



Project Summary

Single-Laboratory Evaluation of Method 8060-Phthalate Esters

Viorica Lopez-Avila, Franklin Constantine, June Milanese, Robert Gale, and
Werner F. Beckert

SW-846 Method 8060 for the determination of phthalate esters in aqueous and solid matrices was modified and evaluated in a single laboratory. The range of compounds of interest was expanded to 16 phthalate esters. A study to determine the sources of phthalate esters contamination in the laboratory, its extent, and ways to minimize background contamination was conducted as part of the evaluation. The packed columns specified for gas chromatographic analysis were replaced with two fused-silica open tubular columns of dissimilar stationary phases. The two fused-silica open tubular columns are connected to an inlet splitter and two electron capture detectors; this setup allows the primary and confirmatory analyses to be conducted simultaneously. Extract cleanup was performed on alumina or on Florisil, however, three of the target compounds were not recovered from the 10-g Florisil column (Method 3620). The use of commercially available Florisil cartridges was evaluated. Our results indicate that this approach is feasible for all 16 compounds. The interferences represented by organochlorine pesticides were evaluated, and possible internal standards and surrogate compounds were identified. The revised method was tested with an estuarine water, a leachate, a groundwater, an estuarine sediment, a municipal sludge, and a sandy loam soil. The results obtained indicated acceptable accuracy and

precision for most of the target analytes.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Regulations for hazardous waste activities under the Resource Conservation and Recovery Act (RCRA) of 1976 and its elements require analytical methodologies that provide reliable data. The document "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Office of Solid Waste Manual SW-846 (1), provides a compilation of methods for evaluating RCRA solid wastes for environmental and human health hazards. One of the methods in this document, Method 8060, addresses the determination of phthalate esters. This method provides conditions for sample extraction (Methods 3510, 3520, 3540, 3550), sample extract cleanup (Methods 3610, 3620, 3640) and gas chromatographic (GC) determination of six phthalates in environmental matrices including groundwater, liquids, and solids. Analyses are performed by gas chromatography (GC) using two packed columns at various temperatures, and the compounds are determined with a flame-ionization (FID) or an electron-capture detector (ECD).

Problems with the current Method 8060 include:

- The primary column specified, a 1.8-m x 4-mm ID glass column packed with 1.5 percent SP-2250/1.95 percent SP-2401 on Supelcoport (100/120 mesh), needs to be operated at two temperatures (180°C and 220°C) in order to chromatograph the six compounds.
- The confirmatory column specified, a 1.8-m x 4-mm ID glass column packed with 3 percent OV-1 on Supelcoport (100/120 mesh), also needs to be operated at two temperatures (200°C and 220°C) in order to chromatograph the six compounds.
- Only six phthalate esters are currently listed, but other phthalates have been found in environmental samples.
- Surrogate compounds are required to be spiked into the sample matrix prior to extraction, yet no compounds are specified or recommended for this purpose. Likewise, internal standards are required whenever internal standard calibration is used for quantification purposes, yet no internal standards are specified or recommended.
- Extract cleanup is performed according to Method 3610 or 3620, yet no data are included on the recovery of the six compounds from the extract cleanup step.
- Many phthalate esters are present as contaminants in or on laboratory equipment and in solvents and reagents (2). Procedures on how to clean glassware and how to remove phthalate esters from solvents and materials should be tested and incorporated in the protocol. Also, examples of typical background contamination of some common laboratory items should be given to make the analyst aware of such problems.

Acurex, under contract to the Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV), conducted an evaluation and improvement study of Method 8060. Since the current protocol was inadequate in certain areas (e.g., in addressing background contamination) and was lacking information in other areas such as the sample cleanup and the GC analysis, the method evaluation and improvement study was approached in two phases.

Phase I, the developmental phase, addressed the following:

- Literature review to gather the relevant information
- Assessment of background contamination of solvents, materials

used in sample cleanup, and apparatus used for sample extraction

- Selection and evaluation of capillary columns for use in the analysis of 16 phthalate esters (Table 1)
 - Evaluation of sample extraction procedures
 - Evaluation of GC/ECD and GC/FID for the analysis of samples containing the test compounds
 - Evaluation of alumina (Method 3610) and Florisil chromatography (Method 3620)
 - Selection of surrogate and internal standards for use in Method 8060
 - Sample preservation studies
- Upon completion of the experimental work in Phase I, the protocol was tested in Phase II on three aqueous matrices and three solid matrices. Performance data generated during the evaluation of the revised Method 8060 include:
- Measures of precision and accuracy
 - Evidence of analyte identification
 - Evidence of resolution of analyte from interfering substances
 - Ruggedness study
 - Method detection limits

Experimental

Apparatus

- (a) Glassware—Essentially as specified in Methods 3510, 3520, 3540, 3550, 3610, and 3620.
- (b) Mixxor-Lidex Technologies, Inc.
- (c) Sonicator-Heat Systems Ultrasonics, Inc., Model W-375.
- (d) Gas chromatographs—Varian 6000 with constant-current/pulsed frequency ECP, interfaced with a Varian Vista 402 data system; Varian 6500 with FID, interfaced with either a Spectra Physics 4290 integrator or a Varian Vista 402 data system. For the simultaneous injection on the DB-5 and DB-1701 columns, the Varian 6000 was equipped with a J&W Scientific press-fit, Y-shape, glass-splitter, and with dual ECDs.
- (e) Autosampler—Varian Model 8000.
- (f) GC Columns—(1) DB-5, (2) Supelcowax-10, (3) DB-210, (4) DB-608, (5) DB-1701, (6) RT_x-5, 30 m x 0.25 mm ID or 30 m x 0.53 mm ID and different film thickness.

Materials

- (a) Solvents and other reagents—As specified in Methods 3510, 3520, 3540, 3550, 3610, and 3620.

