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Single-Laboratory Evaluation of Method 8060--Phthalate Esters

Project Summary/ Project Report

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PROJECT SUMMARY

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ABSTRACT

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.

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.

TABLE 1. PHTHALATE ESTERS INCLUDED IN THE EVALUATION

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

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 ECD, 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 No. 442707, 60/80 mesh, activated at 400°C for 16 hours, then deactivated with water (3 percent by weight).

(c) Alumina—Alumina Woelm N Super I, activated/deactivated as described for Florisil.

(d) C_{18} membrane disks—Analytichem International

(e) Florisil disposable cartridges—Supelclean SPE tubes consisting of serological-grade 6-mL polypropylene tubes, packed each with 1 g LC-Florisil (40-μm particles, 60-A pores) held between polyethylene frits.

(f) Standards—DEP was obtained from Scientific Polymer Products, all other phthalates, as well as benzyl benzoate and diphenyl terephthalate, were obtained from Chem Service (distributed by Bryant Laboratories, Inc.). Purities were stated to be greater than 98 percent. Stock solutions of each compound at 1 mg/mL were prepared in isooctane (Baker Resi-Analyzed, J. T. Baker); working calibration standards were prepared initially in isooctane and later in hexane by 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; 89 percent sand, 7 percent silt, 4 percent clay; cation exchange capacity 7 meq/100 g; total organic carbon content 1,290 ± 185 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 form San Francisco Bay, South San Francisco, California.

- Leachate prepared by Method 1310 from a soil contanimated with lead.

- 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 C_{18}-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 400°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

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

[a]Averages of two to four determinations.
[b]Analyzed 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	[i]	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

[a]20 g Florisil, second immersion with 200 mL hexane/diethyl ether (4:1).
[b]20 g alumina, second immersion with 300 mL hexane/diethyl ether (4:1).
[c]20 g silica gel, second immersion with 300 mL acetone.
[d]40 g anhydrous sodium sulfate, second immersion with 300 mL hexane/acetone (1:1).
[e]5 g glass wool, second immersion with 300 mL hexane/acetone (1:1).
[f]10 g filter paper, second immersion with 100 mL hexane/acetone (1:1).
[g]10 g paper thimbles, second immersion with 100 mL hexane/acetone.
[h]5 g aluminum foil, second imersion with 200 mL hexane/acetone (1:1).
[i]Not able to quantify because of interference.

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 concentrations that can be measured and reported with 99 percent confidence. They ranged from 22 to 640 ng/L for water samples 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.

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.

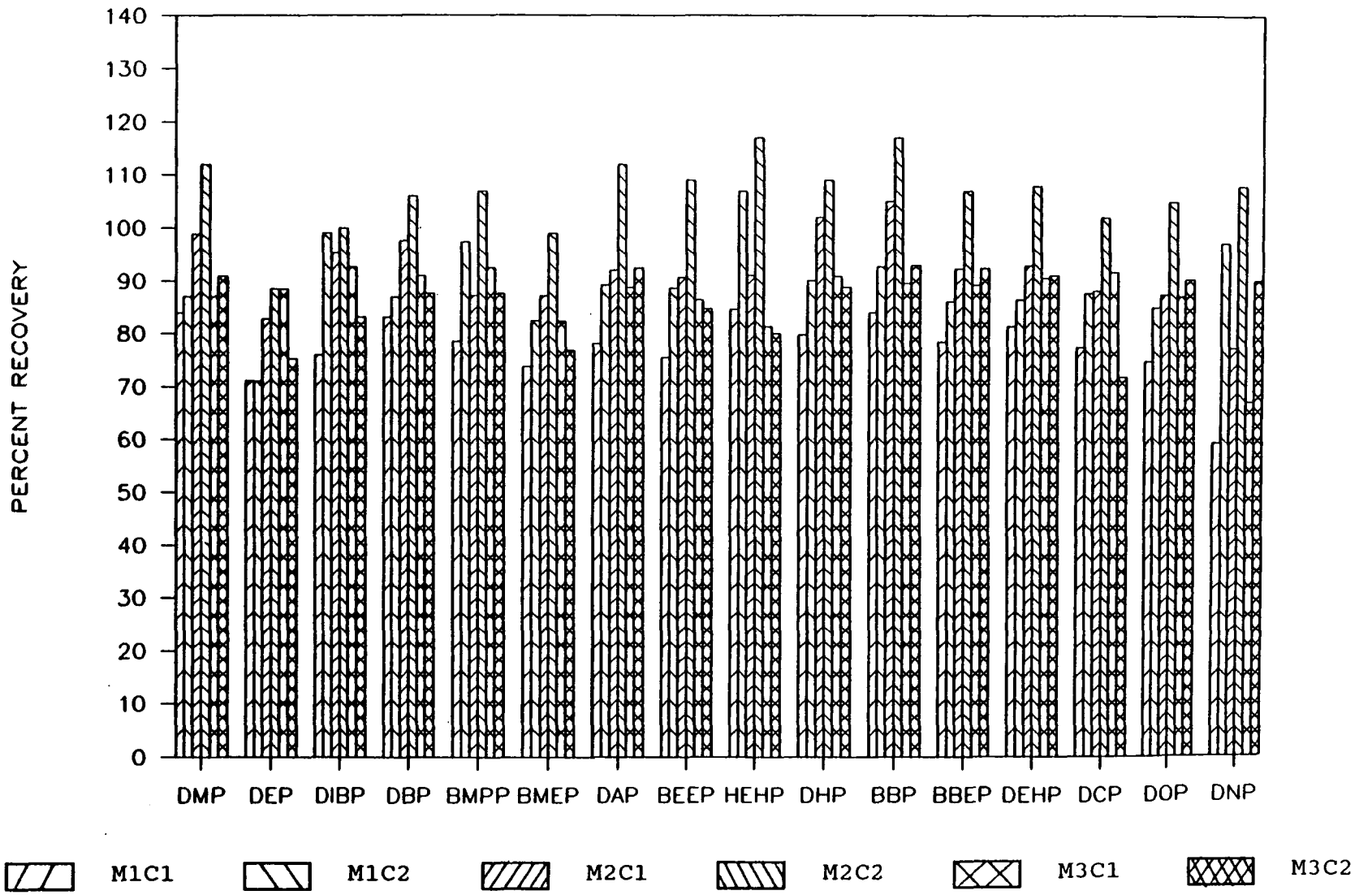

Figure 1. Method accuracy for aqueous matrices (M_1—estuarine water; M_2—leachate; M_3—groundwater; C_1—concentration at 20 μg/L per component; C_2—concentration at 60 μg/L per component).

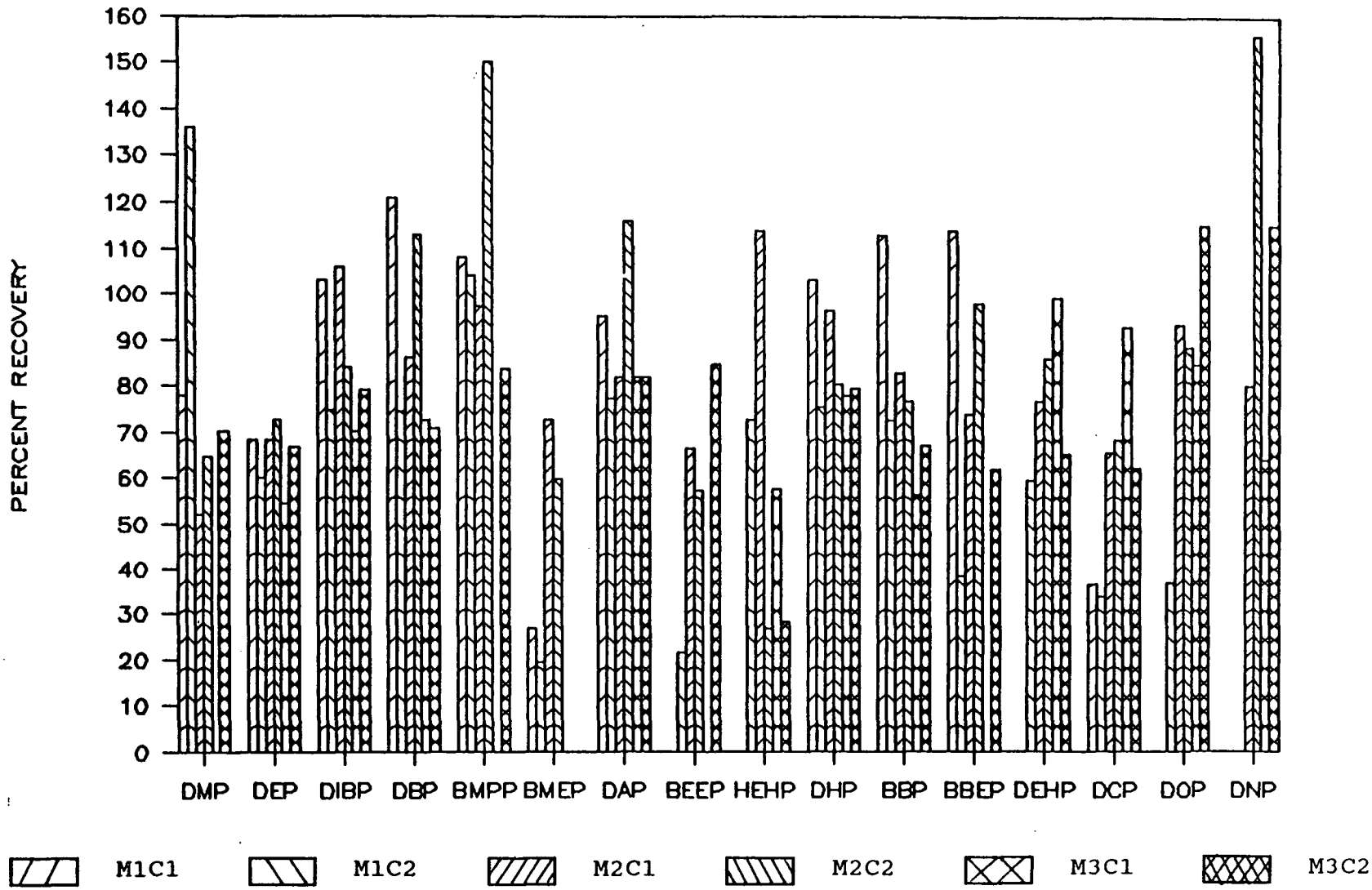

Figure 2. Method accuracy for solid matrices (M_1—estuarine sediment; M_2—municipal sludge; M_3—sandy loam soil; C_1—concentration at 1 μg/g per component; C_2—concentration at 3 μg/g per component).

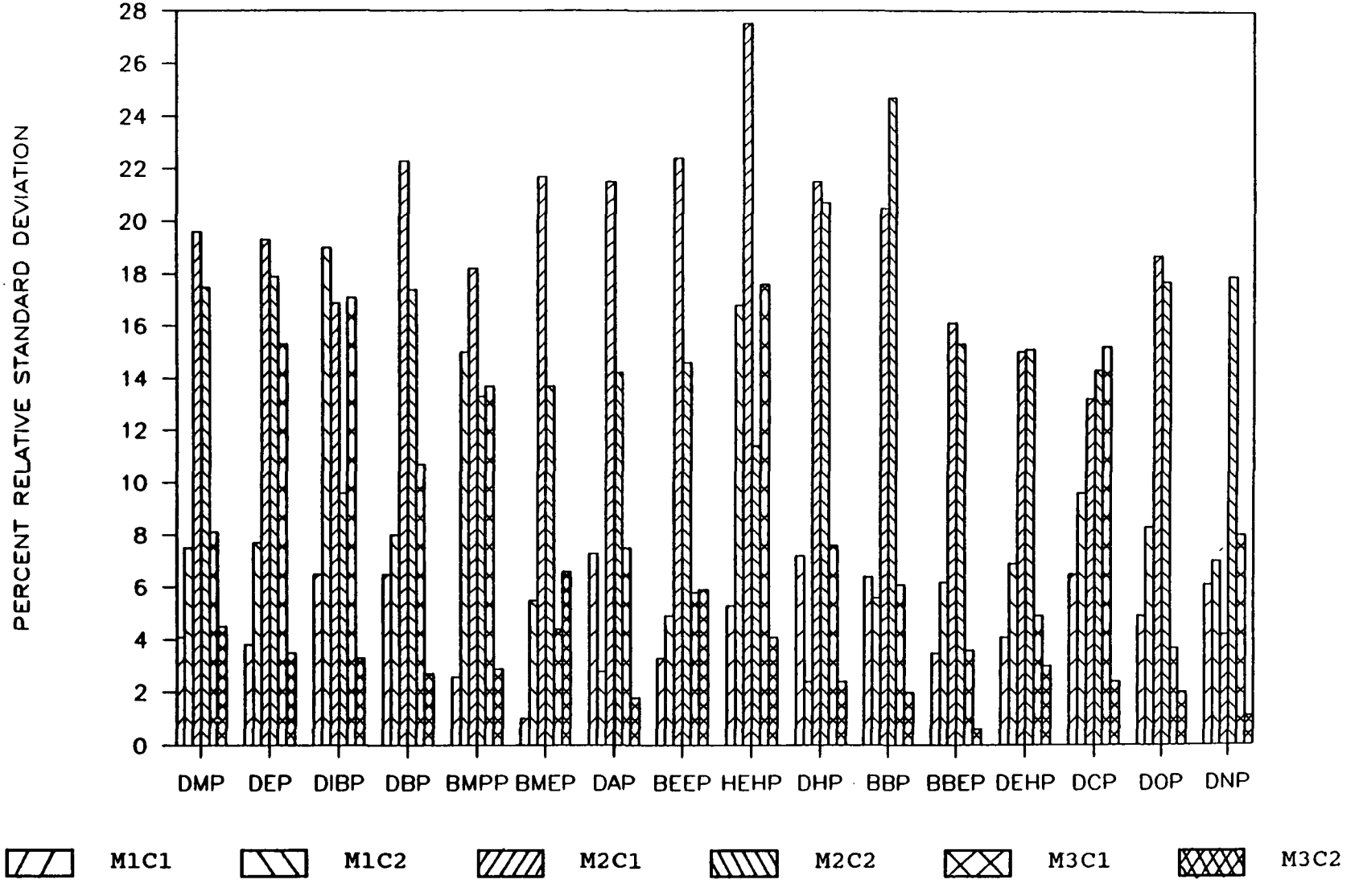

Figure 3. Method precision for aqueous matrices (M_1—estuarine water; M_2—leachate; M_3—groundwater; C_1—concentration at 20 μg/L per component; C_2—concentration at 60 μg/L per component).

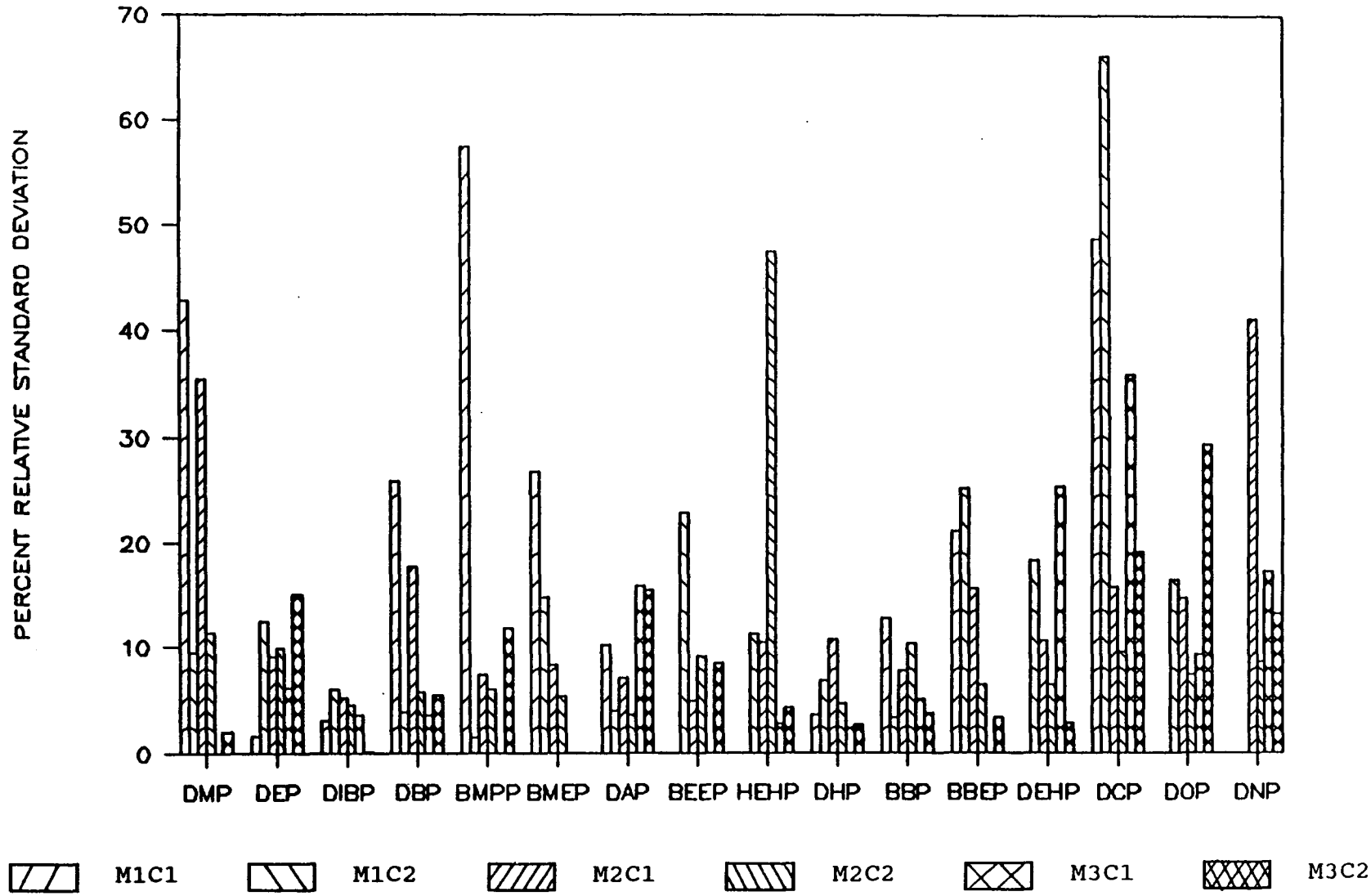

Figure 4. Method precision for solid matrices (M_1—estuarine sediment; M_2—municipal sludge; M_3—sandy loam soil; C_1—concentration at 1 μg/g per component; C_2—concentration at 3 μg/g per component).

Phthalate recoveries from soil 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 11 recoveries >70 percent. When sonication was used, the recoveries ranged from 32 percent for BMPP to 112 percent for DMP, with 13 recoveries >70 percent.

Extract Cleanup

Alumina and Florisil chromatography 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 cartridges 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 ten 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, reagent materials, and glassware used in the 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 C_{18}-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 cartridges was included as an option since it results in quantitative recoveries, reduces contamination, saves chemicals, and reduces laboratory waste.

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 parentheses. 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-1632a	NBS SRM-1633a
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).

