -120
Carbazole	A	< 1	38-50	93	86	8	89	86	3	85	89	4	89	86	3	40 -120
Benzoic acid	A	< 1	38-50	55	58	6	3	4	7	3	8	86	65	68	3	40 -120
Endrin ketone	A	< 1	38-50	90	81	10	89	89	0	77	83	7	87	84	3	40 -120
1,2-Diphenylhydrazine	A	< 1	38-50	83	80	5	80	77	4	70	74	6	86	86	1	40 -120
2,4,5-Trichlorophenol	T	< 1	38-50	92	82	11	82	73	12	77	71	8	84	86	2	40 -120

MIX B (EXPERIMENTS 20/29)																
DCM/ET20, DCM ONLY, DCM/SALT - SINGLE BASE/NEUTRAL EXTRACTION																
HYBRID - ACID/NEUTRAL THEN BASE																
3,3'-Dichlorobenzidine	6,A	< 1	63	88	91	4	90	75	18	86	75	14	80	94	16	1 -262
Benzidine	6	< 1	63	87	89	2	93	78	17	98	83	16	66	89	30	40 -120
2-Picoline	A	< 1	63	50	51	2	63	41	41	79	61	25	59	75	24	40 -120
N-Nitroso-methylethylamine	A	< 1	63	33	34	5	53	34	43	70	54	26	61	75	20	40 -120
N-Nitroso-diethylamine	A	< 1	63	61	61	1	73	49	39	81	62	27	72	88	20	40 -120
N-Nitrosopyrrolidine	A	< 1	63	26	28	7	49	34	37	67	53	24	60	73	20	40 -120
o-Toluidine	A	< 1	63	75	78	3	81	56	37	85	66	25	68	86	23	40 -120
N-Nitroso-morpholine	A	< 1	63	21	24	13	42	29	36	54	43	23	53	66	22	40 -120
N-Nitrosopiperidine	A	< 1	63	60	61	3	72	48	39	76	58	27	73	90	20	40 -120
a,a-Dimethylphenethylamine	A	< 1	63	68	72	5	80	49	49	80	58	32	59	77	25	40 -120
N-Nitrosodibutylamine	A	< 1	63	81	85	5	86	57	40	84	64	26	76	92	19	40 -120
5-Nitro-o-toluidine	A	< 1	63	115	110	5	83	66	22	90	65	32	85	102	18	40 -120
4-Aminobiphenyl	A	< 1	63	82	83	2	84	66	23	80	69	15	72	88	19	40 -120
Dimethylaminoazobenzene	A	< 1	63	77	78	1	80	76	5	95	83	14	78	92	17	40 -120
3,3'-Dimethylbenzidine	A	< 1	63	93	96	4	97	80	18	96	81	16	65	81	21	40 -120
2-Acetylaminofluorene	A	< 1	63	101	105	3	102	86	16	105	90	16	91	104	13	40 -120
1-Naphthylamine	A	< 1	63	176	170	3	123	83	39	114	87	28	79	97	21	40 -120
2-Naphthylamine	A	< 1	63	131	127	3	92	66	33	91	70	25	81	100	21	40 -120
Methapyrilene	A	< 1	63	85	85	0	92	69	29	83	70	17	56	65	15	40 -120
1,4-Benzenediamine	A	< 1	63	6	7	9	11	6	60	5	4	29	0	0	0	40 -120

OVERALL AVERAGE RECOVERY 82 80 76 74 74 71 83 84

MIX C (EXPERIMENT 21 - ACID/NEUTRAL EXTRACTION)																
Hexachloroprene	A	< 1	300	108			84			112			NA	NA		40 -120

**Table 1 Bottle extraction: Replicate results of four techniques *continued***

SEMIVOLATILES	LIST <sup>(1)</sup>	BLANK VALUE µg/L	SPIKE LEVEL µg/L	DCM/Et <sub>2</sub> O			DCM Only			DCM/Salt			HYBRID			QC LIMITS (%) <sup>(2)</sup>
				RECOVERY (%)		D L	RECOVERY (%)		D L	RECOVERY (%)		D L	RECOVERY (%)		D L	
				EXT 1	EXT 2		EXT 1	EXT 2		EXT 1	EXT 2		EXT 1	EXT 2		
<b>ACID EXTRACTABLE SURROGATES</b>																
2-Fluorophenol		67.5	59	64	7	24	24	0	47	39	21	71	72	2	21 -110	
Phenol-d6		67.5	62	62	0	19	21	7	50	40	23	59	59	0	10 -110	
2,4,6-Tribromophenol		67.5	77	73	6	70	68	2	68	73	6	77	77	0	10 -123	
<b>BASE/NEUTRAL SURROGATES</b>																
Nitrobenzene-d5		55.0	80	80	0	69	71	3	69	58	17	82	83	2	35 -114	
2-Fluorobiphenyl		55.0	80	80	0	71	71	0	64	56	12	82	82	0	43 -116	
p-Terphenyl-d14		55.0	85	84	2	80	80	0	58	62	6	85	82	4	33 -141	