- (b) Florisil—J. T. Baker, Lot N 442707, 60/80 mesh, activated 400°C for 16 hours, then deactivated with water (3 percent by weight).
- (c) Alumina—Alumina Woelm N Sup I, activated/deactivated as described for Florisil.
- (d) C₁₈ membrane disks—Analytische International.
- (e) Florisil disposable cartridge—Supelclean SPE tubes consisting of serological-grade 6-n polypropylene tubes, packed each with 1 g LC-Florisil (40-μ particles, 60-A pores) held between polyethylene frits.
- (f) Standards—DEP was obtained from Scientific Polymer Products, other phthalates, as well as benz benzoate and diphenyl terephthalate, were obtained from Chem Service (distributed by Bryant Laboratories, Inc.). Purities were stated to be greater than 99 percent. Stock solutions of each compound at 1 mg/mL were prepared in isooctane (Baker Resin-Analyzed, J. T. Baker) working calibration standards were prepared initially in isooctane and later in hexane. Serial dilutions of a composite stock solution prepared from the individual stock solutions.
- (g) Materials used in contamination evaluation (solvents and other materials used in sample preparation)—Various grades purchased from a variety of suppliers.
- (h) Environmental materials—
 - Sandy loam soil, obtained from Soils Incorporated, Puyallup, Washington, with the following characteristics: pH 5.9 to 6.0; 1 percent sand, 7 percent silt, 92 percent clay; cation exchange capacity 7 meq/100 g; total organic carbon content 1,290 mg/kg.
 - A sediment sample of unknown origin. Analysis of the extract by GC/MS indicated the presence of petroleum hydrocarbons.
 - NBS SRM-1572, Citrus leaves.
 - NBS SRM-1632a, Coal.
 - NBS SRM-1633a, Coal flyash.
 - Estuarine water and sediment collected from San Francisco Bay, South San Francisco, California.
 - Leachate prepared by Method 1310 from a soil contaminated with lead.

Table 1. Phthalate Esters Included in the Evaluation

Compound	CAS No.
<i>Dimethyl phthalate (DMP)</i>	131-11-3
<i>Diethyl phthalate (DEP)</i>	84-66-2
<i>Diisobutyl phthalate (DIBP)</i>	84-69-5
<i>Di-n-butyl phthalate (DBP)</i>	84-74-2
<i>Bis(4-methyl-2-pentyl) phthalate (BMPP)</i>	146-50-9
<i>Bis(2-methoxyethyl) phthalate (BMEP)</i>	117-82-8
<i>Diamyl phthalate (DAP)</i>	131-18-0
<i>Bis(2-ethoxyethyl) phthalate (BEEP)</i>	605-54-9
<i>Hexyl 2-ethylhexyl phthalate (HEHP)</i>	75673-16-4
<i>Dihexyl phthalate (DHP)</i>	84-75-3
<i>Benzyl butyl phthalate (BBP)</i>	85-68-7
<i>Bis(2-n-butoxyethyl) phthalate (BBEP)</i>	117-83-9
<i>Bis(2-ethylhexyl) phthalate (DEHP)</i>	117-81-7
<i>Dicyclohexyl phthalate (DCP)</i>	84-61-7
<i>Pi-n-octyl phthalate (DOP)</i>	117-84-0
<i>Dinonyl phthalate (DNP)</i>	84-76-4

- Ground water collected at a semiconductor plant in Sunnyvale, California.
- Municipal sludge collected from Santa Clara Valley Water District, San Jose, California.
- Sandy loam soil obtained by mixing 20 percent organic soil with 80 percent sand.

Contamination Study

Solvent samples (acetone 150 mL, hexane 150 mL, diethyl ether 30 mL, methylene chloride 180 mL) were individually concentrated by K-D evaporation to 10 mL and further reduced to 1 mL with high-purity nitrogen; only isooctane was not concentrated. At least two replicate samples of each solvent were prepared and analyzed.

Samples of Florisil (20 g), silica gel (20 g), anhydrous sodium sulfate (50 g) and glass wool (5 g) were immersed overnight in solvent which was then separated and concentrated to 1 mL for GC analysis. Two washings were performed in each case and the concentrates analyzed separately. The effect of baking at 400°C for 4 hours was evaluated for anhydrous sodium sulfate and glass wool.

Samples of filter paper (10 g), paper thimbles (10 g) and aluminum foil (5 g) were cut into 0.5-in x 0.5-in pieces and immersed overnight in solvent which was

then separated and concentrated to 1 mL for GC analysis. Two washings were performed in each case and the concentrates analyzed separately.

Gas Chromatography

Operating conditions: DB-5--120°C to 160°C (hold 16 min) at 15°C/min, injector temp. 275°C, detector temp. 320°C; Supelcowax-10--150°C (hold 2 min) to 220°C at 15°C/min, then 260°C (hold 16 min) at 4°C/min, injector temp. 270°C, detector temp. 270°C; DB-210--125°C (hold 1 min) to 240°C (hold 16 min) at 5°C/min, injector temp. 250°C, detector temp. 250°C; DB-5/DB-608; DB-608/DB-1701; DB-608/RT_x-5; DB-5/DB-1701--150°C (hold 0.5 min) to 220°C at 3°C/min, then to 275°C (hold 15 min) at 5°C/min, injector temp. 250°C, detector temp. 320°C.

Sample Extraction

The extraction efficiencies of Methods 3510 (separatory funnel) and 3520 (continuous liquid-liquid extraction) for the target compounds were determined with reagent water. Microextraction of 50 mL samples using a Mixxor device and hexane (10 mL) was also tested. Preconcentration of phthalate esters onto C₁₈-membrane disks (Analytichem International) followed by elution with acetonitrile resulted in quantitative recoveries for all 16 phthalate esters.