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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SINGLE-LABORATORY EVALUATION OF METHOD 8060 -- PHTHALATE ESTERS

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NOTICE

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PREFACE

This is the final report for Work Assignments 2-14 and 3-16, EPA Contract No. 68-03-3226, and Work Assignment 1-16, EPA Contract No. 68-03-3511, "Single-Laboratory Evaluation of Method -- Phthalate Esters," conducted at Acurex Corporation, Project Nos. 8007, 8009, and 8113. These projects were directed by Dr. Viorica Lopez-Avila.

This report was written by Dr. Viorica Lopez-Avila. Technical support for both projects was provided by Mr. Franklin Constantine, Mr. June Milanes, and Dr. Robert Gale.

ABSTRACT

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.

Included in this report as an appendix is an extensive literature review covering analytical methods for the determination of phthalate esters in water, soil, and sediment samples.

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SECTION 1

INTRODUCTION

Regulation of hazardous waste activities under the Resource Conservation and Recovery Act (RCRA) of 1976 and its elements requires use of analytical methodologies that provide reliable data. The document "Test Methods for Evaluating Solid Waste," Office of Solid Waste Manual SW-846, revised recently (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 sample extract cleanup and gas chromatographic conditions for the determination of six compounds (Table 1) in a variety of environmental samples including groundwater, liquids, and solids. Aqueous samples are extracted with methylene chloride in a separatory funnel (Method 3510) or in a continuous liquid-liquid extractor (Method 3520); solid samples are extracted with hexane/acetone (1:1) or methylene chloride/acetone (1:1) using a Soxhlet extractor (Method 3540) or a sonicator (Method 3550). The extracts are cleaned using alumina or Florisil chromatography according to Methods 3610 or 3620, respectively. Organic liquids may be analyzed directly or diluted according to Method 3580. The analysis is performed by gas chromatography (GC) with electron capture detection (ECD) or flame ionization detection (FID). The sensitivity of Method 8060 depends on the level of interferences rather than on instrumental limitations. The method detection limits in reagent water, in the absence of interferences, for the six compounds listed in Method 8060 range from 0.29 μg/L to 3 μg/L. The detection limits for the same compounds in liquid and solid wastes are highly matrix dependent.

The purpose of this study was to evaluate, in a single laboratory, and improve Method 8060 to the extent possible and test the revised protocol on a variety of matrices. A review of the most recent revision of Method 8060 was performed prior to the initiation of this study to identify the areas that required further developmental work. The following comments were made:

- Only six phthalate esters are currently listed in Method 8060, and no CAS registry numbers are given for any of these compounds.

- It is not clear whether the compounds listed in Method 8060 are the only phthalates to be determined by this method. Since the presence in the environment of the phthalate esters probably parallels their production, other phthalate esters such as diisodecyl phthalate and n-hexyl n-decyl phthalate should be considered. Furthermore, several other phthalate esters were reported in water and air samples collected over the United States (2). These include: diisobutyl phthalate, dicyclohexyl phthalate, didecyl phthalate, and dimethyl

TABLE 1. PHTHALATE ESTERS INVESTIGATED IN THIS STUDY

Compound name	Compound abbreviation	CAS No.
Dimethyl phthalate	DMP[a,b]	131-11-3
Diethyl phthalate	DEP[a,b]	84-66-2
Diisobutyl phthalate	DIBP[a,b]	84-69-5
Di-n-butyl phthalate	DBP[a,b]	84-74-2
Bis(4-methyl-2-pentyl) phthalate	BMPP[a,b]	146-50-9
Bis(2-methoxyethyl) phthalate	BMEP[a,b]	117-82-8
Diamyl phthalate	DAP[a,b]	131-18-0
Bis(2-ethoxyethyl) phthalate	BEEP[a,b]	605-54-9
Dihexyl phthalate	DHP[a,b]	84-75-3
Hexyl 2-ethylhexyl phthalate	HEHP[a,b]	75673-16-4
Butyl benzyl phthalate	BBP[a,b]	85-68-7
Bis(2-n-butoxyethyl) phthalate	BBEP[a,b]	117-83-9
Bis(2-ethylhexyl) phthalate	DEHP[a,b]	117-81-7
Dicyclohexyl phthalate	DCP[a,b]	84-61-7
Di-n-octyl phthalate	DOP[a,b]	117-84-0
Dinonyl phthalate	DNP[b]	84-76-4
Diisohexyl phthalate	DIHP	[c]
Diisooctyl phthalate	DIOP	27554-26-3
Diisononyl phthalate	DINP	28553-12-0
Diisodecyl phthalate	DIDP	26761-40-0
Hexyldecyl phthalate	HDP	25724-58-7
Bis(2-ethylhexyl)hexahydro phthalate	BEHHP	[c]
Dimethyl cyclohexyl phthalate	DMCP	[c]
Benzyl 2-ethylhexyl phthalate	BEHP	[c]
Bis[2-(2-ethoxyethoxy)ethyl] phthalate	BEEEP	[c]
Butyl cyclohexyl phthalate	BCP	[c]
Butyl decyl phthalate	BDP	89-19-0
Butyl isodecyl phthalate	BIDP	42343-36-2
Butyl octyl phthalate	BOP	84-78-6
Dicapryl phthalate	DCAP	[c]
Diundecyl phthalate	DUP	[c]
2-Ethylhexyl isodecyl phthalate	EHIDP	[c]
Isodecyl tridecyl phthalate	IDTP	[c]
Octyl decyl phthalate	ODP	119-07-03
Octyl isodecyl phthalate	OIDP	[c]
Isohexyl benzyl phthalate	IHBP	[c]
Dimethyl isophthalate	DMIP	[c]
Dioctyl isophthalate	DOIP	4654-18-6

[a] Compound is currently listed in Method 8060 (SW-846, 3rd Revision).
[b] Compound considered for incorporation in the revised Method 8060.
[c] CAS number not available.

terephthalate. Thus, diisobutyl phthalate, dicyclohexyl phthalate, and didecyl phthalate should also be considered for incorporation in Method 8060.

- The use of ECDs and FIDs is stipulated in the protocol. However, no explanation or suggestion is given when to use one detector versus the other. Such an explanation should be made in relation to the method detection limits.

- Compound confirmation is currently done using a different packed column, and the provisions made in Method 8060 for second column confirmation may not be sufficient, especially when the analysis is performed by GC/FID; GC/MS confirmation should be included in the method as an option.

- Interferences should be addressed in detail. Because of the ubiquitous nature of phthalate esters, it is difficult to perform accurate analyses free of artifacts. Procedures on how to clean glassware and how to purify the solvents and the materials in order to have control over the background contamination should be incorporated. Furthermore, examples of typical background contamination of some common laboratory items should be given in order to make the analysts aware of such problems.

- The ECD temperature should be specified. The variation of sensitivity of the electron capture with detector temperature is well documented. D. Russell and B. McDuffie (3) showed that phthalate ester responses on ECDs decrease with an increase in temperature between 250°C and 340°C. The dibutyl phthalate response increased slightly between 255°C and 260°C, but then decreased from 260°C to 310°C, above which temperature no response was observed. Other phthalate esters (dimethyl, diethyl, dihexyl, diphenyl, dioctyl) also exhibited this phenomenon at temperatures above 300°C to 310°C.

- GC analysis is performed on packed columns. Column 1 (1.5% SP-2250/1.95% SP-2401) requires two isothermal analyses (at 180°C and 220°C), and Column 2 (3% OV-1) also requires two isothermal analyses (at 200°C and 220°C). Isothermal temperature analyses with packed columns are not practical when dealing with complex matrices because material injected onto the column will tend to accumulate at the head of the column, and the higher-boiling materials will emerge from the column at a later time, contributing to cross-contamination of samples. Furthermore, the resolution when using the packed columns is far below that achieved with capillary columns and, consequently, substitution of the packed columns by capillary columns should be investigated.

- No internal standards and surrogate compounds are specified for use in Method 8060.

- The acceptance criteria for accuracy (compound recovery) are quite broad. Four of the six phthalate esters have recovery ranges from

detected (D) to as high as 159 percent. Narrower ranges are desirable at least for clean water samples.

- The sample cleanup procedures (Methods 3610 and 3620) specify the use of large volumes of solvents that may increase the contamination of sample extracts by impurities in the solvents (e.g., 140 mL of 20 percent diethyl ether in hexane for Method 3610 and 100 mL of 20 percent diethyl ether in hexane for Method 3620) and methods requiring less adsorbent and less solvents are therefore desirable. Thuren (4) reported a procedure using 3 g of 3-percent water-deactivated Florisil; the extract was loaded to the Florisil column and eluted with 10 mL petroleum ether followed by 25 mL of 20 percent diethyl ether in petroleum ether. The first fraction (0 to 15 mL) contained polychlorinated biphenyls (PCBs) and DDT, and the second fraction (16 to 35 mL) contained the phthalates esters.

- The protocol lacks any information regarding the recoveries of the six phthalate esters from the cleanup procedures given in Methods 3610 and 3620. Advantages and disadvantages of each method should be stated.

Since the current protocol was inadequate in certain areas (e.g., in addressing background contamination) and was lacking information in other areas such as sample cleanup and 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 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 phthalate esters

- 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 revised and then tested in Phase II on a variety of samples. Performance data generated during the evaluation of the revised Method 8060 include:

- Measures of precision and accuracy

- Evidence of analyte identification
- Evidence for resolution of analyte from interfering substances
- Ruggedness study
- Method detection limits.

Subsequent sections of this report present the conclusions and recommendations of this study, a brief literature review, details of the experimental procedures, and the results and discussion. Appendix A contains the literature review. The revised protocol is included as Appendix B. Appendix C presents the mass spectra of 16 phthalate esters and 6 additional compounds proposed as surrogates and internal standards for Method 8060. Appendix D contains the results of the inorganic analyses of the various aqueous matrices used in the method evaluation.

SECTION 2

CONCLUSIONS

Based on the results presented in this report, several important conclusions can be drawn concerning the determination of phthalate esters in the environmental samples.

- Revision of Method 8060 for the determination of the phthalate esters in environmental samples was necessary because: the packed columns did not have enough resolving power to handle complex environmental samples; the number of compounds listed in the method was limited to six, whereas several other phthalate esters were reported in air and water samples collected throughout the United States; confirmation of compounds by GC/MS was not mentioned; interferences were not addressed in detail; the acceptance criteria for method accuracy were too broad; and sample cleanup procedures did not give any recovery information for the six phthalate esters, and large columns and large volumes of eluting solvents are used which may potentially contaminate samples upon extract concentration.

- Contamination from solvents and reagent materials used in the analysis and glassware limits the detection of phthalate esters at trace levels (ppt-ppb range). Consequently, their determination in environmental samples at ppt-ppb range requires pesticide-grade solvents, thorough cleaning of the glassware followed by heat-treatment (for those that can withstand 400°C temperatures), and a 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 reduces the extraction time, and also minimizes contamination. Preconcentration of aqueous samples on C_{18}-membrane disks followed by extraction of 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 cartridges with hexane/acetone (9:1). The use of Florisil disposable 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 the loss of the lower-molecular-weight esters.

- A 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 time and detector response 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 electron capture detectors.

SECTION 3

RECOMMENDATIONS

- The revised Method 8060 presented in this report has been evaluated in a single laboratory with a few relevant aqueous and solid samples. However, the revised method should be evaluated by other laboratories and with additional samples. This would help identify the applicability range of the method and would define the interlaboratory method performance.

- When applying the revised Method 8060 to samples which have not been previously characterized, identification and quantification of the 16 phthalate esters using the dual-column/dual-detector approach is very reliable. However, determination of the phthalate esters by GC/MS in the selected ion monitoring mode should be considered for future investigation since it would certainly improve the method detection limits, and extract cleanup may not be required.

- Other internal standards and surrogate spiking compounds need to be investigated, and criteria for the selection of internal standards and surrogates need to be developed.

- Standard reference materials certified for phthalate esters need to be developed so interlaboratory method evaluation studies can be conducted.

SECTION 4

LITERATURE REVIEW

In the initial phase of this study, a literature review concerning analytical methods for the determination of phthalate esters in water, soil, sediment, and sludge samples was conducted. This literature review was performed by using the Computerized Chemical Abstracts search as well as several review articles dealing specifically with the analysis of phthalate esters. Furthermore, recent issues of Analytical Chemistry, the Journal of Chromatography, the Journal of Agricultural and Food Chemistry, the Association of Official Analytical Chemists Journal, and Environmental Science and Technology were searched for information that had not yet been entered in the computer data bases.

The computer searches were done using DIALOG. Chemical Abstracts Files were searched back to 1977 for all references containing "phthalate esters," "gas chromatography," "extraction," and "cleanup." Eighty articles judged to be scientifically relevant to the objectives of this study were retrieved from the literature.

The literature review summary is included as Appendix A and presents the material gathered in the following order:

- Sample preservation techniques
- Extraction techniques for water, soil, and sediment samples
- Sample extract cleanup techniques
- GC analysis (columns, retention time information, chromatographic problems, etc.)
- Compound confirmation
- Background contamination by phthalate esters.

From the review presented in this report, it is evident that there is sufficient information in the literature on sample extraction, cleanup, and analysis of phthalate esters to form a data base upon which to design future experiments. However, none of the information retrieved discusses specifically how to determine all of the phthalate esters listed in Method 8060 or those listed in Table 1 in hazardous liquid and solid samples.

SECTION 5

EXPERIMENTAL PROCEDURES

The method development tasks which are presented in this report include evaluation of the extent of background contamination by phthalate esters, sample analysis by GC/ECD and GC/FID using the single column and the dual column approach the sample extraction, and extract cleanup.

5.1 SAMPLE ACQUISITION

All phthalate esters listed in Table 1 were obtained from Chem Service (distributed by Bryant Laboratories, Inc.), except for diethyl phthalate and diisooctyl phthalate which were obtained from Scientific Polymer Products. The purity of the compounds was stated in the catalog to be greater than 98 percent. Stock solutions of each test compound were prepared initially in isooctane (Baker Resi-Analyzed, J. T. Baker) at concentrations of 1 mg/mL. Working calibration standards were prepared initially in isooctane and later in hexane by serial dilution of a composite stock solution prepared from the individual stock solutions.

The organic solvents and the reagent water samples listed in Table 2 were investigated for possible contamination with phthalate esters. Other materials that were investigated included Florisil, alumina, silica gel, filter paper, paper thimbles, aluminum foil, sodium sulfate, and glass wool purchased from various suppliers (Table 3).

The aqueous samples used in the method evaluation included an estuarine water sample taken from the San Francisco Bay, a groundwater sample, and a leachate sample. The leachate sample was prepared from a soil sample, highly contaminated in lead, as follows: 100 g (net weight) of soil was mixed with 1,600 mL deionized water, adjusted to pH 5.2 with 0.5 N acetic acid, and shaken for 24 hrs on a mechanical shaker. Details of procedure are given in Method 1310 of SW-846 Methods Manual. The leachate was filtered through a 0.45-μm Millipore filter (Fisher Scientific, Pittsburgh) prior to extraction with methylene chloride. The results of the inorganic analyses of the three aqueous matrices are included as Appendix D of this report.

The solid matrices used in the method evaluation included three NIST Standard Reference Materials, two sandy loam samples, a sediment of unknown origin contaminated with petroleum hydrocarbons, an estuarine sediment, and a municipal sludge (Table 4).

TABLE 2. IDENTIFICATION OF THE SOLVENT SAMPLES INVESTIGATED

Solvent	Purchased from	Identification	
		Brand	Acurex ID
Acetone	VWR Scientific	Omnisolve, glass-distilled, Lot No. 6352, EM Science	8707-032-1 8707-032-2
Acetone	VWR Scientific	Baker Resi-Analyzed, pesticide residue, Lot No. 643165, J. T. Baker Chemical Co.	8707-032-3 8707-032-4
Acetone	American Scientific	Nanograde, Lot No. 0018-KAXN, Mallinckrodt	8707-032-5 8707-032-6
Acetone	American Scientific	American Burdick & Jackson, Product 010 Lot No. AQ529	8707-032-7 8707-032-8
Acetone	Fisher Scientific	Pesticide grade, UN 1090, Lot No. 870359, Fisher Scientific	8707-032-9 8707-032-10
Acetone	Sargent Welch	Mallinckrodt Nanograde Lot No. 0018 KBDY	8707-032-51 8707-032-52
Acetone	Fisher Scientific	Optima Lot No. 870881	8707-032-63 8707-032-64
Acetone	Caledon Laboratories	Distilled in glass Lot No. 706037	8707-032-71 8707-032-72
Hexane	VWR Scientific	Omnisolve, glass-distilled, Lot No. 6349, EM Science	8707-032-11 8707-032-12
Hexane	VWR Scientific	Baker Resi-Analyzed, Lot No. 604100, J. T. Baker Chemical Co.	8707-032-13 8707-032-14
Hexane	American Scientific	Nanograde, Lot No. 4159KBEZ, Mallinckrodt	8707-032-15 8707-032-16
Hexane	American Scientific	American Burdick & Jackson, Product 217, Lot No. AP783	8707-032-17 8707-032-18

(continued)

TABLE 2. (continued)

Solvent	Purchased from	Identification	
		Brand	Acurex ID
Hexane	Fisher Scientific	Pesticide grade, UN 1208, Lot No. 761495, Fisher Scientific	8707-032-19 8707-032-20
Hexane	Sargent Welch	Mallinckrodt Nanograde Lot No. 4159 KAXD	8707-032-53 8707-032-54
Hexane	Fisher Scientific	Optima Lot No. 873245	8707-032-65 8707-032-66
Hexane	Caledon Laboratories	Distilled in glass Lot No. 706302	8707-032-73 8707-032-74
Isooctane	VWR Scientific	Omnisolve, glass-distilled, Lot No. 6323, EM Science	8707-032-31 8707-032-32
Isooctane	VWR Scientific	Baker Resi-Analyzed, Lot No. 627718, J. T. Baker Chemical Co.	8707-032-33 8707-032-34
Isooctane	American Scientific	Nanograde, Lot No. 6051KBBR Mallinckrodt	8707-032-35 8707-032-36
Isooctane	American Scientific	American Burdick & Jackson, Product 362, Lot No. AP915	8707-032-37 8707-032-38
Isooctane	Fisher Scientific	Pesticide grade, O-297, Lot No. 864429, Fisher Scientific	8707-032-39 8707-032-40
Isooctane	Sargent Welch	Mallinckrodt Nanograde Lot No. 6051 KAPM	8707-032-57 8707-032-58
Isooctane	Fisher Scientific	Optima Lot No. 872894	8707-032-67 8707-032-68
Isooctane	Caledon Laboratories	Distilled in glass Lot No. 707031	8707-032-77 8707-032-78

(continued)

TABLE 2. (continued)