<sup>(1)</sup>LIST 6 = Method 625 analyte A = Appendix IX analyte T = TCLP analyte # = OF SPECIAL NOTE NA = Not Applicable

<sup>(2)</sup> Recovery control ranges are taken from 40 CFR Part 136, Method 625, Table 6, or are arbitrarily set to 40 -120. Surrogate recovery control ranges are taken from the CERCLA, Contract Laboratory Program (CLP) Statement of Work for Organics, OLM04.2.

**Table 2 Bottle extraction: Replicate results of Method 8151A procedure**

HERBICIDES	LIST <sup>(1)</sup>	BLANK VALUE µg/L	SPIKE LEVEL µg/L	SALT/Et <sub>2</sub> O			QC LIMITS (%) <sup>(2)</sup>
				RECOVERY (%)		D L	
				EXT1	EXT2		
<b>FIVE APPX IX HERBICIDES (EXPERIMENT 12 - BASE HYDROLYSIS THEN ACID EXTRACTION)</b>							
2,4-D	A,T	< 0.13	1.3	114	102	11	40 -140
Pentachlorophenol	A	< 0.13	1.3	86	78	10	40 -140
2,4,5-TP (Silvex)	A,T	< 0.13	1.3	102	89	14	40 -140
2,4,5-T	A	< 0.13	1.3	90	75	18	40 -140
Dinoseb	A	< 0.13	1.3	95	83	13	40 -140
<b>AVERAGE RECOVERY</b>				<b>97</b>	<b>85</b>		
<b>SURROGATE</b>							
DCAA		6.7	#	139	132	5	40 -140

<sup>(1)</sup>LIST A = Appendix IX analyte T = TCLP analyte

<sup>(2)</sup> Recovery control ranges are arbitrary

first extractions for both CLLE and SF can be marginal for this analyte, while recoveries are consistently high with BLLE. (Note that Method 625 calls for using SF unless emulsions are encountered and that the extractions be conducted first at an acid pH.)

- Butylbenzylphthalate, diethylphthalate, and dimethylphthalate: These plasticizers are badly suppressed with base-first extractions using either CLLE or BLLE, but are well recovered with either base-first or acid-first SF extractions. (Perhaps SF does not provide enough time for reactions to take place.) With any of the acid-first BLLE procedures, recoveries are excellent. This is an important observation since these are very commonly detected environmental pollutants.
- Phenol: This is also an important compound (being frequently observed in wastewaters) that is recovered poorly using SF but fares substantially better with either acid-first or base-first CLLE or BLLE.
- N-nitrosodimethylamine and pyridine: These basic and volatile components are difficult to extract as well as to retain

through the solvent concentration step. The CLLE and SF data provided here exhibit reasonably good recovery for these compounds, but radical results have been obtained over many years of observation. With BLLE, N-nitrosodimethylamine and pyridine recover about 30% and 20%, respectively, with Procedure A and approximately 40% each with Procedure B. However, 20-40% yields may likely be sufficient to assess these rarely observed analytes, especially if these recoveries are able to be consistently generated.

- Hexachlorocyclopentadiene: The recovery for this analyte is especially good across the board using BLLE, is acceptable with SF, but is very poor with CLLE. (This component is known to be photosensitive. The studies presented in this paper for BLLE were conducted in amber bottles. Environmental samples are recommended to be collected in amber bottles.)
- Aniline: This basic chemical extracts well with SF, CLLE, or BLLE using the Hybrid Procedure B, but is recovered

with lower yield (35-41%) using BLLE with DCM/ether only.