Solid samples were extracted either in a Soxhlet extractor with hexane/acetone (1:1) (Method 3540) or by sonication with methylene chloride/acetone (1:1) (Method 3550).

Extract Cleanup

Florisil and alumina chromatography: glass columns were packed each with 10 g deactivated Florisil or alumina and topped with 1 cm of precleaned anhydrous sodium sulfate. The charged columns were first eluted with 40 mL hexane which was discarded; the phthalate esters were eluted with 4:1 hexane/diethyl ether (100 mL for the Florisil column, 140 mL for the alumina column).

Florisil disposable cartridges: the cartridges were washed with 4 mL pesticide-grade hexane prior to use. The eluting solvents used were hexane, mixtures of hexane and diethyl ether, and mixtures of hexane and acetone. Removal of organochlorine pesticides in the presence of phthalates was attempted with mixtures of 5-percent, 20-percent, 25-percent, and 30-percent methylene chloride and hexane.

Surrogate Compound and Internal Standard Evaluation

Ten compounds were evaluated as possible internal standards and surrogates for Method 8060.

Results and Discussion

Phthalate Ester Contamination Study

Only a brief summary of the results is presented here. Detailed results of the study will be published elsewhere (3).

Solvents

Five organic solvents from up to six different commercial suppliers were analyzed for 11 phthalate esters. As can be seen from the summary results listed in Table 2, six phthalate esters were detected in some or all of these solvents. The only phthalate ester detected in any of the methylene chloride samples above 6 ng/mL was DOP at 8.8 ng/mL in one sample.

Since typical volumes of hexane and acetone used in sample preparation are 200 to 300 mL, the amounts of phthalate esters that can be introduced as contaminants with solvents could be considerable.

Materials

The phthalate contamination summary values (averaged across brands) for the materials listed in Table 3 represent averages of second washings. Florisil, alumina and silica gel showed significant levels of phthalates even in the second washing. Florisil disposable cartridges (not listed in Table 3) in the first washing showed levels from 10 to 460 µg per cartridge for 8 of the 11 phthalate esters listed in Table 3. However, washing of the cartridges just prior to use with 4 mL hexane resulted in acceptable method blanks. Washing alone is not sufficient for sodium sulfate and glass wool, but baking these materials at 40°C for 4 hours followed by solvent washing gave acceptable blanks. High levels were found in filter paper, paper thimbles, and aluminum foil.

Precleaning of these materials is a must when phthalate esters at low nanogram levels are to be quantified.

GC Column Evaluation

Of the six fused-silica capillary columns evaluated, the DB-210 column was found to be the least desirable because of a significant baseline drift during column programming and was therefore eliminated from further consideration.

The retention times of the 16 phthalates of interest on the DB-5 fused-silica capillary column and the Supelcowax-10 fused-silica open tubular

column and the DB-5 and DB-1701 fused-silica open tubular columns are presented in Table 4. The GC conditions were chosen such that all compounds are resolved and the total analysis time is approximately 35 min. All phthalate esters including surrogates were resolved on the DB-5 and DB-1701 columns; these columns were proposed for incorporation in the revised method 8060 since they can be used in the dual-column/dual-detector approach for the determination of Method 8060 phthalate esters.

Sample Extraction

The extraction of reagent water spiked with each of the 16 phthalate esters at 50 µg/L per component for separatory funnel and continuous liquid-liquid extraction and 1 mg/L for the Mixxor extraction gave the following results:

- The continuous liquid-liquid extraction technique had unacceptable reproducibilities for all compounds; for five of the phthalate esters the average recoveries were only 20 to 45 percent.
- Extraction with hexane in the Mixxor device gave unacceptable recoveries and reproducibilities.
- The separatory funnel extraction produced recoveries >70 percent for most compounds, and reproducibilities were better than 10 percent for two-thirds of the compounds.

Further evaluation of the separatory funnel extraction technique at lower spiking levels (25, 10, and 1 µg/L) confirmed its usefulness. At 25 µg/L, the recoveries ranged from 90 to 130 percent, with 11 recoveries between 90 and 110 percent, and at 10 µg/L, the range was 73 to 117 percent, with 10 recoveries between 90 and 110 percent. At 1 µg/L, the recoveries ranged from 53 to 152 percent; only four values were between 90 and 110 percent.

Method Performance

Method performance, as used here, includes method accuracy (percent recovery), method precision (percent relative standard deviation), and method detection limits. In the case of aqueous samples, the method accuracy given as percent recovery of the 16 phthalate esters spiked into an estuarine water, a leachate, and a groundwater at 20 µg/L and 60 µg/L ranged from 59.5 to 117 percent (Figure 1). In the case of solid samples (an estuarine sediment, a municipal sludge, and a sandy loam soil) the recoveries were distributed over a much wider range (Figure 2) indicating that method accuracy is a function of matrix and concentration. Method

precision for aqueous samples (Figure 3) was better than 27.5 percent. Method precision for solid samples (Figure 4) varied from matrix to matrix (Figure 4).

The method detection limits (MDL) were determined for HPLC-grade water from the standard deviations (SD) of seven replicate measurements. They represent the minimum concentration that can be measured and reported with 99 percent confidence. They ranged from 22 to 640 ng/L for water sample subjected to Florisil cleanup and 26 to 320 ng/L for water samples not subjected to Florisil cleanup; in both cases a DB-5 capillary column (single-column approach) was used.

Phthalate recoveries from solid samples, spiked at 1 ppm with the 16 phthalates, using Method 3540 (Soxhlet extraction), ranged from 54 percent for BEEP to 135 percent for DHP with 10 recoveries >70 percent. When sonication was used, the recoveries ranged from 3 percent for BMPP to 112 percent for DMP, with 13 recoveries >70 percent.