Solvent	Purchased from	Identification	
		Brand	Acurex ID
Diethyl Ether	VWR Scientific	Baker Analyzed Lot No. A23099 J. T. Baker Chemical Co.	8707-032-21 8707-032-22
Diethyl Ether	American Scientific	Nanograde, Lot No. 3434KBBA Mallinckrodt	8707-032-23 8707-032-24
Diethyl Ether	American Scientific	American Burdick & Jackson Product 106, Lot No. AQ476	8707-032-25 8707-032-26
Diethyl Ether	Fisher Scientific	HPLC grade, E198-4 Lot No. 871047	8707-032-27 8707-032-28
Diethyl Ether	Fisher Scientific	Spectraanalyzed, E193 Lot No. 861047	8707-032-29 8707-032-30
Diethyl Ether	Sargent Welch	Nanograde, Lot No. 3434KBBA Mallinckrodt	8707-032-55 8707-032-56
Diethyl Ether	Atomergic	Ultrar Lot No. 378950	8707-032-61 8707-032-62
Diethyl Ether	Caledon Laboratories	Distilled in glass Lot No. 706145	8707-032-75 8707-032-76
Methylene chloride	VWR Scientific	Omnisolve, glass-distilled, Lot No. 7057, EM Science	8707-032-41 8707-032-42
Methylene chloride	VWR Scientific	Baker Resi-Analyzed, Lot No. A03137, J. T. Baker Chemical Co.	8707-032-43 8707-032-44
Methylene chloride	American Scientific	Nanograde, Lot No. 3023KBED-A Mallinckrodt	8707-032-45 8707-032-46
Methylene chloride	American Scientific	American Burdick & Jackson, Product 300, Lot No. A0174	8707-032-47 8707-032-48

(continued)

TABLE 2. (concluded)

Solvent	Purchased from	Identification	
		Brand	Acurex ID
Methylene chloride	Fisher Scientific	Pesticide grade D142-4, Lot No. 870226	8707-032-49 8707-032-50
Methylene chloride	Sargent Welch	Nanograde, Lot No. 3023 KAGR-A, Mallinckrodt	8707-032-59 8707-032-60
Methylene chloride	Fisher Scientific	Optima Lot No. 870483	8707-032-69 8707-032-70
Methylene chloride	Caledon Laboratories	Distilled in glass Lot No. 707192	8707-032-79 8707-032-80
Water	American Scientific	Chrom AR Mallinckrodt HPLC grade, Lot No. 6795	8707-034-1 8707-034-2
Water	American Scientific	American Burdick & Jackson Product 365, Lot No. AP643	8707-034-3 8707-034-4
Water	Fisher Scientific	HPLC grade Lot No. 872758	8707-034-5 8707-034-6
Water	VWR Scientific	Baker analyzed HPLC water Lot No. A19097	8707-034-7 8707-034-8
Water	VWR Scientific	Omnisolve EM Science Lot No. 7020	8707-034-9 8707-034-10

TABLE 3. MATERIALS INVESTIGATED FOR POSSIBLE CONTAMINATION WITH PHTHALATE ESTERS

Material	Purchased from	Identification
Florisil	VWR Scientific	J. T. Baker, 60/100 mesh, Lot No. 606721
Florisil PR	VWR Scientific	Supelco, Inc., 60/100 mesh Lot No. 575
Alumina	VWR Scientific	J. T. Baker, aluminum oxide, neutral, Brockman activity, grade I, Lot No. 634733
Alumina	Universal Scientific, Inc.	Alumina Woelm N-Super I, activity grade Super I, Woelm Pharma
Silica gel	VWR Scientific	J. T. Baker Baker-analyzed, 60/200 mesh, Lot No. 610728
Silica gel	VWR Scientific	EM Science, 100/200 mesh, grade 923, Stock No. 7091
Filter paper	VWR Scientific	VWR product, grade 54, 18.5 cm
Filter paper	VWR Scientific	Whatman No. 41, ashless, 18.5 cm
Paper thimbles	Cal Glass	Schleicher & Schuell, 43 x 123 mm, Ref. No. 350267
Paper thimbles	VWR Scientific	Whatman 43 mm x 123 mm
Aluminum foil	Alpha Beta Supermarket	Reynolds Heavy, 75 ft^2
Aluminum foil	Alpha Beta Supermarket	Skaggs Alpha Beta Heavy Duty, 37.5 ft^2
Sodium sulfate	Fisher Scientific	Fisher Scientific, Lot No. 870988
Sodium sulfate	VWR Scientific	EM Science, Stock No. 6183
Glasswool	Alltech Associates, Inc.	Pest grade, Lot No. 7753, Stock No. 4034
Glasswool	Alltech Associates, Inc.	DMCS treated, Lot No. 7651 Stock No. 4037 AA8

TABLE 4. NIST STANDARD REFERENCE MATERIALS AND OTHER SOLID MATRICES USED IN THE METHOD EVALUATION

Material	Description
SRM-1572	Citrus leaves from Lake Alfred area of central Florida. The material was air-dried, ground to pass through a 425-μm screen, dried at 85°C, mixed in a feed blender, and sterilized with Cobalt-60 radiation.
SRM-1632a	Coal obtained from the Humphrey No. 7 mine and coal preparation plant of the Consolidation Coal Co., Osage, West Virginia. Contains approximately 1.8 to 1.9 percent sulfur and was ground to pass through a 60-mesh sieve.
SRM-1633a	Coal flyash, obtained from a coal-fired power plant that uses Pennsylvania and West Virginia coals. The material was sieved to pass through a 90-μm screen.
Sandy loam soil	Mixture of 20 percent organic soil and 80 percent sand.
Sediment sample	Unknown origin, contaminated with petroleum hydrocarbons.
Estuarine sediment	Collected from the San Francisco Bay Area off Seaport Blvd., South San Francisco, California (highly contaminated with elemental sulfur).
Municipal sludge	Obtained from the Santa Clara Valley Water District, San Jose, California.

The revised method 8060 was also evaluated with a series of EPA performance evaluation samples identified as WP 482 Sample 1, WP 482 Sample 2 WP 482 Sample 3, WP 482 Sample 4, WP 485, and WP 281 Sample 2. These samples consisted of concentrated acetone solutions containing some of the target compounds and other organics (e.g., phenols, polynuclear aromatic hydrocarbons, chlorinated benzenes, nitrotoluenes, etc.) at known concentrations. These solutions were diluted with hexane and analyzed by GC/ECD to determine if other organics present in the sample interfere with the target compounds.

5.2 BACKGROUND CONTAMINATION STUDY

A portion of each solvent (150 mL for acetone and hexane, 30 mL for diethyl ether, and 180 mL for methylene chloride) was condensed by Kuderna-Danish evaporation to approximately 10 mL, and then to 1 mL using a gentle stream of high-purity nitrogen (99.999 percent), which was directed across the mouth of the Kuderna-Danish receiver. No concentration was performed for isooctane. At least two replicate samples of each solvent were prepared and analyzed by GC/ECD, with the exception of methylene chloride concentrates which were analyzed by GC/FID. The volumes of solvents used are those specified in Method 8060 and in the 3500 series methods. For example, Method 3510 specifies extraction of aqueous sample with three 60-mL portions of methylene chloride and Method 3620 specifies elution of a Florisil column with 140 mL of 20 percent diethyl ether in hexane.

Materials such as Florisil, alumina, silica gel, anhydrous sodium sulfate, and glass wool were immersed overnight in 200 or 300 mL of solvent. The exact volume and the solvent used are specified in the Results and Discussion section. The solvent was then decanted and concentrated to 1 mL for GC analysis. The amounts of Florisil, alumina, and anhydrous sodium sulfate are twice as large as those recommended in Method 3620, 3610, and 3510, respectively. For glass wool we used arbitrarily 5 g.

Other materials such as filter paper, paper thimbles, and aluminum foil were cut into 0.5 in. x 0.5 in. pieces and immersed into 100 or 200 mL of hexane/acetone (1:1). The solvent was then separated and concentrated to 1 mL for GC analysis.

5.3 EVALUATION OF GAS CHROMATOGRAPHY

GC with ECD and FID was evaluated only with fused-silica capillary columns. The gas chromatographs used throughout this study were a Varian 6000 equipped with a constant current pulsed-frequency ECD and interfaced with a Varian Vista 402 data system, a Varian 6500 gas chromatograph equipped with a FID and interfaced with either a Spectra Physics 4290 integrator or a Varian Vista 402 data system, and a Varian 3400 gas chromatograph equipped with a constant current pulsed-frequency ECD and interfaced to a Varian Vista 402 data system. All injections were performed with Varian Model 8000 autosamplers.

Three fused-silica capillary columns were investigated for the single column approach. The GC operating conditions for each column are given in Table 5.

TABLE 5. GC OPERATING CONDITIONS FOR THE SINGLE-COLUMN APPROACH

	Column 1	Column 2	Column 3
Instrument	Varian 6000 (ECD)	Varian 6500 (FID)	Varian 3400 (ECD)
Column dimensions	30 m x 0.25 mm ID	30 m x 0.53 mm ID	30 m x 0.53 mm ID
Liquid phase	DB-5 (J&W Scientific)	Supelcowax-10 (Supelco Inc.)	DB-210 (J&W Scientific)
Film thickness (μm)	0.25	1.0	1.0
Carrier gas	Helium	Helium	Helium
Carrier flowrate (cm/sec)	5* (33 psi)	(40 psi)	11.5 mL/min
Makeup gas	Nitrogen	Helium	Nitrogen
Makeup flowrate (mL/min)	65	30	28
Temperature program:	(1) 150°C to 275°C at 15°C/min (2) 120°C to 260°C at 15°C/min, then 260°C to 300°C at 2°C/min (3) 120°C to 260°C at 15°C/min, then 260°C to 280°C at 2°C/min	100°C (2-min hold) to 240°C (14-min hold) at 10°C/min	125°C (1-min hold) to 240°C (16-min hold) at 5°C/min
Injector temperature (°C)	275	250	250
Detector temperature (°C)	285 and 310	250	250
Injection volume (μL)	1.0 (isooctane)	1.0 (isooctane)	1.4 (hexane)
Type of injection	Splitless	Splitless	On-column
Splitless time (sec)	45	45	--
Split flow (mL/min)	60	100	--

*Measured at 120°C.

Four 30 m x 0.53 mm ID fused-silica open tubular columns were investigated for the dual-column/dual-detector approach. The four columns were paired as shown in Table 6, using two different injection tees.

5.4 EXTRACTION TECHNIQUES

5.4.1 Sample Extraction

The extraction efficiencies for the Method 8060 compounds were determined for HPLC-grade water at pH 2, 7, and 9, using separatory funnel extraction with methylene chloride (Method 3510) and continuous liquid-liquid extraction (Method 3520). The compounds were spiked into each water sample at 5 µg/L; quantification was performed by GC/ECD using a DB-5 fused-silica capillary column and external standard calibration.

Microextraction of 50-mL spiked HPLC-grade water samples using a Mixxor device (Lidex Technologies, Inc.) and hexane (10 mL) as the extraction solvent was also tested. The solvent and the aqueous sample were added to the upper reservoir, the cap was tightened, and the piston was moved up and down in the mixing chamber five or six times. The hexane layer was decanted into a 40-mL vial and dried with precleaned anhydrous sodium sulfate. The hexane layer was then transferred to another vial and concentrated to 1 mL under a gentle stream of high-purity nitrogen. Quantification was performed by GC/ECD using a DB-5 fused-silica capillary column and external standard calibration.

Evaluation of C_8- and C_{18}-membrane disks (Analytichem International) was performed with HPLC-grade water and groundwater spiked at 25 µg/L and 100 µg/L. The aqueous matrix (500 mL) was filtered through the membrane disk installed in a Millipore filtration apparatus at a flowrate of approximately 25 mL/min. The C_8- or the C_{18}-membrane disk was preconditioned, immediately prior to use, with 10 mL methanol followed by 10 mL HPLC-grade water. To improve the extraction efficiency of the membrane disk, 2.5 mL methanol were added to each aqueous sample prior to filtration. The target compounds were extracted from the membrane disk with 10 mL acetonitrile. The acetonitrile extract was concentrated to a final volume of 1 mL using a gentle stream of high-purity nitrogen (99.999 percent) and analyzed by GC/ECD using the dual-column/dual-detector approach.

Soil or sediment samples were extracted either with hexane/acetone (1:1) in a Soxhlet extractor (Method 3540) or with methylene chloride/acetone (1:1) using a sonic probe (Heat Systems Ultrasonics, Inc., Model W-375) following the procedures specified in Method 3550.

5.4.2 Soil Spiking

The following procedure was used for spiking soil samples that were used in comparing Methods 3540 and 3550. One hundred grams potting soil and 400 g sand were mixed with 200 mL deionized water and were blended at full speed for 2 min in a Waring laboratory blender, Waring Products Division, Dynamics Corporation of America, New Hartford, Connecticut. Twenty milliliters of an isooctane solution containing the Method 8060 compounds at concentrations of 35 µg/mL were added, and blending was continued for 10 min with intermittent cooling to yield a smooth slurry. Immediately after blending, the slurry was

TABLE 6. GC OPERATING CONDITIONS FOR THE DUAL-COLUMN/DUAL-DETECTOR APPROACH

	DB-5/DB-608	DB-608/DB-1701	RT_x-5/DB-608	DB-5/DB-1701
Instrument	Varian 6500/Vista 604 data system	Varian 6000/Vista 402 data system	Vista 6500/Vista 402 data system	Vista 6000/Vista 402 data system
Column dimensions	30 m x 0.53 mm ID	30 m x 0.53 mm ID	30 m x 0.53 mm ID	30 m x 0.53 mm ID
Liquid phase (Film thickness)	DB-5 (1.5 μm) DB-608 (0.83 μm)	DB-608 (0.83 μm) DB-1701 (1.0 μm)	RT_x-5 (0.5 μm) DB-608 (0.83 μm)	DB-5 (1.5 μm) DB-1701 (1.0 μm)
Carrier gas and flowrate	Helium (6 mL/min)	Helium (6 mL/min)	Helium (6 mL/min)	Helium (6 mL/min)
Makeup gas	Nitrogen	Nitrogen	Nitrogen	Nitrogen
Makeup flowrate (mL/min)	19	19	19	19
Temperature Program:	150°C (0.5-min hold) to 220°C at 5°C/min, then to 275°C (18-min hold) at 3°C/min	150°C (0.5-min hold) to 220°C at 5°C/min, then to 275°C (18-min hold) at 3°C/min	150°C (0.5-min hold) to 220°C at 5°C/min then to 275°C (18 min hold) at 3°C/min	150°C (0.5-min hold) to 220°C at 5°C/min, then to 275°C (18-min hold) at 3°C min
Injector temperature (°C)	250	250	250	250
Detector temperature (°C)	320	320	320	320
Injection volume (μL)	2	2	2	2
Type of injection tee	Supelco, 8-in injection tee	Supelco, 8-in injection tee	Supelco, 8-in injection tee	J&W Scientific press-fit Y shape splitter

separated into 35-g portions. The slurry was stirred 10 sec after each portion removal from the blender.

The portions were serially labeled in the order in which the removal was done. Those portions that carried even numbers were analyzed immediately. The portions with odd numbers were either frozen for up to 1-1/2 months at -10°C or stored at 4°C in a walk-in refrigerator.

5.5 EXTRACT CLEANUP

5.5.1 Florisil Chromatography

Florisil from J. T. Baker (60/80 mesh size; Lot No. 442707) was activated for 16 hrs at 400°C, allowed to cool in a precleaned amber glass jar, and then deactivated with distilled water (3 percent by weight). The glass jar was rolled for 10 min and then allowed to sit for at least 2 hrs. Ten grams of the deactivated Florisil were loaded to a chromatographic column (20 mm ID x 500 mm length) and topped with 1 cm (bed height) of precleaned anhydrous sodium sulfate. The columns were first eluted with 40 mL hexane which was discarded; hexane standards or sample extracts were loaded to the columns, and the phthalate esters were eluted with 100 mL of 20 percent diethyl ether in petroleum ether. The fractions were concentrated to 10 mL by Kuderna-Danish evaporation.

Florisil disposable cartridges (Supelco, Inc.) containing LC-Florisil 40 µm particles (60 Å pores) were each prewashed with 4 mL pesticide grade hexane prior to use. Florisil cartridges were eluted in sets of 12 on a Supelclean™ vacuum manifold (Supelco, Inc.) that provided increased sample throughput while the volume of the eluting solvent was kept to a minimum. The eluting solvents evaluated with the Florisil disposable cartridges are given in Section 6.4.

5.5.2 Alumina Chromatography

Alumina Woelm N Super I, W200 series was activated for 16 hours at 400°C, allowed to cool in a precleaned amber glass jar, and then deactivated with distilled water (3 percent by weight). The glass jar was rolled for 10 min and then allowed to sit for at least 2 hrs. Ten grams of the deactivated alumina were loaded to a chromatographic column (20 mm ID x 500 mm length) and topped with 1 cm (bed height) of precleaned anhydrous sodium sulfate. The columns were first eluted with 35 mL hexane which was discarded; hexane standards or sample extracts were loaded to the columns and the phthalate esters were eluted with 140 mL of 20 percent diethyl ether in hexane. The fractions were concentrated to 10 mL by Kuderna-Danish evaporation.

5.6 SAMPLE PRESERVATION

Preservation studies were carried out for both water and soil samples. Fourteen 1-L reagent water samples were spiked with the test compounds at one concentration and stored in the dark at 4°C for up to 21 days. Two samples were extracted immediately; other samples were removed at day 1, 3, 7, 10, 14, and 21 and analyzed for the 16 test compounds. Duplicate measurements were performed at each time event. In addition, six 1-L samples were spiked with

the test compounds at one concentration and were adjusted to pH 2 with 6N H_2SO_4. Two samples were extracted immediately; the other samples were stored at 4°C for 7 days and 14 days. This experiment was repeated at pH 9.

Thirty-gram portions of sandy loam soil spiked with the 16 phthalate esters at 1 µg/g per component were stored frozen at -10°C for 1 month. At day 3, 7, 14, and 28 they were removed and analyzed for the target compounds.

5.7 GC/MS METHODOLOGY

A Finnigan 4510B GC/MS system interfaced to a Finnigan Nova 4X data system was used in this study. The GC was equipped with a split/splitless injector. The column was a 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 µm film thickness) supplied by J&W Scientific, Inc. The GC instrumental conditions were as follows:

- Temperature program -- 40°C to 300°C at 8°C/min
- Injector temperature -- 250°C
- Transfer line temperature -- 260°C
- Injection volume -- 1 µL
- Solvent -- methylene chloride
- Carrier gas -- helium at 10 psi at 40°C

The MS conditions were as follows:

- Ion source tuning -- as per EPA DFTPP requirement
- Ion source temperature -- 190°C
- Scanning mass range -- 45 to 450 amu
- Scan rate -- 1 sec/cycle
- Electron energy -- 70 eV
- Multiplier voltage -- 1,400 eV

5.8 GLASSWARE CLEANUP

All glassware used in this study, except the continuous liquid-liquid extractors, Soxhlet extractors, and the volumetric glassware, were washed with Alconox detergent and hot water, were rinsed with tap water and with deionized water, and were finally baked at 400°C for 2 hrs unless otherwise indicated. The continuous liquid-liquid extractors, the Soxhlet extractors, and the volumetric glassware were washed as described above and were rinsed with American Burdick & Jackson acetone immediately after washing and again prior to use.