- 3- and 4-Nitroanilines: These species often exhibit erratic (usually high) recovery, probably due to chromatographic chemical activity. There is apparently no problem extracting them with any of the techniques.
- Methyl methanesulfonate: With BLLE, this Appendix IX compound recovers about 28% with Procedure A and approx. 42% with Procedure B. SF and CLLE comparison data are not available for this component.
- Benzoic acid: This frequently observed but usually unregulated chemical is extracted well using either BLLE Procedure A or B, but is suppressed when only DCM or DCM/salt alone is used to extract. SF and CLLE comparison data are not available for this component.
- N-nitrosomethylethylamine and N-nitrosodiethylamine: With BLLE, these Appendix IX compounds recover about 30% with Procedure A and approx. 65% with Procedure B. SF and CLLE comparison data are not available for these components.
- 1,4-Benzenediamine: This chemical was recovered poorly with Procedure A and not at all with Procedure B (acid first) at the spike levels used in this study. Benzenediamine was also found to extract extremely poorly using either SF or CLLE. The partitioning is not favorable for this compound and the problem appears to be universal. It should be noted that this compound occasionally will appear to recover using CLLE if improperly fortified. Due to the mechanics of the glassware, CLLEs are commonly fortified after solvent has been added to the water. This can result in a false assessment of recovery.

Table 3 BLLE, CLLE, and SF extractions (base-first vs acid-first extractions)