Extract Cleanup

Alumina and Florisil chromatographs were performed with standards in hexane according to Methods 3610 and 3620, respectively (Table 5). For the Florisil cartridge cleanup, various solvents and solvent combinations were tried on standards in hexane and on standards in the presence of organochlorine pesticides. It was found that the organochlorine pesticides can be removed efficiently from the cartridge with hexane/methylene chloride (4:1) under these conditions, the phthalate esters are retained on the Florisil cartridge and can be recovered with hexane/acetone (9:1). The recoveries are presented in Tables 5 and 6. Additional details on the Florisil cartridge cleanup method can be found in Reference 4.

Surrogate Compound and Internal Standard

Of 10 compounds evaluated, benzyl benzoate was selected as internal standard and diphenyl phthalate, diphenyl isophthalate, and dibenzyl phthalate were considered as surrogate compounds. The selection was based primarily on the observation that both compounds are resolved from the other phthalate esters under the conditions of the GC analysis.

Conclusions

Contamination from solvents, reagents, materials, and glassware used in the

Table 2. Phthalate Ester Contamination Ranges in Common Solvents^a (ng/mL)

Phthalate	Acetone	Hexane	Diethyl ether	Isooctane	Methylene ^b chloride
Dimethyl	<0.10	<0.10	<0.20 - 3.45	<10	<6
Diethyl	<0.10 - 0.40	<0.10	<0.20	<10	<6
Diisobutyl	<0.10 - 0.35	<0.10 - 0.35	<0.20	<10	<6
Di-n-butyl	<0.10 - 0.50	<0.10	<0.20 - 2.9	<10 - 103	<6
Diamyl	<0.10	<0.10	<0.20	<10	<6
Dihexyl	<0.10 - 0.45	<0.10 - 0.87	<0.20 - 0.75	<10 - 42	<6
Benzyl butyl	<0.10 - 0.46	<0.10	<0.20	<10	<6
Bis(2-ethylhexyl)	<0.10 - 0.45	<0.10 - 0.40	<0.20 - 2.2	<10 - 69	<6
Dicyclohexyl	<0.10	<0.10	<0.20	<10	<6
Di-n-octyl	<0.10	<0.10	<0.20	<10	8.8
Dinonyl	<0.10	<0.10	<0.20	<10	<6
No. of diff. brands	8	8	8	8	8
Below det. limit	1	2	0	0	7
Concentr. factor	150	150	30	1	180

^aAverages of two to four determinations.^bAnalyzed by GC/FID which resulted in high detection limits.**Table 3. Representative Phthalate Ester Contamination Values of Laboratory Materials (ng/g)**

Phthalate	Florisil ^a	Alumina ^b	Silical gel ^c	Sodium sulfate ^d	Glass wool ^e	Filter paper ^f	Paper thimbles ^g	Aluminum foil ^h
Dimethyl	6.2	129	1	0.7	27.4	67.5	35	24
Diethyl	5.3	28	15	1.8	2.2	<1.0	2.3	0.6
Diisobutyl	0.9	29	0.6	0.8	3	11.5	2.3	0.7
Di-n-butyl	<0.5	14	0.8	3.5	<2.0	6.5	<2.0	0.5
Diamyl	<0.5	5.8	<0.5	0.5	<2.0	<1.0	<2.0	<0.5
Dihexyl	0.8	1.2	3.8	3.3	13	15.5	17.0	3.0
Benzyl butyl	<0.5	0.6	18	4.7	4	3.3	3.0	2.5
Bis(2-ethylhexyl)	2.3	4.8	1.3	1.0	4.4	11	2.8	2.5
Dicyclohexyl	<0.5	<0.5	<0.5	<0.5	<2.0	<1.0	<2.0	<0.5
Di-n-octyl	1.5	<0.5	0.7	<0.5	5	<1.0	<2.0	1.1
Dinonyl	2.3	<0.5	<0.5	<0.5	<2.0	1.0	<2.0	1.0
No. of diff. brands	2	2	2	2	2	1	1	2

^a20 g Florisil, second immersion with 200 mL hexane/diethyl ether (4:1).^b20 g alumina, second immersion with 300 mL hexane/diethyl ether (4:1).^c20 g silica gel, second immersion with 300 mL acetone.^d40 g anhydrous sodium sulfate, second immersion with 300 mL hexane/acetone (1:1).^e5 g glass wool, second immersion with 300 mL hexane/acetone (1:1).^f10 g filter paper, second immersion with 100 mL hexane/acetone (1:1).^g10 g paper thimbles, second immersion with 100 mL hexane/acetone.^h5 g aluminum foil, second immersion with 200 mL hexane/acetone (1:1).ⁱNot able to quantify because of interference.

analysis limit the detection of phthalate esters at trace levels (ppt-ppb range). Consequently, their determinations in environmental samples at ppt-ppb range require pesticide-grade solvents, thorough cleaning of the glassware followed by heat-treatment (for those items that can withstand 400°C temperatures), and the minimum number of steps in sample workup.

Extraction of water samples in a separatory funnel was desired over the continuous liquid-liquid extraction since it

gave good recoveries and reproducibilities for most target analytes, greatly reduced the extraction time, and also minimizes contamination. Preconcentration of aqueous samples on C₁₈ membrane disks followed by extraction of the phthalate esters with acetonitrile gave quantitative recoveries and good reproducibilities and was therefore incorporated in the revised Method 8060.