SECTION 6

RESULTS AND DISCUSSION

6.1 BACKGROUND CONTAMINATION STUDY

This study was undertaken in conjunction with the evaluation of EPA Method 8060 for the determination of phthalate esters in environmental samples. Since contamination of samples could not be avoided even with the highest degree of precaution, we wanted to know the sources of contamination and the conditions under which we might be able to reduce the background contamination. Various solvents recommended for use in Method 8060 were obtained from six commercial suppliers and were concentrated up to 180-fold to determine background levels of 11 phthalate esters. Reagent water samples from three commercial suppliers, totaling five different brands, were analyzed for 16 phthalate esters. Materials used in sample workup that were investigated in this study include: Florisil, alumina, silica gel, filter paper, paper thimbles, aluminum foil, anhydrous sodium sulfate, and glass wool. In each case, a minimum of two brands of each material was obtained from commercial suppliers. Solvent washing, as well as high temperature (400°C) treatment followed by solvent washing, was employed to remove traces of phthalate esters. The solvent washings were analyzed for 11 phthalate esters. Finally, the likelihood of contamination of laboratory glassware subjected to common laboratory cleanup procedures, and the likelihood of contamination of hexane and isooctane stored in sample vials of different sizes and capped with metal foil or Teflon-lined crimp-top caps were addressed.

6.1.1 Organic Solvents

Five organic solvents from 6 different commercial suppliers were analyzed for 11 of the most common phthalate esters. The results are summarized in Tables 7 through 11. Five phthalate esters that were detected in these solvents include: DIBP, DBP, DHP, BBP, and DEHP. Their levels range from 0.1 to 0.87 ng/mL for hexane and acetone, 0.2 to 3.6 ng/mL for diethyl ether, and 10 to 115 ng/mL for isooctane. No phthalate esters were detected in any of the methylene chloride solvents, except for DOP in one sample; however, the detection limits were much higher than for the other solvent, since the condensates were analyzed by GC/FID.

Since typical volumes of hexane and acetone used in sample workup are 200 to 300 mL, then the amounts of the phthalate esters which will be introduced as contaminants with the organic solvent may be as high as 260 ng per compound. This amount will result in concentrations of 26 ng/g of sample for a 10 g sample extracted with hexane/acetone.

TABLE 7. BACKGROUND LEVELS OF PHTHALATE ESTERS IN VARIOUS BRANDS OF ACETONE

Supplier	Brand	Lot No.	Concentration (ng/mL)[a]										
			DMP	DEP	DIBP	DBP	DAP	DHP	BBP	DEHP	DCP	DOP	DNP
VWR Scientific	Omnisolve, glass distilled, EM Science	6352	<0.10	<0.10	<0.10	0.20	<0.10	<0.10	0.10	0.17	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	0.24	<0.10	<0.10	0.22	0.16	<0.10	<0.10	<0.10
VWR Scientific	Baker Resi-Analyzed, pesticide residue, J. T. Baker Chemical Co.	643135	<0.10	<0.10	<0.10	0.47	<0.10	<0.10	0.41	0.15	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	0.40	<0.10	<0.10	0.40	0.18	<0.10	<0.10	<0.10
American Scientific	Mallinkrodt, Nanograde	0018 KAXN	<0.10	<0.10	<0.10	0.44	<0.10	<0.10	<0.10	0.40	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	0.40	<0.10	<0.10	<0.10	0.36	<0.10	<0.10	<0.10
American Scientific	American Burdick & Jackson, Product 010	AQ529	<0.10	<0.10	0.33	<0.10	<0.10	<0.10	0.41	0.11	<0.10	<0.10	<0.10
			<0.10	<0.10	0.37	<0.10	<0.10	<0.10	0.20	0.13	<0.10	<0.10	<0.10
Fisher Scientific	Fisher Scientific, pesticide grade, UN 1090	870359	[b]	[b]	<0.10	<0.10	<0.10	<0.10	0.42	0.10	<0.10	<0.10	<0.10
			[b]	[b]	<0.10	<0.10	<0.10	<0.10	0.57	0.43	<0.10	<0.10	<0.10
			[b]	[b]	<0.10	<0.10	<0.10	<0.10	0.40	0.44	<0.10	<0.10	<0.10
Fisher Scientific	Optima	870881	<0.10	0.40	<0.10	<0.10	<0.10	0.10	<0.10	<0.10	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	<0.10	<0.10	<0.20	<0.10	<0.10	<0.10	<0.10	<0.10
Caledon Laboratories	Distilled in glass	706037	<0.10	<0.10	<0.10	0.50	<0.10	0.40	<0.10	0.50	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	0.50	<0.10	0.50	<0.10	0.40	<0.10	<0.10	<0.10
Sargent Welch	Mallinkrodt, nanograde	0018 KBDY	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10

[a]Concentration factor is 150. Analyses were performed by GC/ECD using a 30 m x 0.25 mm ID DB-5 fused-silica capillary column. Two replicate samples were analyzed from each brand of acetone, except for Fisher Scientific brand where three replicates were analyzed.
[b]Not able to quantify compound because of interference.

TABLE 8. BACKGROUND LEVELS OF PHTHALATE ESTERS IN VARIOUS BRANDS OF HEXANE

			Concentration (ng/mL)*										
Supplier	Brand	Lot No.	DMP	DEP	DIBP	DBP	DAP	DHP	BBP	DEHP	DCP	DOP	DNP
VWR Scientific	Omnisolve, glass distilled, EM Science	6349	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
VWR Scientific	Baker Resi-Analyzed, J. T. Baker Chemical Co.	604100	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.13	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
American Scientific	Mallinkrodt, Nanograde	4159KBEZ	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.23	<0.10	<0.10	<0.10
			<0.10	<0.10	0.33	<0.10	<0.10	<0.10	<0.10	0.67	<0.10	<0.10	<0.10
			<0.10	<0.10	0.37	<0.10	<0.10	<0.10	<0.10	0.21	<0.10	<0.10	<0.10
American Scientific	American Burdick & Jackson, Product 217	AP783	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Fisher Scientific	Fisher Scientific, pesticide grade, UN 1208	761495	<0.10	<0.10	<0.10	<0.10	<0.10	0.87	<0.10	<0.10	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	<0.10	<0.10	0.87	<0.10	<0.10	<0.10	<0.10	<0.10
Fisher Scientific	Optima	873245	<0.10	<0.10	0.20	<0.10	<0.10	<0.10	<0.10	0.20	<0.10	<0.10	<0.10
			<0.10	<0.10	0.20	<0.10	<0.10	0.50	<0.10	0.40	<0.10	<0.10	<0.10
Caledon Laboratories	Distilled in glass	706302	<0.10	<0.10	<0.10	<0.10	<0.10	0.30	<0.10	0.40	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	<0.10	<0.10	0.30	<0.10	0.40	<0.10	<0.10	<0.10
Sargent Welch	Mallinkrodt, nanograde	4159 KBXD	<0.10	<0.10	<0.10	<0.10	<0.10	0.10	<0.10	0.30	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	<0.10	<0.10	0.10	<0.10	<0.10	<0.10	<0.10	<0.10

*Concentration factor is 150. Analyses were performed by GC/ECD using a 30 m x 0.25 mm ID DB-5 fused-silica capillary column. Two replicate samples were analyzed from each brand of hexane, except for Mallinkrodt Nanograde brand where four replicates were analyzed.

TABLE 9. BACKGROUND LEVELS OF PHTHALATE ESTERS IN VARIOUS BRANDS OF ISOOCTANE

			Concentration (ng/mL)*										
Supplier	Brand	Lot No.	DMP	DEP	DIBP	DBP	DAP	DHP	BBP	DEHP	DCP	DOP	DNP
VWR Scientific	Omnisolve, glass distilled, EM Science	6323	<10	<10	<10	93	<10	<10	<10	15	<10	<10	<10
			<10	<10	<10	81	<10	<10	<10	21	<10	<10	<10
VWR Scientific	Baker Analyzed, J. T. Baker Chemical Co.	627718	<10	<10	<10	91	<10	<10	<10	12	<10	<10	<10
			<10	<10	<10	79	<10	<10	<10	10	<10	<10	<10
American Scientific	Mallinkrodt, Nanograde	6051KBBR	<10	<10	<10	110	<10	<10	<10	12	<10	<10	<10
			<10	<10	<10	115	<10	<10	<10	57	<10	<10	<10
			<10	<10	<10	79	<10	<10	<10	<10	<10	<10	<10
			<10	<10	<10	110	<10	<10	<10	<10	<10	<10	<10
American Scientific	American Burdick & Jackson, Product 362	AP915	<10	<10	<10	76	<10	<10	<10	17	<10	<10	<10
			<10	<10	<10	80	<10	<10	<10	17	<10	<10	<10
Fisher Scientific	Fisher Scientific, pesticide grade, 0-297	864429	<10	<10	<10	94	<10	<10	<10	<10	<10	<10	<10
			<10	<10	<10	100	<10	<10	<10	11	<10	<10	<10
Fisher Scientific	Optima	872894	<10	<10	<10	<10	<10	<10	<10	22	<10	<10	<10
			<10	<10	<10	<10	<10	<10	<10	25	<10	<10	<10
Caledon Laboratories	Distilled in glass	707031	<10	<10	<10	<10	<10	44	<10	77	<10	<10	<10
			<10	<10	<10	<10	<10	40	<10	61	<10	<10	<10
Sargent Welch	Mallinkrodt, nanograde	6051 KAPM	<10	<10	<10	<10	<10	<10	<10	32	<10	<10	<10
			<10	<10	<10	<10	<10	14	<10	11	<10	<10	<10

*Concentration compound is 1. Analyses were performed by GC/ECD using a 30 m x 0.25 mm ID DB-5 fused-silica capillary column. Two replicate samples were analyzed from each brand of isooctane, except for Mallinkrodt Nanograde brand where four replicates were analyzed.

TABLE 10. BACKGROUND LEVELS OF PHTHALATE ESTERS IN VARIOUS BRANDS OF DIETHYL ETHER

			Concentration (ng/mL)*										
Supplier	Brand	Lot No.	DMP	DEP	DIBP	DBP	DAP	DHP	BBP	DEHP	DCP	DOP	DNP
VWR Scientific	Baker Analyzed, J. T. Baker Chemical Co.	A23099	<0.80	<0.80	<0.20	1.8	<0.20	0.70	0.18	0.90	<0.05	<0.20	<0.20
			<0.80	<0.80	<0.20	2.8	<0.20	0.60	0.14	1.0	<0.05	<0.20	<0.20
American Scientific	Mallinkrodt, Nanograde	3434KBBA	3.6	<0.80	<0.20	2.9	<0.20	0.83	0.16	1.3	<0.05	<0.20	<0.20
			3.3	<0.80	<0.20	2.9	<0.20	0.67	0.13	1.3	<0.05	<0.20	<0.20
American Scientific	American Burdick & Jackson, Product 106	AQ476	<0.80	<0.80	<0.20	2.5	<0.20	0.59	0.14	1.1	<0.05	<0.20	<0.20
			<0.80	<0.80	<0.20	1.8	<0.20	<0.20	<0.05	0.30	<0.05	<0.20	<0.20
Fisher Scientific	HPLC grade E198-4	871047	<0.80	<0.80	<0.20	2.5	<0.20	<0.20	<0.05	0.27	<0.05	<0.20	<0.20
			<0.80	<0.80	<0.20	1.7	<0.20	<0.20	<0.05	0.36	<0.05	<0.20	<0.20
Fisher Scientific	Spectra-Analyzed E193	861047	1.1	<0.80	<0.20	2.7	<0.20	0.55	0.13	1.1	<0.05	<0.20	<0.20
			1.5	<0.80	<0.20	3.1	<0.20	0.60	0.11	0.92	<0.05	<0.20	<0.20
Atomergic	Atomergic	378950	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.20	<0.10	<0.10	<0.10
			<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.20	<0.10	<0.10	<0.10
Caledon Laboratories	Distilled in glass	706145	<0.80	<0.80	<0.20	<0.20	<0.20	1.6	<0.05	2.2	<0.05	<0.20	<0.20
			<0.80	<0.80	<0.20	<0.20	<0.20	1.4	<0.05	2.2	<0.05	<0.20	<0.20
Sargent Welch	Mallinkrodt, nanograde	3434 KBBA	2.0	<0.80	<0.20	<0.20	<0.20	0.20	<0.05	<0.20	<0.05	<0.20	<0.20
			2.2	<0.80	<0.20	<0.20	<0.20	0.20	<0.05	0.30	<0.05	<0.20	<0.20

*Concentration factor is 30. Analyses were performed by GC/ECD using a 30 m x 0.25 mm ID DB-5 fused-silica capillary column. Two replicate samples were analyzed from each brand of diethyl ether.

TABLE 11. BACKGROUND LEVELS OF PHTHALATE ESTERS IN VARIOUS BRANDS OF METHYLENE CHLORIDE[a]

Supplier	Brand	Lot No.	Concentration (ng/mL)[a]										
			DMP	DEP	DIBP	DBP	DAP	DHP	BBP	DEHP	DCP	DOP	DNP
VWR Scientific	Omnisolve, glass distilled, EM Science	7057	<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
			<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
VWR Scientific	Baker Resi-Analyzed, J. T. Baker Chemical Co.	A03137	<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
			<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
American Scientific	Mallinkrodt, Nanograde	3023KBED-A	<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
			<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
American Scientific	American Burdick & Jackson, Product 300	A0174	<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	8.8	<6.0
			<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
Fisher Scientific	Pesticide grade, D142-4	870226	<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
			<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
Fisher Scientific	Optima	870483	<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
			<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
Caledon Laboratories	Distilled in glass	707192	<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
			<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
Sargent Welch	Mallinkrodt, nanograde	3023KAGR-A	<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0
			<3.0	<3.0	<3.0	<3.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0	<6.0

[a]Concentration factor is 180. Analyses were performed by GC/FID using a 30 m x 0.53 mm ID Supelcowax-10 fused-silica open tubular column. Two replicate samples were analyzed from each brand of methylene chloride.

6.1.2 Reagent Water

No phthalate esters were detected in any of the five different brands of reagent water at levels above 0.5 or 1.0 μg/L. The results are presented in Table 12. Analyses were performed by GC/FID.

The HPLC-grade water samples from Fisher Scientific (Lot No. 874716) were selected to be analyzed by GC/ECD following extraction with methylene chloride (American Burdick & Jackson, lot AT 348) and solvent-exchange with hexane (American Burdick & Jackson, log AQ 406). Four phthalate esters, DBP, DHP, BBP, and DHP, were detected in seven samples at levels ranging from 0.1 to 0.2 μg/L. None of the other 12 phthalate esters were detected. The method detection limits, estimated from the instrument detection limits, were approximately 0.02 μg/L.

6.1.3 Materials

Tables 13 through 19 present data on the background levels of the phthalate esters in various materials such as Florisil, alumina, silica gel, filter paper, paper thimbles, aluminum foil, anhydrous sodium sulfate, and glass wool. GC/ECD chromatograms of solvent washings obtained from these materials are shown in Figures 1 through 5.

Florisil, alumina, and silica gel (Table 13) showed significant levels, and, therefore, use of these materials in sample cleanup should be employed cautiously. Washing of these materials, prior to use, with the solvent(s) used for elution during the extract cleanup step was helpful.

Use of Florisil disposable cartridges (1 g Florisil per cartridge) has been investigated to determine if contaminant levels will decrease as the amount of Florisil and the volume of the eluting solvent are proportionally decreased. The phthalate esters detected in the method blanks obtained from Florisil disposable cartridges are shown in Table 14. Their levels ranged from 10 to 460 ng with 5 phthalate esters in the 105 to 460 ng range. It is possible that the plastic material used in manufacturing these cartridges contributed these contaminants.

Complete removal of the phthalate esters does not seem possible, and it is desirable to keep the steps involved in sample preparation to a minimum. If cleanup must be used, then method blanks must be obtained prior to sample workup in order to select the cleanest adsorbent. Furthermore, solvent volumes should be kept to a minimum, and solvents from various commercial suppliers should be tested, if information regarding the background levels of phthalate esters is not available.

The filter paper and paper thimble samples were first precleaned in a Soxhlet extractor with acetone for 72 hrs, using fresh solvent which was changed at 24-hr intervals. Following precleaning, samples were cut in small pieces and were immersed in hexane/acetone (1:1) overnight. Figures 3 and 4 present GC/ECD chromatograms obtained before precleaning and after precleaning. It is quite obvious from the results presented in Tables 15 and 16 that washing of the paper filter or paper thimble with solvent, prior to use, is not adequate. Even after Soxhlet extraction for 72 hrs with acetone,

TABLE 12. BACKGROUND LEVELS OF PHTHALATE ESTERS IN VARIOUS BRANDS OF REAGENT WATERS

			Concentration (μg/L)[a]							
Supplier	Brand	Lot No.	DMP	DEP	DIBP	DBP	DMPP	BMEP	DAP	BEEP
American Scientific	Chrom AR Mallinkrodt HPLC grade	6795	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<1.0
			<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<1.0
American Scientific	American Burdick & Jackson, Product 365	AP643	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<1.0
			<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<1.0
Fisher Scientific	HPLC grade	872758[b]	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<1.0
			<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<1.0
VWR Scientific	Baker Analyzed HPLC Water	A19097	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<1.0
			<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<1.0
VWR Scientific	Omnisolve EM Science	7020	<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<1.0
			<0.5	<0.5	<0.5	<0.5	<0.5	<1.0	<0.5	<1.0

(continued)

[a]One-liter water sample was extracted in a separatory funnel, three times, with 60 mL methylene chloride (American Burdick & Jackson, Lot No. A0174), the extract dried with anhydrous sodium sulfate (Fisher Scientific Lot No. 872983, heated at 400°C for 4 hours) and concentrated in a Kuderna-Danish evaporator to 1 mL. Analyses were performed by GC/FID using a 30 m x 0.53 mm ID Supelcowax-10 fused-silica open tubular column. Two replicate samples were analyzed from each brand of reagent water.

[b]Another lot of HPLC-grade water from Fisher Scientific (lot 874716) was analyzed by GC/ECD.

TABLE 12. (concluded)

Supplier	Brand	Lot No.	Concentration (μg/L)[a]							
			HEHP	DHP	BBP	DEHP	BBEP	DCP	DOP	DNP
American Scientific	Chrom AR	6795	<0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
	Mallinkrodt HPLC grade		<0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
American Scientific	American Burdick & Jackson, Product 365	AP643	<0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
			<0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Fisher Scientific	HPLC grade	872758[b]	<0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
			<0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
VWR Scientific	Baker Analyzed HPLC Water	A19097	<0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
			<0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
VWR Scientific	Omnisolve EM Science	7020	<0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
			<0.5	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0

[a]One-liter water sample was extracted in a separatory funnel, three times, with 60 mL methylene chloride (American Burdick & Jackson, Lot No. A0174), the extract dried with anhydrous sodium sulfate (Fisher Scientific Lot No. 872983, heated at 400°C for 4 hours) and concentrated in a Kuderna-Danish evaporator to 1 mL. Analyses were performed by GC/FID using a 30 m x 0.53 mm ID Supelcowax-10 fused-silica open tubular column. Two replicate samples were analyzed from each brand of reagent water.

[b]Another lot of HPLC-grade water from Fisher Scientific (Lot 874716) was analyzed by GC/ECD.