SEMIVOLATILES	LIST <sup>(1)</sup>	SPIKE LEVEL µd/L	BASE FIRST THEN ACID EXTRACTION			ACID FIRST THEN BASE EXTRACTION				QC LIMITS (%) <sup>(2)</sup>
			RECOVERY %			RECOVERY (%)				
			DCM/ETHER AVE REPS	CLLE AVE REPS	SF SINGLE	HYBRID AVE REPS	DCM/ETHER AVE REPS	CLLE AVE REPS	SF AVE REPS	
MIX D										
1,2,4-Trichlorobenzene	6,A	38 - 50	87	81	72	74	79	57	58	44 -142
1,2-Dichlorobenzene	6,A	38 - 50	91	81	77	75	83	55	56	32 -129
1,3-Dichlorobenzene	6,A	38 - 50	90	77	76	71	82	51	54	1 -172
1,4-Dichlorobenzene	6,A	38 - 50	91	78	77	73	84	53	55	20 -124
2,4,6-Trichlorophenol	6,A,T	38 - 50	87	84	79	109	81	85	76	37 -144
2,4-Dichlorophenol	6,A	38 - 50	85	81	75	78	80	74	72	39 -135
2,4-Dimethylphenol	6,A	38 - 50	94	43	80	77	88	26	79	32 -119
2,4-Dinitrophenol	6,A	38 - 50	101	104	100	76	88	85	73	1 -191
2,4-Dinitrotoluene	6,A,T	38 - 50	102	104	97	105	95	93	77	39 -139
2,6-Dinitrotoluene	6,A	38 - 50	90	101	87	101	83	86	71	50 -158
2-Chloronaphthalene	6,A	38 - 50	96	101	80	103	87	65	59	60 -118
2-Chlorophenol	6,A	38 - 50	85	83	76	92	80	64	61	23 -134
2-Nitrophenol	6,A	38 - 50	86	94	78	87	79	72	66	29 -182
4,6-Dinitro-2-methylphenol	6,A	38 - 50	103	115	110	78	100	87	77	1 -181
4-Bromophenyl phenyl ether	6,A	38 - 50	89	101	85	77	87	86	73	53 -127
4-Chloro-3-methylphenol	6,A	38 - 50	96	98	85	74	90	84	77	22 -147
4-Chlorophenyl phenyl ether	6,A	38 - 50	91	98	81	102	86	84	70	25 -158
4-Nitrophenol	6,A	38 - 50	110	128	49	101	102	104	41	1 -132
Acenaphthene	6,A	38 - 50	67	99	79	109	68	81	71	47 -145
Acenaphthylene	6,A	38 - 50	94	99	82	101	86	76	69	33 -145
Anthracene	6,A	38 - 50	98	101	97	77	89	85	75	27 -133
Benzo(a)anthracene	6,A	38 - 50	77	102	98	83	83	88	78	33 -143
Benzo(a)pyrene	6,A	38 - 50	66	94	99	81	77	85	80	17 -163
Benzo(b)fluoranthene	6,A	38 - 50	63	94	92	82	74	87	78	24 -159
Benzo(ghi)perylene	6,A	38 - 50	68	116	105	77	87	75	81	1 -219
Benzo(k)fluoranthene	6,A	38 - 50	62	101	97	80	78	79	79	11 -162
bis(2-Chloroethoxy)methane	6,A	38 - 50	78	81	66	76	72	64	59	33 -184
bis(2-Chloroethyl)ether	6,A	38 - 50	89	87	76	84	79	64	58	12 -158
bis(2-Chloroisopropyl)ether	6,A	38 - 50	108	104	93	91	99	75	67	36 -166
bis(2-ethylhexyl)phthalate	6,A	38 - 50	75	109	112	84	97	93	84	8 -158
Butyl benzyl phthalate	6,A	38 - 50	19	25	99	78	92	92	81	1 -152
Chrysene	6,A	38 - 50	78	107	103	82	85	91	81	17 -168
Dibenz(ah)anthracene	6,A	38 - 50	61	116	109	80	86	84	86	1 -227
Diethylphthalate	6,A	38 - 50	27	36	90	103	91	86	72	1 -114
Dimethylphthalate	6,A	38 - 50	9	14	73	100	81	84	72	1 -112
Di-n-butylphthalate	6,A	38 - 50	46	51	105	82	95	91	80	1 -118
Di-n-octylphthalate	6,A	38 - 50	60	106	111	80	83	92	85	4 -146
Fluoranthene	6,A	38 - 50	94	103	99	83	91	85	73	26 -137
Fluorene	6,A	38 - 50	92	97	82	100	86	84	71	59 -121
Hexachlorobenzene	6,A,T	38 - 50	79	96	85	78	81	86	74	1 -152
Hexachloroethane	6,A,T	38 - 50	94	82	79	72	84	50	54	40 -113
Hexachlorobutadiene	6,A,T	38 - 50	79	79	70	66	73	51	56	24 -116
Indeno(1,2,3-cd)pyrene	6,A	38 - 50	64	113	107	79	87	82	83	1 -171
Isophorone	6,A	38 - 50	99	105	84	68	89	85	76	21 -196
Naphthalene	6,A	38 - 50	91	90	78	77	84	64	63	21 -133
Nitrobenzene	6,A,T	38 - 50	97	97	82	89	88	74	67	35 -180
N-Nitroso-di-n-propylamine	6,A	38 - 50	110	111	94	94	99	85	76	1 -230
Pentachlorophenol	6,A,T	38 - 50	79	82	86	76	79	85	74	14 -176
Phenanthrene	6,A	38 - 50	96	102	95	77	89	85	73	54 -120
Phenol	6,A	38 - 50	70	86	34	94	67	71	35	5 -112
Pyrene	6,A	38 - 50	95	102	98	76	89	94	78	52 -115
N-Nitrosodimethylamine	6,A	38 - 50	26	87	56	38	26	69	48	40 -120
Hexachlorocyclopentadiene	6,A	38 - 50	70	9	68	80	85	16	53	40 -120
Pyridine	A,T	38 - 50	14	37	31	46	19	66	47	40 -120
Aniline	A	38 - 50	35	83	66	73	41	85	87	40 -120
Benzyl alcohol	A	38 - 50	97	138	73	72	71	68	72	40 -120
2-Methylphenol	A,T	38 - 50	89	91	72	118	83	69	70	40 -120
3-& 4-Methylphenol	A,T	38 - 50	87	91	66	93	83	72	63	40 -120
4-Chloroaniline	A	38 - 50	72	99	81	67	54	93	90	40 -120
2-Methylnaphthalene	A	38 - 50	94	96	79	64	85	70	65	40 -120
2-Nitroaniline	A	38 - 50	105	118	99	98	95	93	78	40 -120
3-Nitroaniline	A	38 - 50	112	153	138	78	93	119	106	40 -120
Dibenzofuran	A	38 - 50	100	100	82	103	92	83	70	40 -120
2,3,4,6-Tetrachlorophenol	A	38 - 50	92	88	90	112	89	84	71	40 -120
4-Nitroaniline	A	38 - 50	142	164	161	101	134	124	114	40 -120
1-Methylnaphthalene	A	38 - 50	93	94	75	63	85	70	66	40 -120
Carbazole	A	38 - 50	103	106	102	80	96	90	77	40 -120
2,4,5-Trichlorophenol	T	38 - 50	86	89	79	97	81	85	76	40 -120