Extract cleanup using Florisil disposable cartridges and elution with

hexane/acetone (9:1) gave quantitative recoveries for all 16 phthalate esters proposed for incorporation in Method 8060. Organochlorine pesticides overlap with the phthalate esters when the GC is performed on a DB-5 fused-silica capillary column. Use of Florisil disposable cartridges and elution with 20 percent methylene chloride in hexane helps to remove the organochlorine pesticides. Phthalate esters are then recovered from the Florisil cartridge with hexane/acetone (9:1). The use of Florisil disposable

Table 4. GC Retention Times for the Phthalates^a

Phthalate	Retention time (min)			
	DB-5 ^b 30 m x 0.25 mm ID	Supelco- wax-10 ^b 30 m x 0.53 mm ID	DB-5 ^c 30 m x 0.53 mm ID	DB-1701 ^c 30 m x 0.53 mm ID
Dimethyl	3.42	5.62	7.06	6.37
Diethyl	3.45	6.11	9.30	8.45
Diisobutyl	6.48	7.26	14.44	12.91
Di-n-butyl	7.14	8.43	16.26	14.66
Bis(4-methyl-2-pentyl)	7.96	8.14	18.77	16.27
Bis(2-methoxyethyl)	7.40	12.05	17.02	16.41
Diamyl	8.41	10.15	20.25	18.08
Bis(2-ethoxyethyl)	8.17	12.41	19.43	18.21
Hexyl 2-ethylhexyl	8.63	11.13	21.07	18.97
Dihexyl	9.62	12.21	24.57	21.85
Benzyl butyl	9.69	16.36	24.86	23.08
Bis(2-n-butoxyethyl)	10.53	16.94	27.56	25.24
Bis(2-ethylhexyl)	11.13	13.31	29.23	25.67
Dicyclohexyl	10.98	16.66	28.88	26.35
Di-n-octyl	13.03	17.25	33.33	29.83
Dinonyl	16.00	20.73	38.80	33.84
Benzyl benzoate (IS)	5.77	7.87	12.71	11.07
Diphenyl phthalate (SU)	d	d	29.46	28.32
Diphenyl isophthalate (SU)	d	d	32.99	31.37
Dibenzyl phthalate (SU)	d	d	34.40	32.65

^a The GC conditions have been specified under "Gas Chromatography."

^b Single-column approach.

^c Dual-column/dual-detector approach. The two columns were connected to a J&W Scientific press-fit, Y-shape, glass-splitter.

^d Not available.

cartridges was included as an option since it results in quantitative recoveries, reduces contamination, saves chemicals, and reduces laboratory waste.

Preservation of aqueous samples at neutral and acidic pH and 4°C is adequate for 21 days. Preservation of water samples at pH 9 and 4°C should be avoided since most compounds show significant decrease in concentration after 14 days of storage. Storage of spiked soil samples at -10°C is preferred over refrigeration at 4°C, since it minimizes loss of the lower-molecular-weight esters.

The dual-column/dual-detector approach for the analysis of phthalate

esters increases sample throughput by allowing the primary and confirmatory column analyses to be performed simultaneously. Excellent reproducibilities of the retention times and detector responses were achieved with two 30 m x 0.53-mm ID fused-silica open tubular columns of dissimilar stationary phases connected to an injection tee and two ECDs

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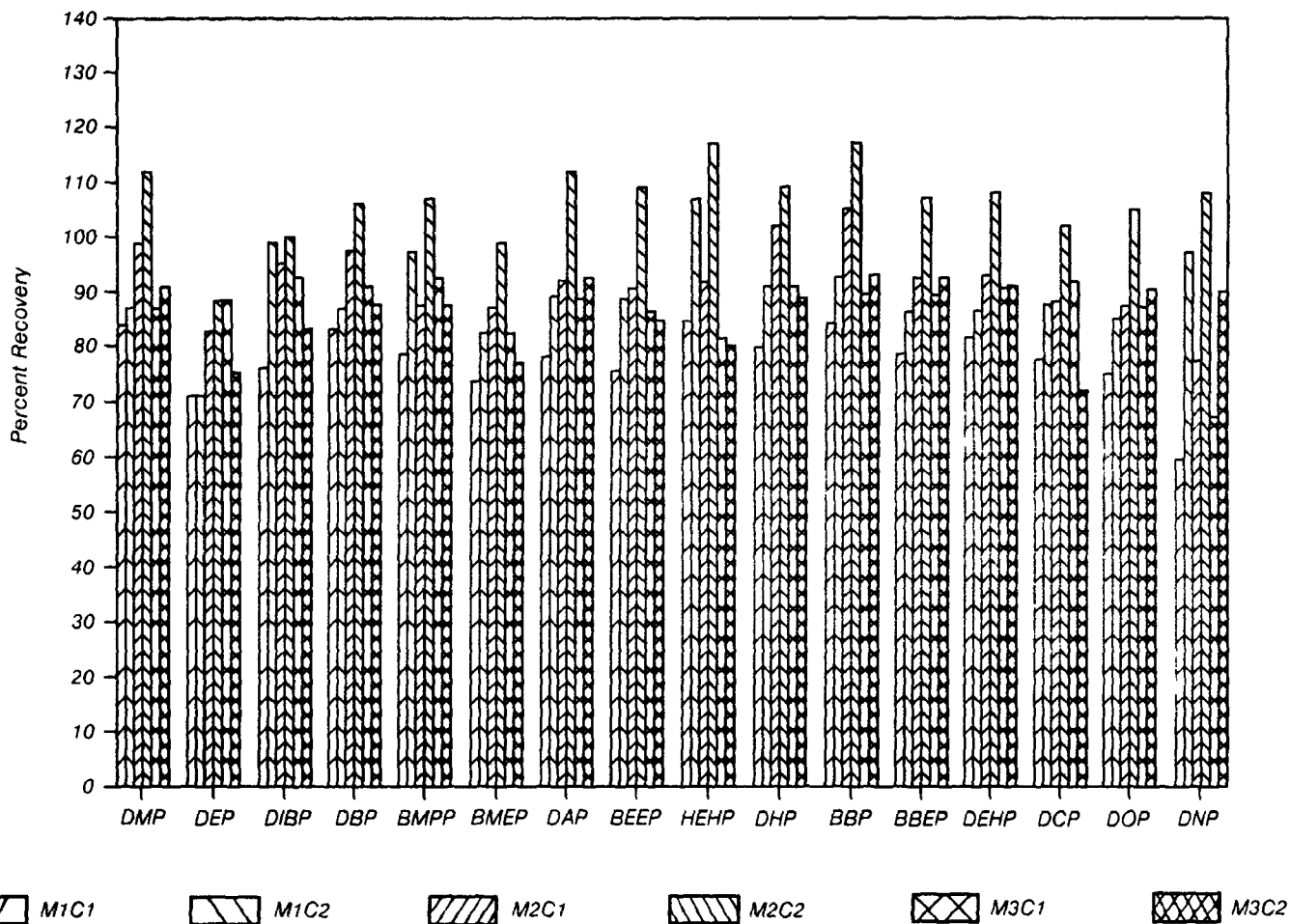