TABLE 13. TYPICAL LEVELS OF PHTHALATE ESTERS REMOVED FROM FLORISIL, ALUMINA, AND SILICA GEL BY 20 PERCENT DIETHYL ETHER IN HEXANE AND ACETONE[a]

	Florisil J. T. Baker Lot No. 606721 (60/100 mesh)				Florisil PR Supelco Inc. Lot No. 575 (60/100 mesh)				Alumina Woelm N Super I Woelm Pharma (Universal Scientific, Inc.)		
Compound	First washing		Second washing		First washing		Second washing		First[b] washing	Second washing	
DMP	110	160	110	110	74	110	160	110	420	c	c
DEP	190	110	160	130	50	120	88	48	130	1,300	420
DIBP	48	22	18	12	22	24	20	24	60	1,300	480
DBP	140	100	<10	<10	<10	12	<10	<10	14	880	110
DAP	20	<10	<10	<10	<10	<10	<10	<10	150	120	140
DHP	10	12	12	12	14	12	10	32	18	32	40
BBP	24	<10	<10	<10	<10	<10	<10	<10	<10	18	<10
DEHP	100	70	62	48	40	54	38	38	68	d	40
DCP	<10	<10	<10	<10	<10	<10	<10	<10	<10	d	<10
DOP	<10	<10	<10	<10	58	92	34	68	<10	d	<10
DNP	<10	<10	<10	<10	52	96	120	68	<10	d	<10

(continued)

[a] 20 percent diethyl ether in hexane was used for Florisil and alumina; 200 and 300 mL, respectively. Acetone (300 mL) was used in the case of silica gel. In each case 20 g of materials were used. $V_{extract}$ was 1 mL. Values given are in ng/mL of extract, and they represent measurements from duplicate experiments.
[b] Duplicate experiments were performed in this case; however, one of the washings was lost during solvent concentration.
[c] Not able to quantify because of interference from solvent.
[d] Not able to quantify because of high background.

TABLE 13. (concluded)

Compound	Aluminum oxide, neutral, J. T. Baker Brockmann Activity Grade 1 Lot No. 634733				Silica gel J. T. Baker analyzed Lot No. 610728 (60/100 mesh)				Silica gel E. M. Science Grade 923 (100/200 mesh)			
	First washing		Second washing		First washing		Second washing		First washing		Second washing	
DMP	640	1,200	1,960	3,200	c	c	c	c	c	c	c	c
DEP	52	66	340	160	<100	<100	190	150	<10	110	400	470
DIBP	38	84	220	340	2,300	2,100	11	14	<10	33	<10	<10
DBP	24	56	32	88	550	220	<10	<10	31	30	36	<10
DAP	160	110	62	140	650	990	14	<10	<10	<10	<10	<10
DHP	40	18	14	14	420	380	92	130	24	25	33	50
BBP	20	<10	<10	<10	1,300	1,800	780	680	<10	<10	<10	<10
DEHP	600	300	200	46	1,200	1,100	24	25	40	349	31	22
DCP	<10	<10	<10	<10	340	400	<10	<10	<10	<10	<10	<10
DOP	<10	<10	<10	<10	1,000	1,300	16	18	25	<10	<10	<10
DNP	<10	<10	<10	<10	1,000	600	<10	<10	<10	<10	<10	<10

[a] 20 percent diethyl ether in hexane was used for Florisil and alumina; 200 and 300 mL, respectively. Acetone (300 mL) was used in the case of silica gel. In each case 20 g of materials were used. $V_{extract}$ was 1 mL. Values given are in ng/mL of extract, and they represent measurements from duplicate experiments.
[b] Duplicate experiments were performed in this case; however, one of the washings was lost during solvent concentration.
[c] Not able to quantify because of interference from solvent.
[d] Not able to quantify because of high background.

TABLE 14. PHTHALATE ESTERS DETECTED IN PROCEDURAL BLANKS FROM FLORISIL CARTRIDGES

Compound	Average amount ± standard deviation[a] (ng/cartridge)
DMP	456 ± 42
DEP	159 ± 66
DIBP	105 ± 10
DBP	136 ±17
BMPP	89 ± 41
BMEP	262 ± 72
DAP	53 ± 49
BEEP	66 ± 4
HEHP	24 ± 17
DHP	33 ± 2
BBP	18 ± 3
BBEP	41 ± 12
DEHP	291 ± 37
DCP	<10
DOP	<10
DNP	<10

[a] The number of determinations was 5. Each Florisil cartridge was eluted with 5 mL of 20 percent methylene chloride in hexane (Fraction 1), which was discarded, followed by 5 mL of hexane/acetone (9:1) which was concentrated to 1 mL and analyzed by GC/ECD.

TABLE 15. TYPICAL LEVELS OF PHTHALATE ESTERS REMOVED FROM FILTER PAPER BY HEXANE/ACETONE (1:1)[a]

Compound	Concentration (ng/mL extract)				Concentration (ng/g)
	First washing		Second washing		
DMP	3,100	[b]	710	640	380
DEP	<10	<10	<10	<10	<1.0
DIBP	260	240	110	120	37
DBP	170	210	68	62	26
DAP	44	35	<10	<10	4.0
DHP	260	280	140	170	43
BBP	54	72	28	38	9.6
DEHP	160	220	89	130	30
DCP	<10	<10	<10	<10	<1.0
DOP	<10	<10	<10	<10	<1.0
DNP	<10	<10	<10	<10	<1.0

[a] Whatman #41 (VWR Scientific) filter paper was precleaned three times in a Soxhlet extractor with American Burdick & Jackson acetone, each time using fresh solvent which was changed at 24-hr intervals. Samples were then cut into 0.5 in. x 0.5 in. pieces; 10 g were immersed in 100 mL of hexane/acetone (1:1) overnight. $V_{extract}$ was 1 mL. Values given represent measurements from duplicate experiments.

[b] Not able to quantify.

TABLE 16. TYPICAL LEVELS OF PHTHALATE ESTERS REMOVED FROM PAPER THIMBLES BY HEXANE/ACETONE (1:1)[a]

Compound	Concentration (ng/mL extract)				Concentration (ng/g)
	First washing		Second washing		
DMP	960	1,000	330	400	140
DEP	35	12	22	24	4.7
DIBP	94	89	23	23	12
DBP	12	27	<10	<10	2.8
DAP	14	12	<10	<10	2.2
DHP	470	800	140	200	80
BBP	110	130	31	29	15
DEHP	76	76	28	28	10
DCP	<10	<10	<10	<10	<1.0
DOP	<20	<20	22	<20	<2.0
DNP	<20	<20	23	<10	<2.0

[a]Whatman 43 mm x 123 mm paper thimble (VWR Scientific); each thimble was precleaned three times in a Soxhlet extractor with American Burdick & Jackson acetone, each time using fresh solvent which was changed at 24-hr intervals. Samples were then cut into 0.5 in. x 0.5 in. pieces; 10 g were immersed in 100 mL of hexane/acetone (1:1) overnight. $V_{extract}$ was 1 mL. Values given represent measurements from duplicate experiments.

TABLE 17. TYPICAL LEVELS OF PHTHALATE ESTERS REMOVED FROM ALUMINUM FOIL BY HEXANE/ACETONE (1:1)[a]

	Reynolds heavy-duty aluminum foil					Skaggs Alpha Beta heavy-duty aluminum foil	
			After baking at 400°C			Before baking at 400°C	
Compound	Before baking at 400°C Second washing		First washing		Second washing[b]	Second washing	
DMP	290	260	150	180	410	202	210
DEP	<10	<10	33	14	17	<10	<10
DIBP	<10	<10	<10	<10	14	<10	<10
DBP	<10	<10	22	<10	140	<10	<10
DAP	<10	<10	<10	<10	18	<10	<10
DHP	36	34	96	26	140	24	25
BBP	32	28	84	11	170	19	21
DEHP	36	13	<10	20	18	19	37
DCP	<10	<10	<10	<10	<10	10	<10
DOP	11	<10	<10	<10	105	<10	19
DNP	15	<10	<10	<10	<10	13	<10

[a]Aluminum foil (5 g), before or after baking at 400°C, was cut into 0.5 in. pieces which were immersed into 200 mL of hexane/acetone (1:1) overnight. $V_{extract}$ was 1 mL. Values given are in ng/mL of extract, and they represent measurements from duplicate experiments.
[b]The duplicate extract was lost during solvent concentration.

TABLE 18. TYPICAL LEVELS OF PHTHALATE ESTERS REMOVED FROM ANHYDROUS SODIUM SULFATE BY HEXANE/ACETONE (1:1)[a]

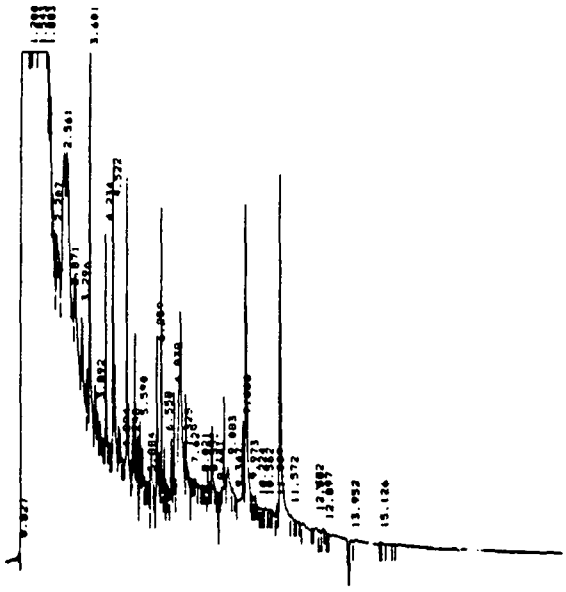
	Fisher Scientific Lot No. 870988						EM Science 6183	
Compound	Second washing before baking at 400°C		First washing after baking at 400°C		Second washing after baking at 400°C		Second washing before baking at 400°C	
DMP	<10	<10	<10	<10	<10	<10	<23	<10
DEP	<10	<10	<10	<10	<10	<10	67	55
DIBP	20	23	<10	<10	<10	<10	<10	14
DBP	80	70	54	39	100	11	69	63
DAP	11	10	<10	<10	<10	<10	<10	<10
DHP	100	88	130	100	88	38	62	16
BBP	110	110	120	100	70	22	85	70
DEHP	22	22	150	<10	39	10	10	30
DCP	<10	<10	<10	<10	<10	<10	<10	<10
DOP	<10	<10	<10	<10	<10	<10	<10	<10
DNP	<10	<10	<10	<10	<10	<10	<10	<10

[a]A volume of 300 mL hexane/acetone (1:1) was used for each portion of 50 g of anhydrous sodium sulfate, $V_{extract}$ was 1 mL. Values given are in ng/mL of extract, and they represent measurements from duplicate experiments.

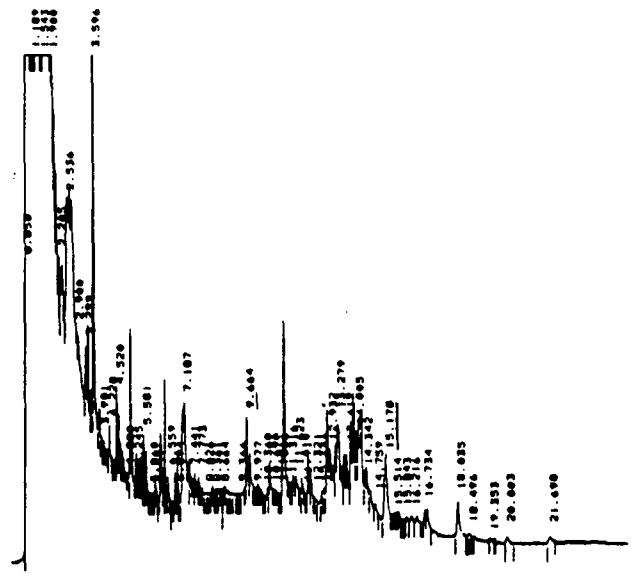
TABLE 19. TYPICAL LEVELS OF PHTHALATE ESTERS REMOVED FROM GLASS WOOL BY HEXANE/ACETONE (1:1)[a]

Compound	Glass wool, Alltech Associates DMCS treated					Glass wool, Alltech Associates Pesticide grade					
	First washing		Second washing		Average concentration (ng/g)	First washing before baking at 400°C	Second washing before baking at 400°C	Average concentration (ng/g)	First washing after baking at 400°C		Average concentration (ng/g)
DMP	86	77	40	81	28	210	290	100	85	<24	11
DEP	109	17	10	<10	13	<10	14	2.8	<10	<10	<2.0
DIBP	36	30	21	13	10	<10	<10	<2.0	<10	<10	<2.0
DBP	14	14	<10	<10	2.8	<10	<10	<2.0	<10	<10	<2.0
DAP	<10	<10	10	11	<2.0	<10	<10	<2.0	<10	<10	<2.0
DHP	125	121	89	70	41	33	35	6.8	<10	<10	<2.0
BBP	51	43	26	18	14	<10	17	3.4	<10	<10	<2.0
DEHP	63	21	27	21	13	51	18	14	<10	<10	<2.0
DCP	<10	<10	<10	<10	<2.0	<10	<10	<2.0	<10	<10	<2.0
DOP	<10	<10	27	35	6.2	<10	<10	<2.0	<10	<10	<2.0
DNP	<10	<10	<10	<10	<2.0	<10	<10	<20	<10	<10	<2.0

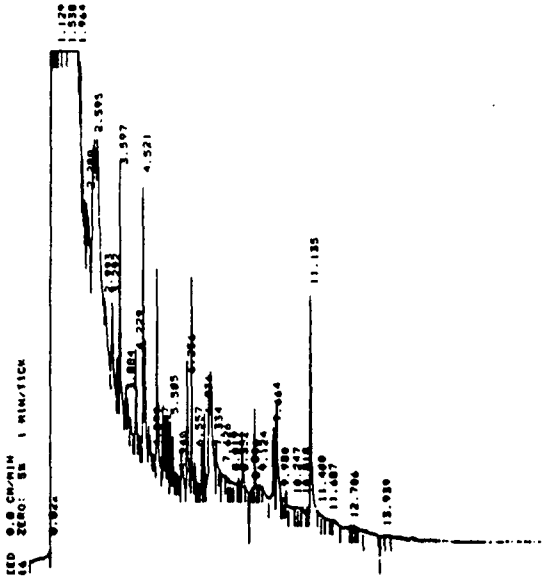
[a]5 g of glass wool were weighed out in a 500-mL amber jar, then allowed to soak twice for 16 hours, each time with fresh hexane/acetone (1:1), 300 mL. The solvent washings were concentrated to 1 mL by Kuderna-Danish evaporation. Values given are in ng/mL of extract, and they represent measurements from duplicate experiments.



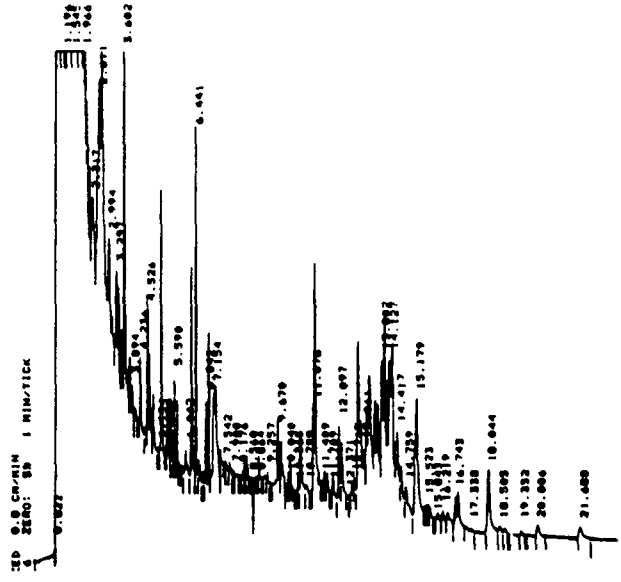
Florisil, VWR Scientific
(Baker Analyzed)
First washing



Florisil, Supelco
First washing

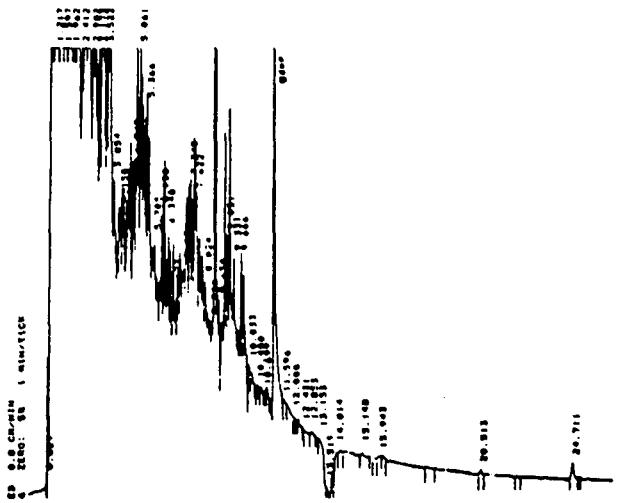


Florisil, VWR Scientific
(Baker Analyzed)
Second washing

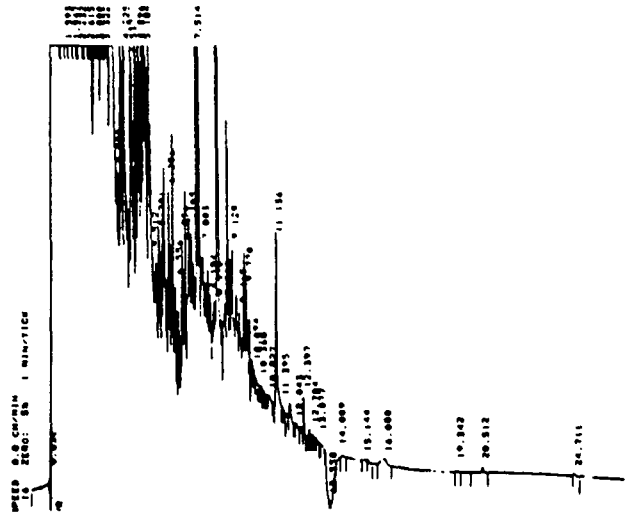


Florisil, Supelco
Second washing

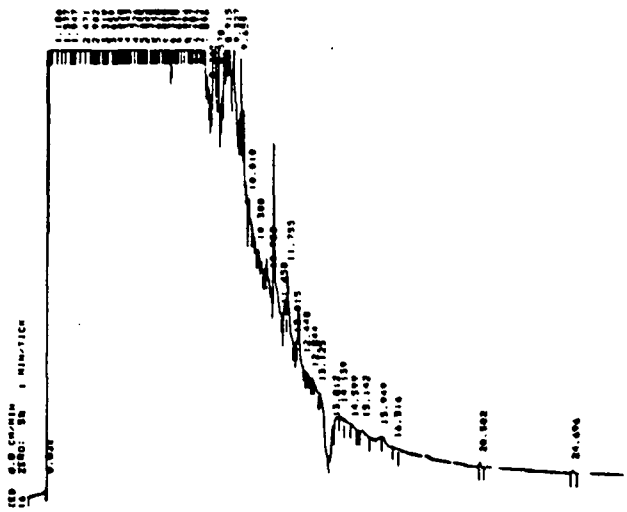
Figure 1. GC/ECD chromatograms of solvent washings obtained from two different brands of Florisil.