continued

**Table 3** BLLE, CLLE, and SF extractions (base-first vs acid-first extractions) *continued*

SEMIVOLATILES	LIST <sup>(1)</sup>	SPIKE LEVEL µg/L	BASE FIRST THEN ACID EXTRACTION			ACID FIRST THEN BASE EXTRACTION				QC LIMITS (%) <sup>(2)</sup>
			DCM/ETHER AVE REPS	CLLE AVE REPS	SF SINGLE	HYBRID AVE REPS	DCM/ETHER AVE REPS	CLLE AVE REPS	SF AVE REPS	
AVERAGE RECOVERY			82	92	86	84	83	78	71	
<b>ACID EXTRACTABLE SURROGATES</b>										
2-Fluorophenol	47 - 75		NS	63	NS	61	NS	48	37	21 -110
Phenol-d6	47 - 75		NS	76	NS	56	NS	63	29	10 -110
2,4,6-Tribromophenol	47 - 75		NS	81	NS	75	NS	84	70	10 -123
<b>BASE/NEUTRAL SURROGATES</b>										
Nitrobenzene-d5	47 - 75		NS	94	NS	80	NS	66	61	35 -114
2-Fluorobiphenyl	47 - 75		NS	93	NS	100	NS	68	62	43 -116
p-Terphenyl-d14	47 - 75		NS	102	NS	80	NS	82	70	33 -141

<sup>(1)</sup> LIST 6 = Method 625 analyte A = Appendix IX analyte T = TCLP analyte

<sup>(2)</sup> Recovery control ranges are taken from 40 CFR Part 136, Method 625, Table 6 or are arbitrarily set to 40 -120.

Surrogate recovery control ranges are taken from the Contract Laboratory Program (CLP) Statement of Work for Organics, OLM04.2.

# = OF SPECIAL NOTE

NS - NOT SPIKED

• Phenol-d5: This isotopically labeled surrogate not surprisingly closely mimics its native homolog, often recovering poorly using SF but faring well with either acid-first or base-first BLLE or with CLLE. It is interesting to note that, using DCM alone to extract, BLLE results are even poorer than SF results.

For a given dual pH extraction using SF, 60 × 6 (360 mL) of DCM would be consumed while CLLE typically uses about 450 mL. BLLE utilizes only 180 mL, exactly half that of the SF technique. With the SF procedure, a few samples may be extracted in a couple of hours by a technician working full time. With CLLE, a large rack (if available) of extractors may be set up in that same couple of hours, but the full process will take two days. With SF and especially CLLE, the glassware used must be carefully cleaned between each use using a number of sometimes elaborate techniques. With BLLE, 30 or more disposable sample bottles may be set up in 1 hr, turned on a rack (each rack designed to hold 30 or more bottles; see Figure 1), and a dual pH extraction completed in 1 day.

BLLE uses much less solvent and is faster than CLLE. Recovery variations due to condenser water temperature and drip rate are eliminated, hexachlorocyclopentadiene is recovered in high yield, and recovery problems with either 2,4-dimethylphenol (acid-first extraction) or the phthalates (base-first extraction) are avoided. Maintenance of the expensive glassware required

for CLLE, which is too easily and too often broken, is not a factor with BLLE.

Emulsions are not observed with BLLE, but are all too frequent with SF. While a few samples can be extracted faster using SF, it would take a single technician a couple of days to extract 30 samples, whereas a technician with multiple BLLE racks could prepare over hundreds of samples in one day. BLLE uses less solvent and is significantly less labor intensive.

Procedure A is the easiest to employ in that ordinary solvents and reagents routinely used in most laboratories may be used directly. This procedure could be used for virtually all applications. The sodium chloride needed for Procedure B (obtained from several sources) was found to require baking to eliminate trace levels of phthalates. While this requires some effort, baking sodium sulfate, an identical procedure for an identical reason, is a common practice in most laboratories.

An elevation of detection limit due to slightly smaller starting sample volumes required for BLLE may be compensated for by a commensurate reduction of final extract volume or by calibrating instruments to slightly lower levels. Alternatively, slightly larger sample bottles could be used.

### Conclusion

BLLE can be used in place of SF or CLLE to save labor, solvent, overall cost, and/or time. It is inherently more precise. Recov-

ery requirements of Method 625 will be more readily met with BLLE than with either SF or CLLE.

Laboratory analysis professionals may determine the best method to employ for their specific water liquid-liquid extraction needs by assessing these data provided or by generating their own. In view of the task at hand, the target analyte required, data quality objectives, and operational expenses, BLLE will serve best for most applications.

### References

1. U.S. EPA Office of Solid Waste and Emergency Response, SW-846, Third Edition, Revision 3, December 1996.
2. Base/Neutrals and Acids. 40 Code of Federal Regulations, Part 136, Appendix A, Method 625; Office of the Federal Register, National Archives & Records Administration.
3. Groundwater Monitoring List. 40 Code of Federal Regulations, Part 264, Appendix IX; Office of the Federal Register, National Archives & Records Administration.

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