Figure 1. Method accuracy for aqueous matrices (M_1 --estuarine water; M_2 --leachate; M_3 --groundwater; C_1 --concentration at 20 $\mu\text{g/L}$ per component; C_2 --concentration at 670 $\mu\text{g/L}$ per component)

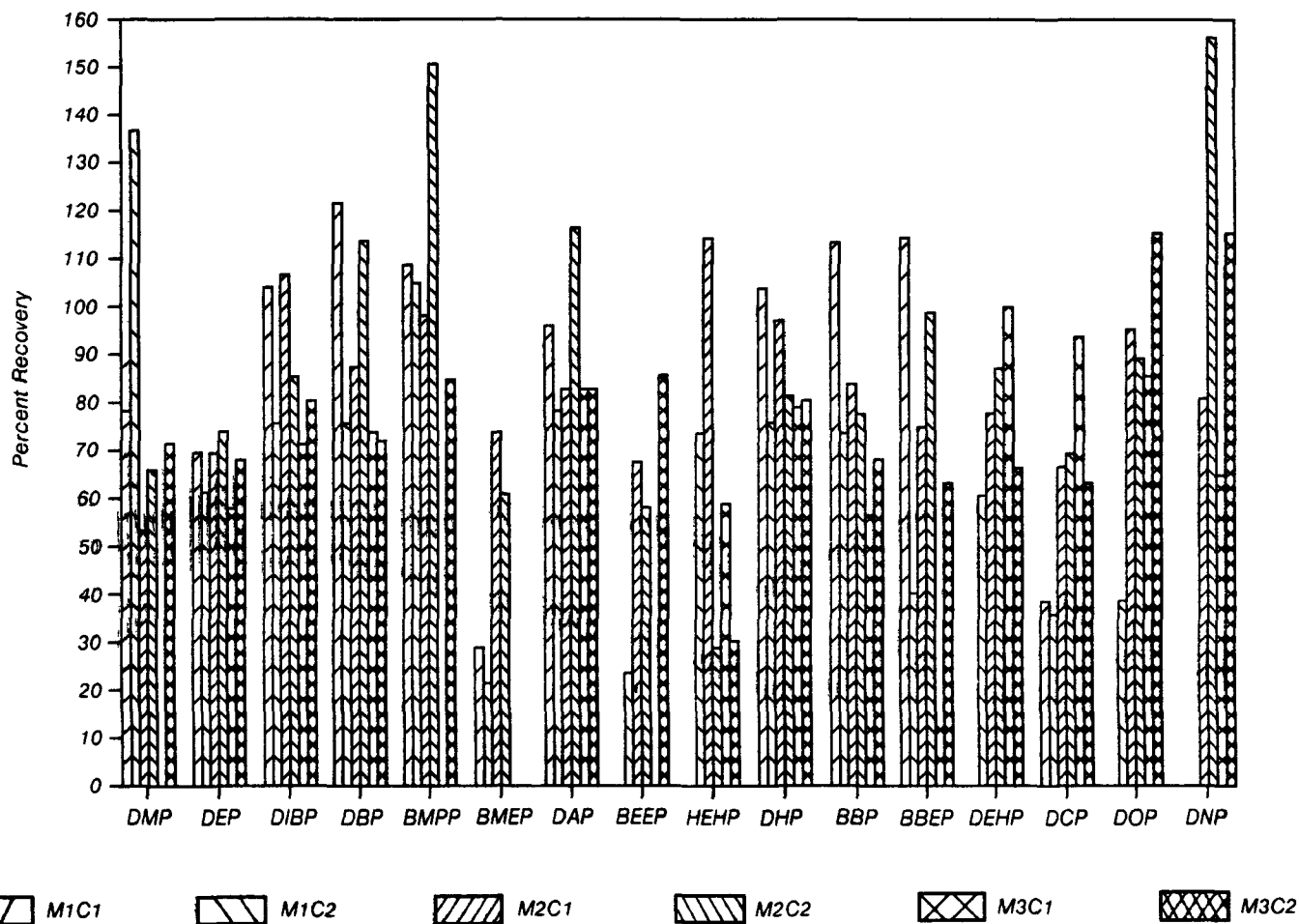


Figure 2. Method accuracy for solid matrices (M_1 --estuarine sediment; M_2 --municipal sludge; M_3 --sandy loam soil; C_1 --concentration at 1 μg per component; C_2 --concentration at 3 $\mu\text{g/g}$ per component).