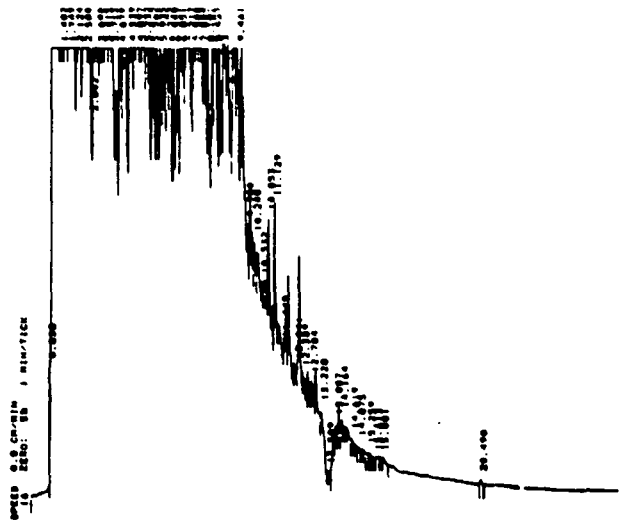
Alumina, Woelm Pharma
First washing



Alumina, VWR Scientific
(Baker Analyzed)
First washing



Alumina, Woelm Pharma
Second washing



Alumina, VWR Scientific
(Baker Analyzed)
Second washing

Figure 2. GC/ECD chromatograms of solvent washings obtained from two different brands of alumina.

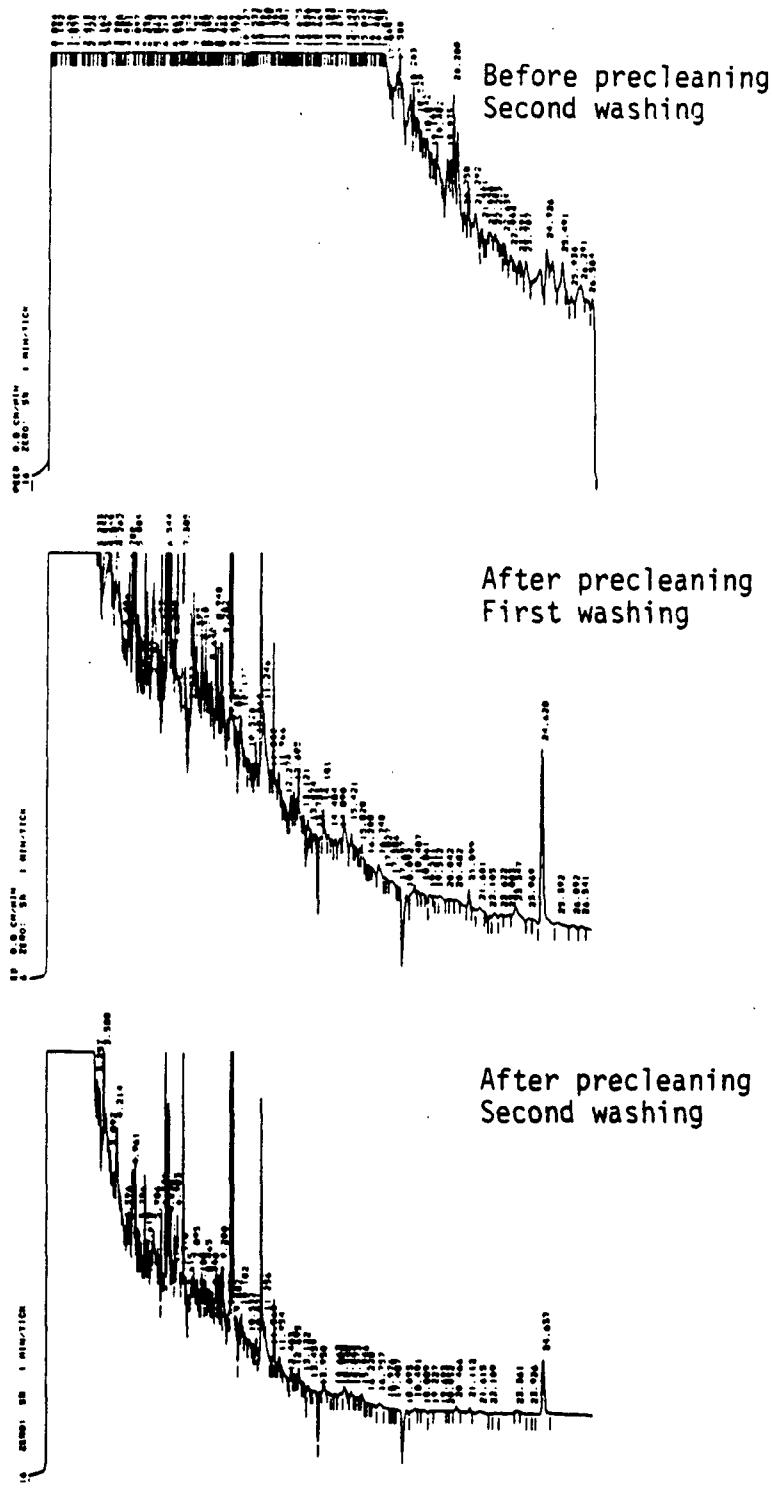
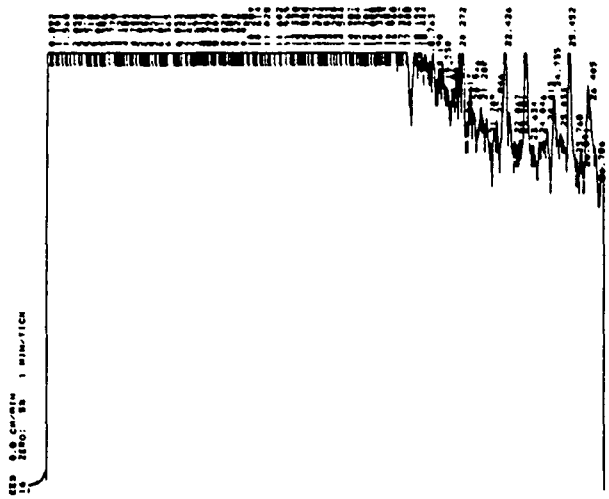
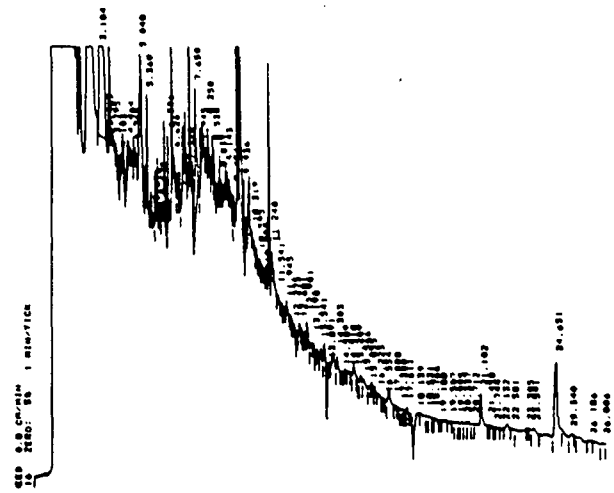


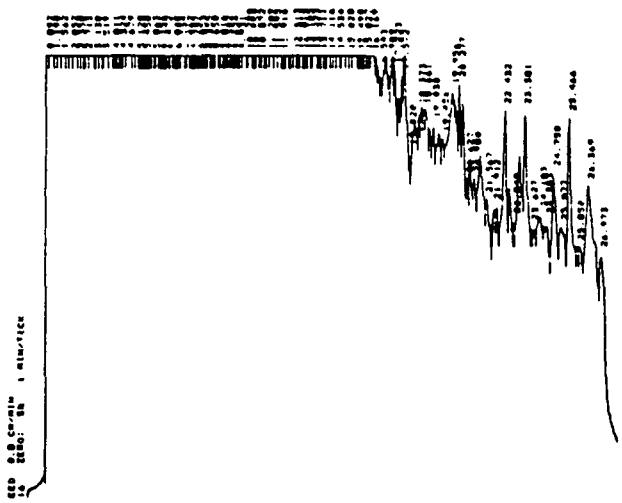
Figure 3. GC/ECD chromatograms of solvent washings of filter paper (Whatman No. 41) before precleaning (top) and after precleaning (middle and bottom).



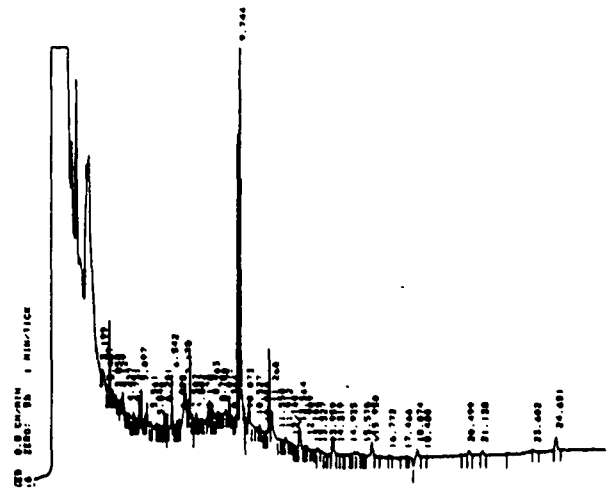
Before precleaning
First washing



After precleaning
First washing



Before precleaning
Second washing



After precleaning
Second washing

Figure 4. GC/ECD chromatograms of solvent washings obtained from paper thimbles (Whatman 23 x 123) before precleaning and after precleaning.

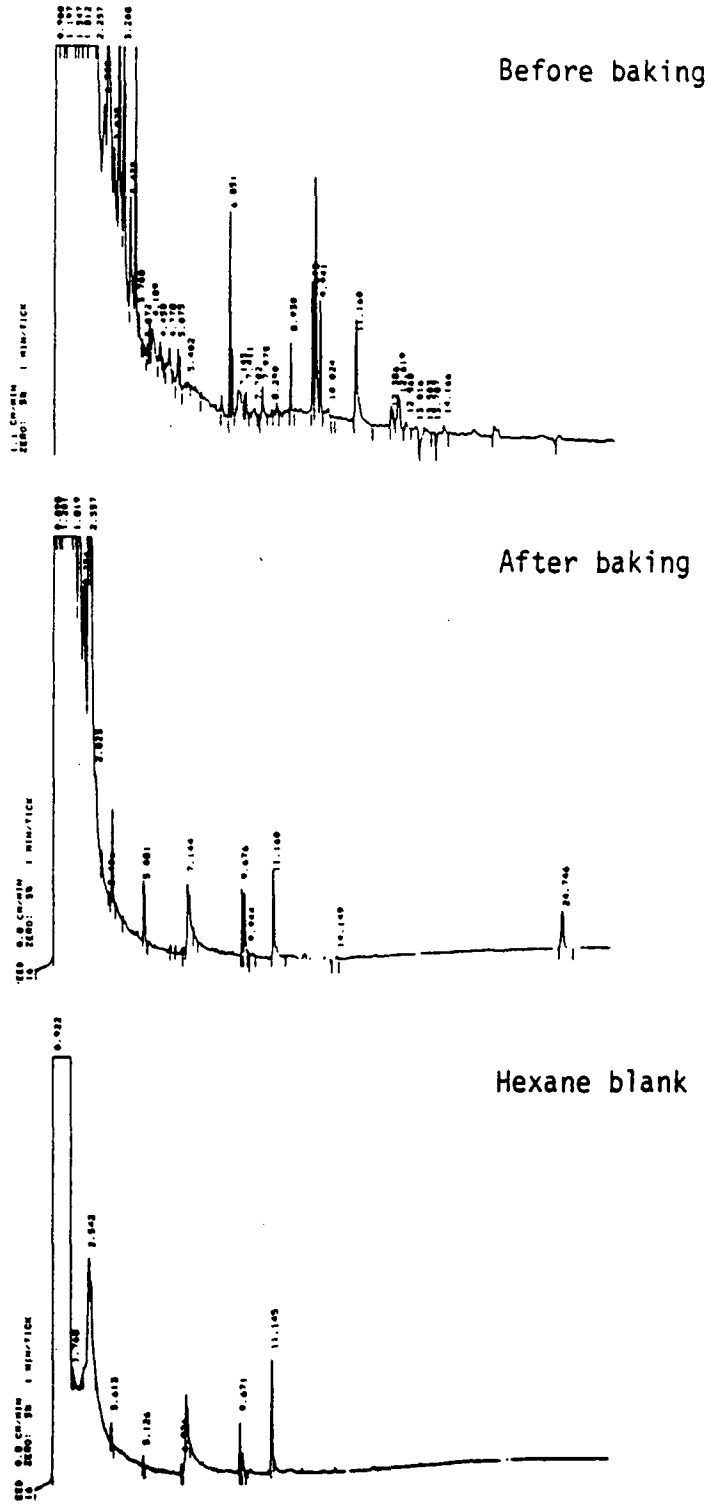


Figure 5. GC/ECD chromatograms of solvent washings from Alltech pest grade glass wool before baking and after baking at 400°C.

there were still detectable levels of 6 phthalate esters on the filter paper and 8 phthalate esters on the paper thimble in the second washing of the material.

Therefore, paper thimbles and filter paper must be exhaustively washed with the solvent that is going to be used in the sample extraction. Soxhlet extraction for 12 hours with fresh solvent should be repeated at least three times. Method blanks should be obtained before any of the precleaned thimbles or filter papers are used. Storage of precleaned thimbles and filter paper in precleaned glass jars covered with aluminum foil is recommended.

Washing of the aluminum foil with hexane/acetone (1:1) seem to be sufficient in removing any contaminants. The levels of the target compounds detected in the first washing after baking at 400°C for 4 hrs remained low. A second washing indicated levels in excess of 100 ng/mL of extract (Table 17). Possible contamination by the laboratory glassware may be a reasonable explanation.

Washing alone is not sufficient for sodium sulfate and glass wool, but baking these materials at 400°C for 4 hrs followed by solvent washing gave acceptable blanks (Tables 18 and 19).

6.1.4 Glassware

Typical levels (in nanograms) of the 16 test compounds present on laboratory glassware before and after baking at 400°C for 4 hours are given in Table 20. The data shown in Table 20 indicate the removal of phthalate esters by baking the glassware at 400°C for 4 hours is quite adequate. Storage of glassware in the laboratory introduces contamination even if the glassware is wrapped in aluminum foil (Table 21). Furthermore, washing of continuous liquid-liquid extractors and Soxhlet extractors with detergent, thorough rinsing with hot tap water, followed by deionized water, and acetone, is not adequate. Even after the Soxhlet extractor was refluxed with acetone for 3 days, and the solvent changed daily, the levels of DEHP were as high as 500 ng.

6.1.5 Sample Vials

Storage of hexane and isooctane in 1.8 mL- and 15-mL glass vials capped with metal foil liners or Teflon-lined rubber liners resulted in some contamination; however, only five contaminants were detected, and their levels ranged from 20 to 50 ng/mL of uncondensed solvent (Tables 22 and 23).

6.2 EVALUATION OF GAS CHROMATOGRAPHY

The following fused-silica columns were chosen for evaluation: a 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness), a 30 m x 0.53 mm ID Supelcowax-10 fused-silica open tubular column (1.0 μm film thickness), and a 30 m x 0.53 mm ID DB-210 fused-silica open tubular column (1.0 μm film thickness); a 30 m x 0.53 mm ID DB-5 fused-silica open tubular column (1.5 μm film thickness), a 30 m x 0.53 mm ID RT_x-5, fused-silica open tubular column (0.5 μm film thickness), a 30 m x 0.53 mm ID DB-608 fused-silica open tubular column (0.83 μm film thickness), and a 30 m x 0.53 mm ID

TABLE 20. TYPICAL LEVELS (IN NANOGRAMS PER PIECE OF GLASSWARE) OF PHTHALATE ESTERS CONTAMINATION REMAINING ON LABORATORY GLASSWARE THAT WAS SUBJECTED TO COMMON LABORATORY CLEANUP PROCEDURES BEFORE AND AFTER BAKING AT 400°C TEMPERATURES FOR 4 HRS[a]

	Precleaned amber bottle				Precleaned amber bottle spiked with 5,000 ng of each compound and heated for 4 hours at 400°C			
Compound	First washing		Second washing		First washing		Second washing	
DMP	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
DEP	37	42	127	25	18	41	19	56
DIBP	7.0	6.6	11	<5.0	12	13	<5.0	9.9
DBP	115	62	26	36	29	37	25	56
BMPP	6.2	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	5.5
BMEP	<5.0	<5.0	7.5	<5.0	<5.0	9.9	8.8	5.4
DAP	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	12
BEEP	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	8.9
HEHP	<5.0	<5.0	<5.0	<5.0	<5.0	5.6	<5.0	11
DHP	62	50	19	29	32	41	28	37
BBP	52	30	<5.0	16	13	23	15	29
BBEP	<5.0	<5.0	<5.0	<5.0	5.3	<5.0	<5.0	<5.0
DEHP	105	61	29	46	41	58	35	41
DCP	<5.0	<5.0	<5.0	6.1	6.8	6.6	6.5	7.0
DOP	5.5	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
DNP	6.8	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0

[a]Values given are in nanograms per piece of glassware and they represent measurements from duplicate experiments (i.e., two different sets of glassware treated the same).

TABLE 21. TYPICAL LEVELS (IN NANOGRAMS PER PIECE OF GLASSWARE) OF PHTHALATE ESTERS CONTAMINATION ON LABORATORY GLASSWARE SUBJECTED TO COMMON LABORATORY CLEANUP PROCEDURES, BEFORE AND AFTER STORAGE IN AN ANALYTICAL LABORATORY ENVIRONMENT

Compound	After storage separatory funnel (precleaned, stored on shelf in laboratory)		After storage continuous liquid-liquid extractor (precleaned, stored on shelf in laboratory)		Before storage amber jar (precleaned)		After storage amber jar (precleaned, stored on shelf in laboratory)		Before storage Soxhlet extractor (precleaned)		After storage Soxhlet extractor (precleaned, stored on shelf in laboratory)	
DMP	61	37	2100	2100	<5.0	<5.0	<5.0	<5.0	36	55	45	102
DEP	28	37	47	36	12	<5.0	29	20	42	24	15	12
DIBP	17	8.3	75	16	15	12	14	7.3	14	23	19	10
DBP	47	73	173	155	11	11	27	17	62	67	43	20
BMPP	5.9	<5.0	15	5.9	<5.0	<5.0	<5.0	<5.0	8.0	43	19	20
BMEP	17	29	54	3.5	17	28	16	16	47	64	8.0	5.0
DAP	<5.0	7.9	22	9.3	<5.0	<5.0	<5.0	<5.0	35	63	26	20
BEEP	<5.0	5.5	7.0	6.4	<5.0	<5.0	<5.0	<5.0	14	20	11	9.0
HEHP	<5.0	<5.0	15	<5.0	<5.0	<5.0	<5.0	<5.0	13	22	34	8.0
DHP	51	52	190	110	50	36	38	29	53	94	130	100
BBP	59	74	230	140	32	11	30	9.0	74	220	72	90
BBEP	<5.0	<5.0	12	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	22	22
DEHP	140	100	490	110	24	48	67	32	77[a]	500[a]	90[a]	150[a]
DCP	<5.0	<5.0	9.3	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	45[a]	56[a]
DOP	9.0	10	32	7.0	<5.0	<5.0	10	<5.0	18[a]	94[a]	22[a]	22[a]
DNP	6.6	<5.0	<5.0	<5.0	<5.0	<5.0	22	<5.0	45[a]	170[a]	8.9[a]	8.9[a]

[a] Value given is approximate since it was estimated from the peak area.

TABLE 22. TYPICAL LEVELS OF PHTHALATE ESTERS CONTAMINATION IN HEXANE STORED IN SAMPLE VIALS FOR UP TO 61 DAYS AT 4°C

Solvent	Day	Vial size (mL)	Type of liner	Concentration (ng/mL of uncondensed solvent)															
				DMP	DEP	DIBP	DBP	BMPP	BMEP	DAP	BEEP	HEHP	DHP	BBP	BBEP	DEHP	DCP	DOP	DNP
Hexane	2	1.8	metal	<10	<10	<10	<10	<10	<10	<10	<10	<10	15	<10	<10	39	<10	<10	<10
Hexane	2	1.8	Teflon	<10	<10	<10	37	<10	<10	<10	<10	<10	16	<10	<10	38	<10	<10	<10
Hexane	2	15	metal	<10	<10	<10	<10	<10	<10	<10	<10	<10	16	75	<10	36	<10	<10	<10
Hexane	2	15	Teflon	<10	<10	<10	<10	<10	<10	<10	<10	<10	15	<10	<10	42	<10	<10	<10
Hexane blank				<10	<10	<10	<10	<10	<10	<10	<10	<10	16	<10	<10	38	<10	<10	<10
Hexane	12	1.8	metal	<10	31	<10	19	<10	<10	<10	<10	<10	11	<10	<10	33	<10	<10	<10
Hexane	12	1.8	Teflon	<10	31	<10	28	<10	<10	<10	<10	<10	15	<10	<10	36	<10	<10	<10
Hexane	12	15	metal	<10	34	<10	22	<10	<10	<10	<10	<10	14	<10	<10	33	<10	<10	<10
Hexane	12	15	Teflon	<10	38	<10	27	<10	<10	<10	<10	<10	20	<10	<10	34	<10	<10	<10
Hexane	20	1.8	metal	<10	<10	<10	<10	*	*	<10	*	*	<10	<10	*	29	<10	<10	<10*
Hexane	20	1.8	Teflon	<10	<10	<10	<10	*	*	<10	*	*	<10	<10	*	29	<10	<10	<10
Hexane	20	15	metal	<10	<10	<10	<10	*	*	<10	*	*	<10	<10	*	27	<10	<10	<10
Hexane blank	20	15	Teflon	<10	<10	<10	<10	*	*	<10	*	*	<10	<10	*	25	<10	<10	<10
Hexane	61	1.8	metal	<10	13	<10	<10	<10	<10	<10	<10	<10	29	<10	<10	33	15	<10	<10
Hexane	61	1.8	Teflon	<10	20	<10	17	<10	<10	<10	<10	<10	15	<10	<10	28	16	<10	<10
Hexane	61	15	metal	<10	19	<10	16	<10	<10	<10	<10	<10	19	<10	<10	30	17	<10	<10
Hexane	61	15	Teflon	<10	19	<10	14	<10	<10	<10	<10	<10	17	<10	<10	23	14	<10	<10
Hexane blank				<10	19	<10	<10	12	<10	<10	<10	<10	15	<10	<10	38	16	<10	<10

*Data not available.
Hexane used was a Burdick & Jackson product, Lot No. AQ075.

TABLE 23. TYPICAL LEVELS OF PHTHALATE ESTERS CONTAMINATION IN ISOOCTANE STORED IN SAMPLE VIALS FOR UP TO 61 DAYS AT 4°C

Solvent	Day	Vial size (mL)	Type of liner	Concentration (ng/mL of uncondensed solvent)															
				DMP	DEP	DIBP	DBP	BMPP	BMEP	DAP	BEEP	HEHP	DHP	BBP	BBEP	DEHP	DCP	DOP	DNP
Isooctane	2	1.8	metal	<50	<50	<10	<10	*	*	<10	*	*	44	<10	*	13	<10	<10	<10*
Isooctane	2	1.8	Teflon	<50	<50	<10	<10	*	*	<10	*	*	30	<10	*	12	<10	<10	<10
Isooctane	2	15	metal	<50	<50	<10	<10	*	*	<10	*	*	30	<10	*	<10	<10	<10	<10
Isooctane	2	15	Teflon	<50	<50	<10	<10	*	*	<10	*	*	34	<10	*	13	<10	<10	<10
Isooctane	8	1.8	metal	<50	<50	<10	<10	*	*	<10	*	*	30	<10	*	13	<10	<10	<10*
Isooctane	8	1.8	Teflon	<50	<50	<10	<10	*	*	<10	*	*	39	<10	*	13	<10	<10	<10
Isooctane	8	15	metal	<50	<50	<10	<10	*	*	<10	*	*	21	<10	*	17	<10	<10	<10
Isooctane	8	15	Teflon	<50	<50	<10	<10	*	*	<10	*	*	58	<10	*	17	<10	<10	<10
Isooctane	12	1.8	metal	<10	26	<10	23	<10	<10	<10	<10	<10	16	<10	<10	35	<10	<10	<10
Isooctane	12	1.8	Teflon	<10	36	<10	24	<10	<10	<10	<10	<10	14	<10	<10	33	<10	<10	<10
Isooctane	12	15	metal	<10	25	<10	35	<10	<10	<10	<10	<10	16	82	<10	36	<10	<10	<10
Isooctane	12	15	Teflon	<10	33	<10	24	<10	<10	<10	<10	<10	17	<10	<10	36	<10	<10	<10
Isooctane blank	12	15	metal	<10	31	<10	20	<10	<10	<10	<10	<10	16	<10	<10	36	<10	<10	<10
Isooctane	20	1.8	metal	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	22	<10	<10	<10
Isooctane	20	1.8	Teflon	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	18	<10	<10	<10
Isooctane	20	15	metal	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	24	14	<10	<10
Isooctane	20	15	Teflon	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	24	14	<10	<10
Isooctane blank	20	15	metal	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	24	<10	<10	<10
Isooctane	61	1.8	metal	<10	<10	22	15	<10	<10	<10	<10	<10	24	<10	<10	26	15	<10	<10
Isooctane	61	1.8	Teflon	<10	<10	19	<10	<10	<10	<10	<10	<10	22	<10	<10	26	15	<10	<10
Isooctane	61	15	metal	<10	<10	27	17	<10	<10	<10	<10	<10	29	<10	<10	36	<10	<10	<10
Isooctane	61	15	Teflon	<10	<10	25	<10	<10	<10	<10	<10	<10	35	<10	<10	28	<10	<10	<10
Isooctane blank				<10	<10	17	<10	<10	<10	<10	<10	<10	35	<10	<10	25	15	<10	<10

*Data not available.
Isooctane used was a Fisher Scientific product, Lot No. 864429 pesticide grade.

DB-1701 fused-silica open tubular column (1.0 μm film thickness). The GC operating conditions for the first three columns are given in Table 5. The columns were connected to either an ECD or an FID. The other four columns were tested in pairs using an injection tee to split the standard or sample extract introduced into the injector to two different fused-silica open tubular columns, each connected to an ECD. The single-column approach is discussed in Section 6.2.1; the dual-column/dual-detector approach is discussed in Section 6.2.2.

6.2.1 Single-Column Approach

The experimental work began with the evaluation of a DB-5 fused-silica capillary column. Thirty-eight phthalate esters standards were analyzed individually to establish their elution order when the DB-5 column was programmed from 150°C to 275°C at 15°C/min (Tables 24 and 25), or 120°C to 250°C at 15°C/min, and then from 250°C to 300°C at 2°C/min (Table 24).

Some of the compounds (e.g., diisohexyl phthalate, diisooctyl phthalate, diisononyl phthalate, diisodecyl phthalate, hexyl decyl phthalate, and butyl decyl phthalate) were found to contain multiple peaks and were eliminated from further consideration. GC/ECD chromatograms of a composite standard containing 16 compounds and GC/ECD chromatograms of some of the phthalate esters found to give multiple peaks are presented in Figures 6 through 9. Other compounds that had identical retention times on the DB-5 fused-silica capillary column were not included in the composite standard. For example, dimethyl cyclohexyl phthalate and dioctyl phthalate and benzyl 2-ethylhexylphthalate had retention times of 12.12 min, 12.18 min, and 12.12 min, respectively, and didecyl phthalate and bis(2-ethylhexyl)phthalate had retention times of 10.82 min and 10.85 min, respectively. Following this preliminary work, the group of 16 compounds listed in Table 24 were selected for further evaluation. The GC conditions were optimized to get the best separation of the 16 compounds and the total analysis time not to exceed 30 min.

Retention times of the 16 compounds analyzed on the Supelcowax-10 fused-silica open tubular column are given in Tables 26 and 27. GC/FID chromatograms obtained during the optimization of the GC analysis are presented in Figures 10 through 15. Attempts made to connect the Supelcowax-10 column to an ECD were unsuccessful because of a high detector background caused by column bleed.

Table 28 presents the results for a DB-210 fused-silica open tubular column, and Figure 16 shows a GC/ECD chromatogram of a standard containing 11 phthalate esters which was analyzed on the DB-210 fused-silica open tubular column. This column was found to be the least desirable because of a significant drift in baseline during column programming. Since this column was not acceptable for the 11 phthalate esters tested, additional phthalate esters were not considered.

Our ECD was originally optimized at 285°C, and all experimental work for the single-column approach was carried out at 285°C. In addition, we also performed requirements in which the detector temperature was raised to 310°C or 320°C. Quite often we had to bake the detector at higher temperatures in

TABLE 24. RETENTION TIMES (MIN) OF METHOD 8060 COMPOUNDS ANALYZED ON A DB-5 FUSED-SILICA CAPILLARY COLUMN

Compound No.	Compound	Retention time (min)					
		Individual standards[a] (10 ng/μL)		Composite standard[a] (10 ng/μL)		Composite standard[b] (10 ng/μL)	Composite standard[c] (10 ng/μL)
1	DMP	3.01	2.97	2.97	3.01	3.48 to 3.49	4.22
2	DEP	4.10	4.10	4.13	4.09	4.50 to 4.51	5.37
3	DIBP	6.34	6.34	6.36	6.34	6.52 to 6.53	7.50
4	DBP	7.06	7.06	7.08	7.05	7.19 to 7.20	8.18
5	BMPP	8.02					
6	BMEP	7.47					
7	DAP	8.40	8.39	8.41	8.39	8.46 to 8.48	9.47
8	BEEP	8.25					
9	HEHP	8.69					
10	DHP	9.62	9.63	9.64	9.63	9.68 to 9.70	10.81
11	BBP	9.70	9.69	9.71	9.70	9.75 to 9.77	10.89
12	BBEP	10.60					
13	DEHP	10.85	10.85	10.86	10.85	11.13 to 11.15	12.57
14	DCP	10.76	10.75	10.77	10.76	11.01 to 11.02	12.39
15	DOP	12.18	12.19	12.20	12.19	12.84 to 12.85	14.69
16	DNP	14.08	14.08	14.09	14.08	15.14 to 15.16	17.56

[a]GC operating conditions are given in Table 5; the temperature program is 150°C to 275°C at 15°C/min; injector temperature 275°C; detector temperature 285°C. Duplicate determinations.
[b]Values given represent the range of retention times for five consecutive determinations performed with an autosampler. GC conditions are given in Table 5; the temperature program is 120°C to 260°C at 15°C/min; then to 280°C at 2°C/min; injector temperature 275°C; detector temperature 310°C.
[c]GC conditions are given in Table 5; the temperature program is 120°C to 250°C at 15°C/min; then 250°C to 300°C at 2°C/min; injector temperature 275°C; detector temperature 310°C.

TABLE 25. RETENTION TIMES OF THE ADDITIONAL PHTHALATE ESTER STANDARDS ANALYZED ON A DB-5 FUSED-SILICA CAPILLARY COLUMN

Compound	Retention time[a] (min)
DIHP	See Figure 7
DIOP	See Figure 7
DINP	See Figure 7
DIDP	See Figure 8
HDP	See Figure 8
BEHHP	10.70
DMCP	12.12
BEHP	11.20 and 12.12
BEEEP	11.16
BCP	9.00
BDP	See Figure 9
BIDP	[b]
BOP	9.78 (small peaks at 7.22 and 12.95)
DCAP	11.18
DUP	[b]
EHIDP	[b]
IDTP	9.05 to 9.74 (multiple peaks)
ODP	[b]
OIDP	[b]
IHBP	9.08 and 10.83
DMIP	[b]
DOIP	[b]

[a]For GC operating conditions, refer to Table 5; the temperature program is 150°C to 275°C at 15°C/min; detector temperature 285°C.
[b]No peak was observed at 10 ppm concentration.

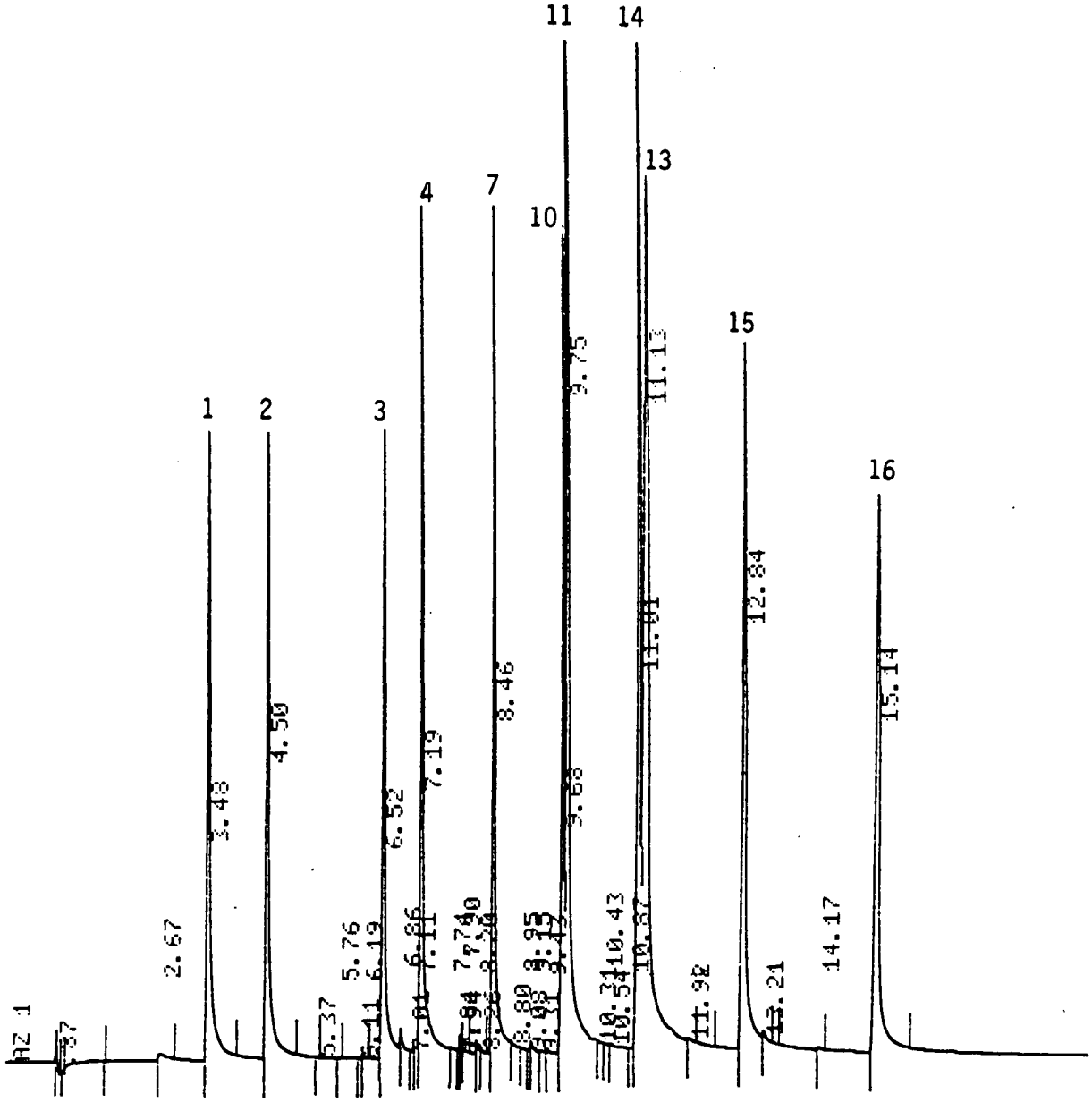


Figure 6. GC/ECD chromatogram of composite phthalate esters standard analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column. For GC operating conditions refer to Table 24, footnote b. Peak assignments are given in Table 24.

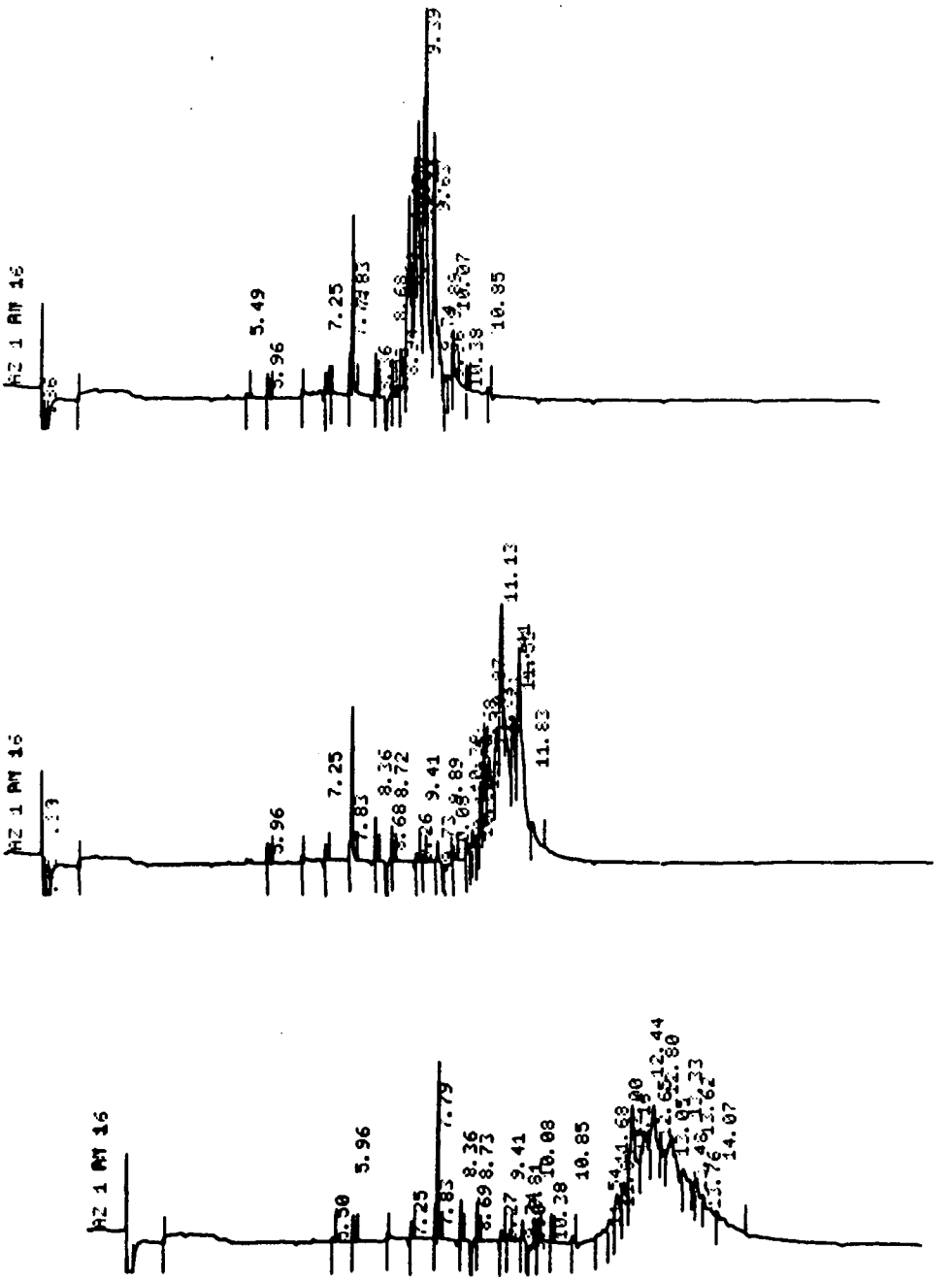


Figure 7. GC/ECD chromatograms of diisohexyl phthalate (top), diisooctyl phthalate (middle), and diisononyl phthalate (bottom) analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column. For GC operating conditions, refer to Table 5; the temperature program is 150°C to 275°C at 15°C/min; detector temperature 285°C.