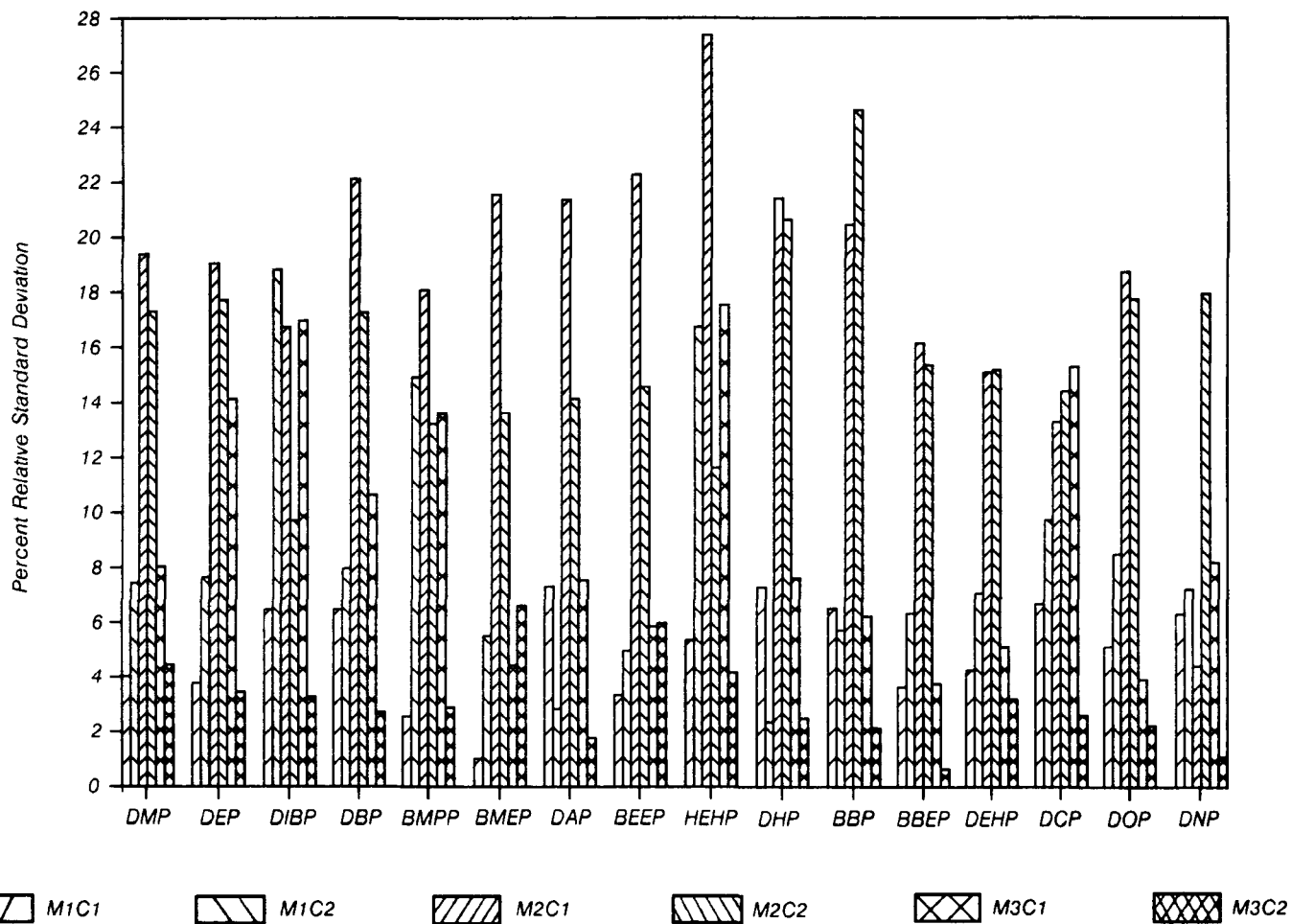


Figure 3. Method precision for aqueous matrices (M_1 --estuarine water; M_2 --leachate; M_3 --groundwater; C_1 --concentration at 20 $\mu\text{g/L}$ per component; C_2 --concentration at 60 $\mu\text{g/L}$ per component).

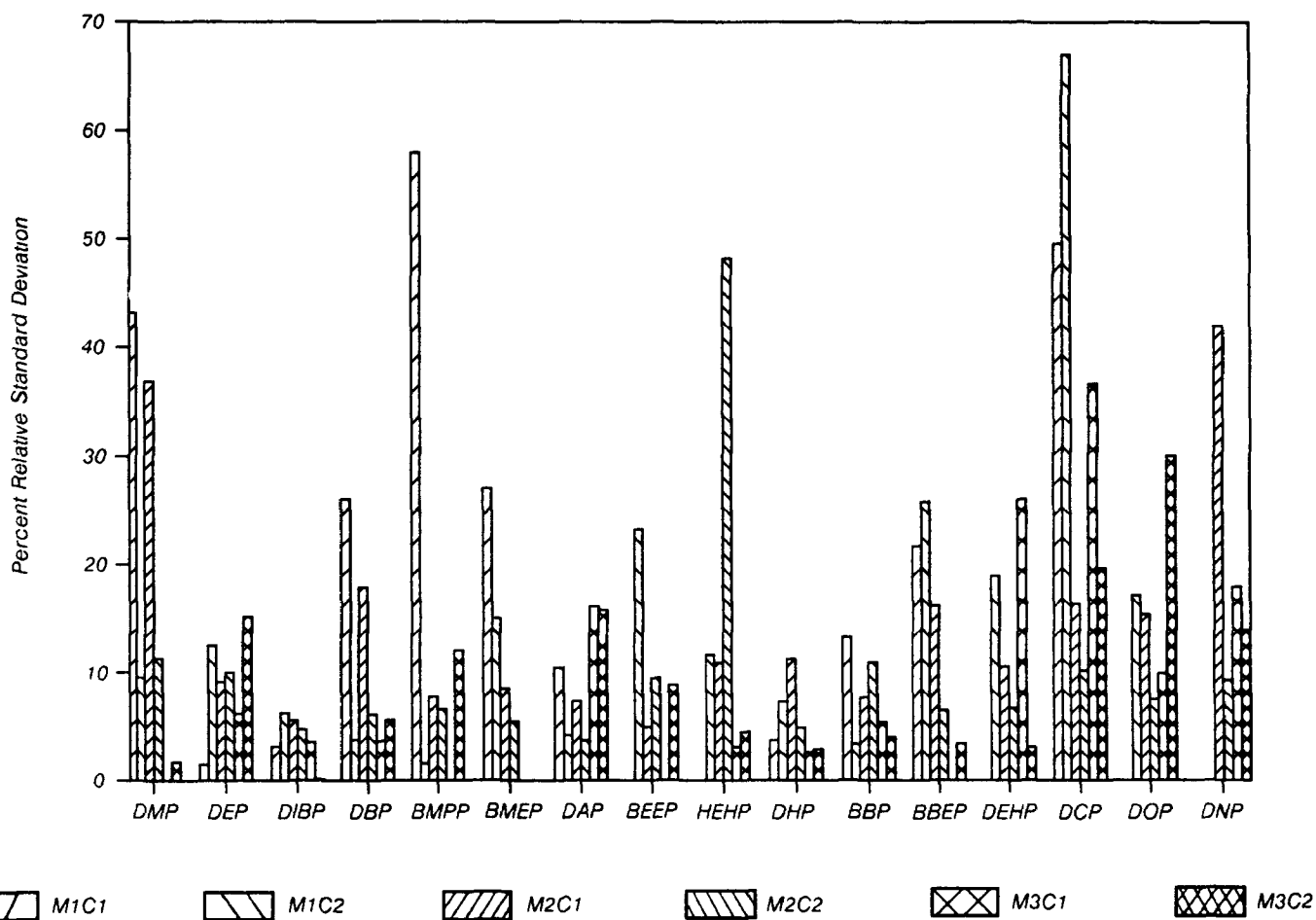


Figure 4. Method precision for solid matrices (M_1 --estuarine sediment; M_2 --municipal sludge; M_3 --sandy loam soil; C_1 --concentration at 1 μ g per component; C_2 --concentration at 3 μ g/g per component).

Table 5. Extract Cleanup Recoveries (in Percent)

Phthalate	Florisil ^a	Alumina ^a	Florisil Cartridges ^b	
			Fraction 1	Fraction 2
Dimethyl	43	65	0	130 (52)
Diethyl	57	62	0	88 (2.8)
Diisobutyl	80	77	0	118 (16)
Di-n-butyl	85	77	12	121 (13)
Bis(4-methyl-2-pentyl)	85	89	0	123 (5.7)
Bis(2-methoxyethyl)	0	70	0	32 (31)
Diamyl	82	75	3.3	94 (8.3)
Bis(2-ethoxyethyl)	0	67	0	82 (19)
Hexyl 2-ethylhexyl	105	91	0	94 (8.3)
Dihexyl	74	72	0	126 (6.4)
Benzyl butyl	90	87	0	62 (15)
Bis(2-n-butoxyethyl)	0	63	0	98 (6.5)
Bis(2-ethylhexyl)	82	91	0	110 (2.7)
Dicyclohexyl	84	84	0	106 (3.3)
Di-n-octyl	115	108	0	123 (7.0)
Dinonyl	73	71	0	102 (8.7)

^a Average of two determinations.

^b Averages of three determinations, RSDs given in parenthesis.

Fraction 1 was eluted with 5 ml hexane/methylene chloride (4:1) and Fraction 2 with 5 mL hexane/acetone (9:1).

Table 6. Percent Recoveries of Phthalate Esters from Various Matrices by Florisil Cartridge Cleanup with Hexane/Methylene Chloride (4:1) and Hexane/Acetone (9:1) as Eluants^a

Phthalate	Sandy Loam Soil	Sediment	NBS SRM-1572	NBS SRM-1632 ^a	NBS SRM-1633 ^a
Dimethyl	78	75	80	76	82
Diethyl	79	79	89	79	84
Diisobutyl	79	82	90	108	86
Dibutyl	74	78	84	83	83
Bis(4-methyl-2-pentyl)	77	84	102	91	86
Diamyl	82	86	100	76	89
Bis(2-ethoxyethyl)	37	24	62	32	33
Hexyl 2-ethylhexyl	80	88	95	93	81
Dihexyl	78	88	86	92	80
Benzyl butyl	82	99	114	102	98
Bis(butoxyethyl)	86	94	98	106	98
Bis(2-ethylhexyl)	74	85	108	88	112
Dicyclohexyl	91	96	106	98	95
Dioctyl	80	92	104	95	88
Dinonyl	84	96	106	111	92

^a Spiking level is 50 ng/mL for each compound. Data shown are for Fraction 2 which was eluted with 5 mL hexane/acetone (9:1).

Viorica Lopez-Avila, Franklin Constantine, June Milanese, and Robert Gale are with Acurex Corp., Mountain View, CA 94039. The EPA author, **Werner F. Beckert** (also the EPA Project Officer, see below) is with the Environmental Monitoring Systems Laboratory, Las Vegas, NV 89193-3478. The complete report, entitled "Single-Laboratory Evaluation of Method 8060--Phthalate Esters," (Order No. PB 90-191 776/AS; Cost: \$39.00, subject to change) will be available only from:

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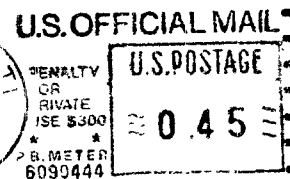
The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Las Vegas, NV 89193-3478

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