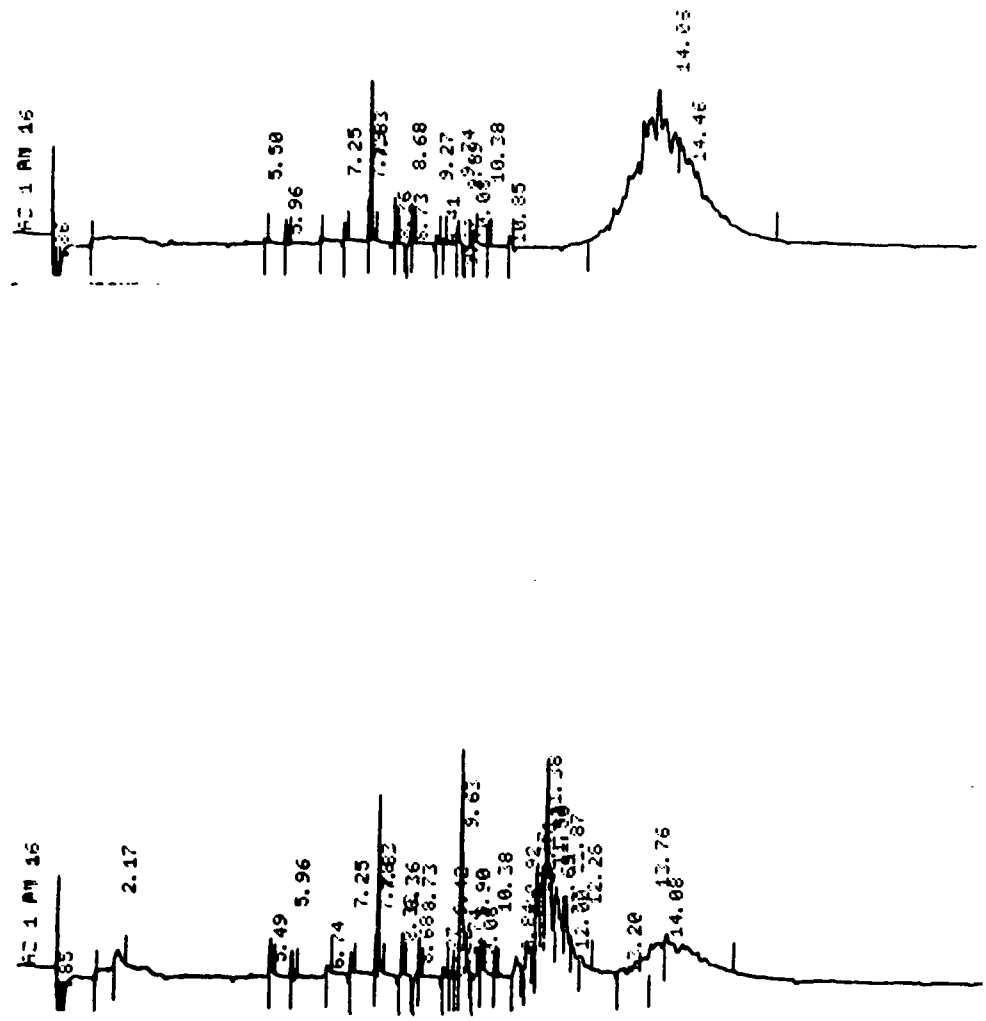


Figure 8. GC/ECD chromatograms of diisodecyl phthalate (top) and hexyl decyl phthalate (bottom) analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column. For GC operating conditions, refer to Table 5; the temperature program is 150°C to 275°C at 15°C/min; detector temperature 285°C.

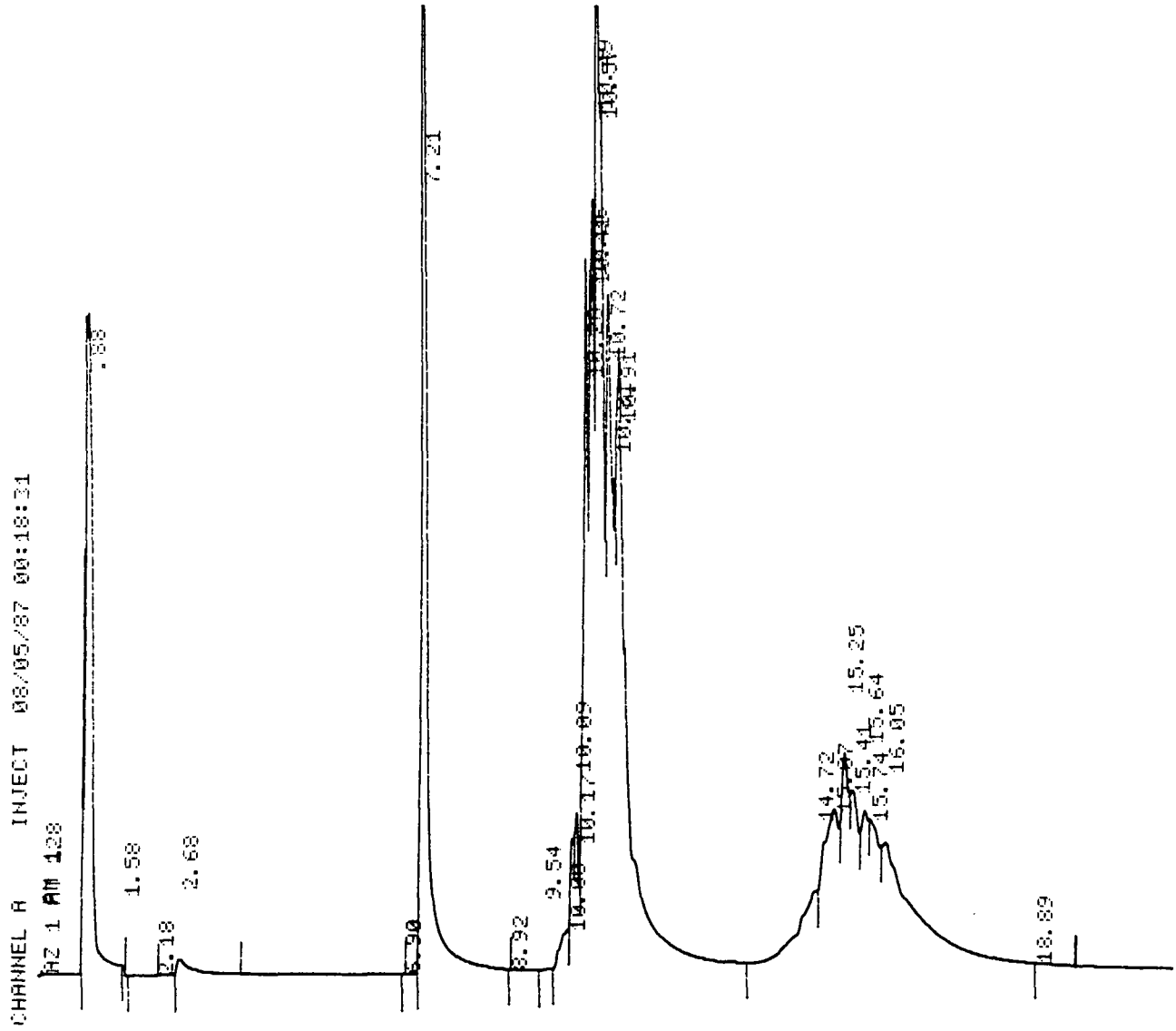


Figure 9. GC/ECD chromatogram of butyl decyl phthalate analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column. For GC operating conditions, refer to Table 5; the temperature program is 150°C to 275°C at 15°C/min; detector temperature 285°C.

TABLE 26. RETENTION TIMES (MIN) OF METHOD 8060 COMPOUNDS ANALYZED ON A SUPELCOWAX-10 FUSED-SILICA OPEN TUBULAR COLUMN

Compound no.	Compound	Retention time (min)[a] Individual standards (50 ng/μL)	Composite standard (50 ng/μL)	
1	DMP	10.04	10.04	10.03
2	DEP	10.72	10.73	10.72
3	DIBP	12.25	12.27	12.26
4	DBP	13.56	13.55	13.55
7	DAP	15.02	15.04	15.04
10	DHP	16.51	16.54	16.51
11	BBP	20.61	20.68	20.69
12	DEHP	17.36	17.36	17.34
14	DCP	20.80	20.87	20.87
15	DOP	21.40	21.44	21.46
16	DNP	25.97	26.00	26.05

[a]GC operating conditions are given in Table 5. Duplicate determinations.

TABLE 27. RETENTION TIMES OF 16 PHTHALATE ESTER STANDARDS ANALYZED ON A SUPELCOWAX-10 FUSED-SILICA OPEN TUBULAR COLUMN

Compound No.	Compound	Retention time (min)				
		Figure 11[a]	Figure 12[a]	Figure 13[a]	Figure 14[a]	Figure 15[a]
1	DMP	10.02	7.33	11.24	5.67	[b]
2	DEP	10.72	7.81	12.24	6.17	6.11
3	DIBP	12.26	9.17	14.46	7.33	7.26
4	DBP	13.54	10.67	16.26	8.51	8.43
5	BMPP	13.28	10.29	15.89	8.21	8.14
7	DAP	15.04	12.85	18.43	10.24	10.15
8	BEEP	16.50	15.62	20.66	12.51	12.41
9	HEHP	15.70	14.04	19.38	11.22	11.13
10	DHP	16.50	15.37	20.47	12.31	12.21
11	BBP	20.74	[c]	[c]	16.47	16.36
12	BBEP	20.74	[c]	[c]	17.05	16.94
13	DEHP	17.36	16.71	21.42	13.41	13.31
14	DCP	20.74	[c]	[c]	16.77	16.66
15	DOP	22.63	20.86	24.19	18.15	18.28
16	DNP	25.88	24.70	26.48	20.86	20.73

[a]The GC operating conditions are listed in Figures 11 through 15.
[b]Compound not added to the composite standard.
[c]Compounds were resolved; however, the integrator did not give retention time.

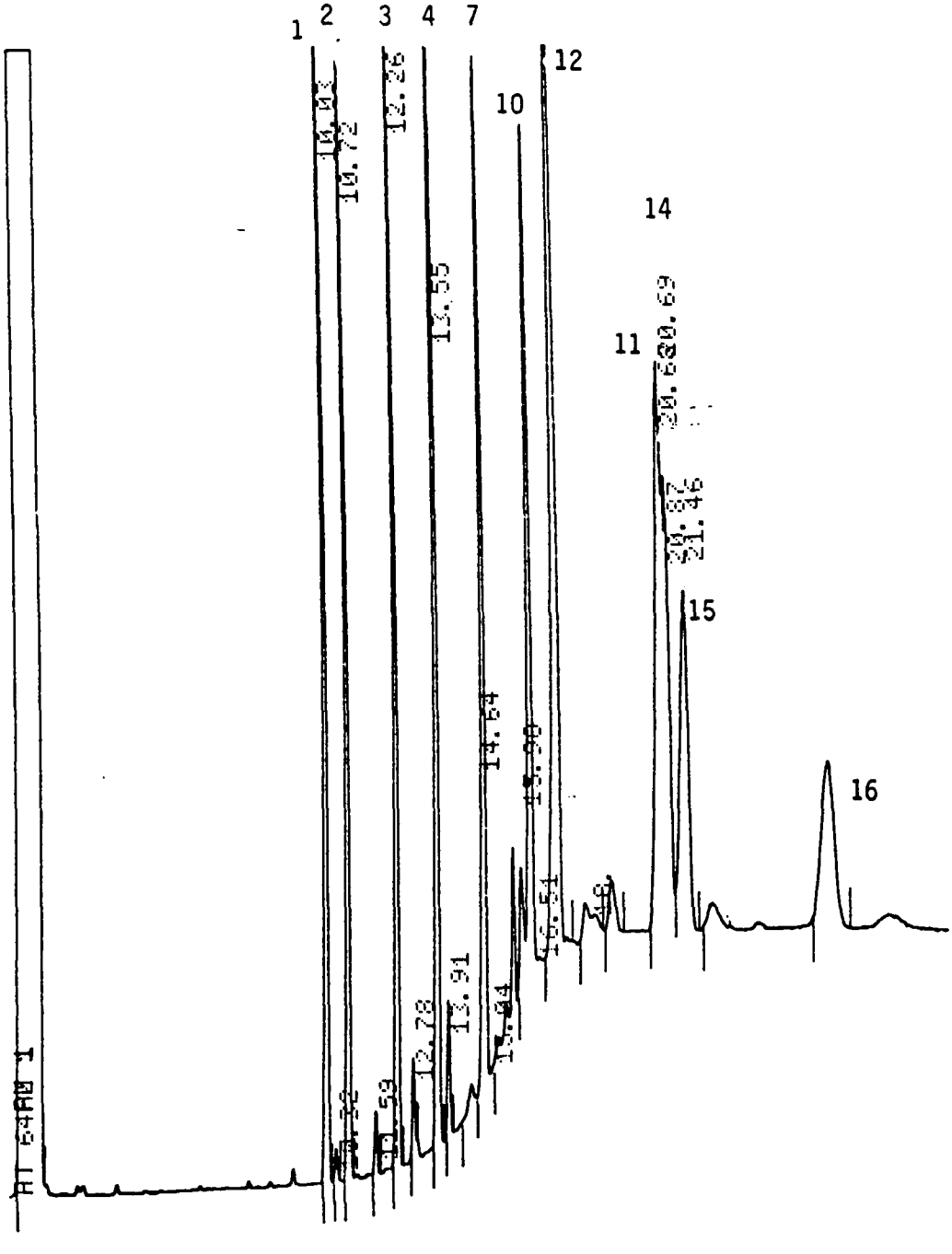


Figure 10. GC/FID chromatogram of composite phthalate esters standard analyzed on a 30 m x 0.53 mm ID Supelcowax-10 fused-silica open tubular column. For GC operating conditions, refer to Table 5. Peak assignments are given in Table 26.

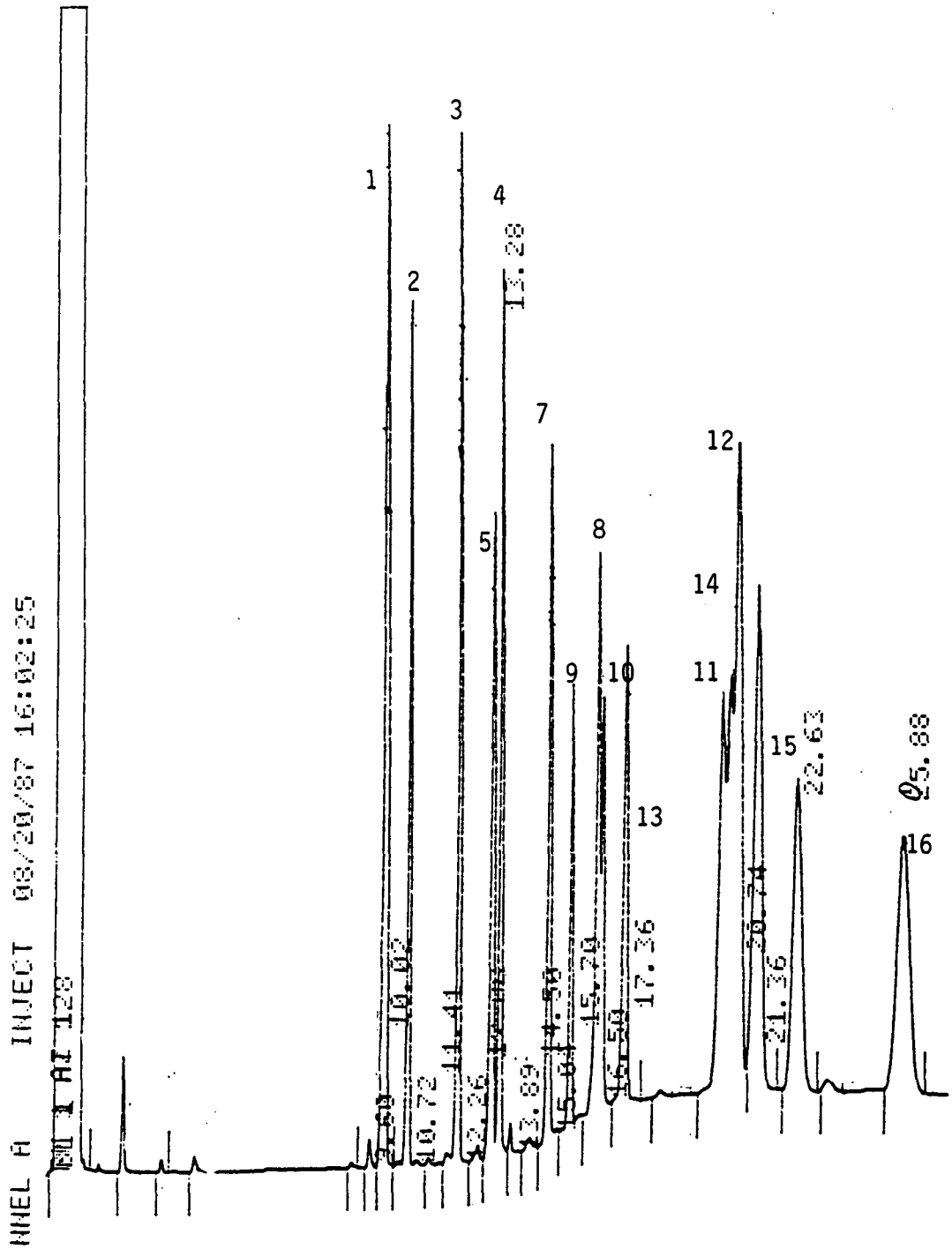


Figure 11. GC/FID chromatogram of composite phthalate esters standard analyzed on a Supelcowax-10 fused-silica open tubular column. Temperature program: 100°C (hold 2 min) to 240°C (hold 19 min) at 10°C/min; helium at 33 psi.

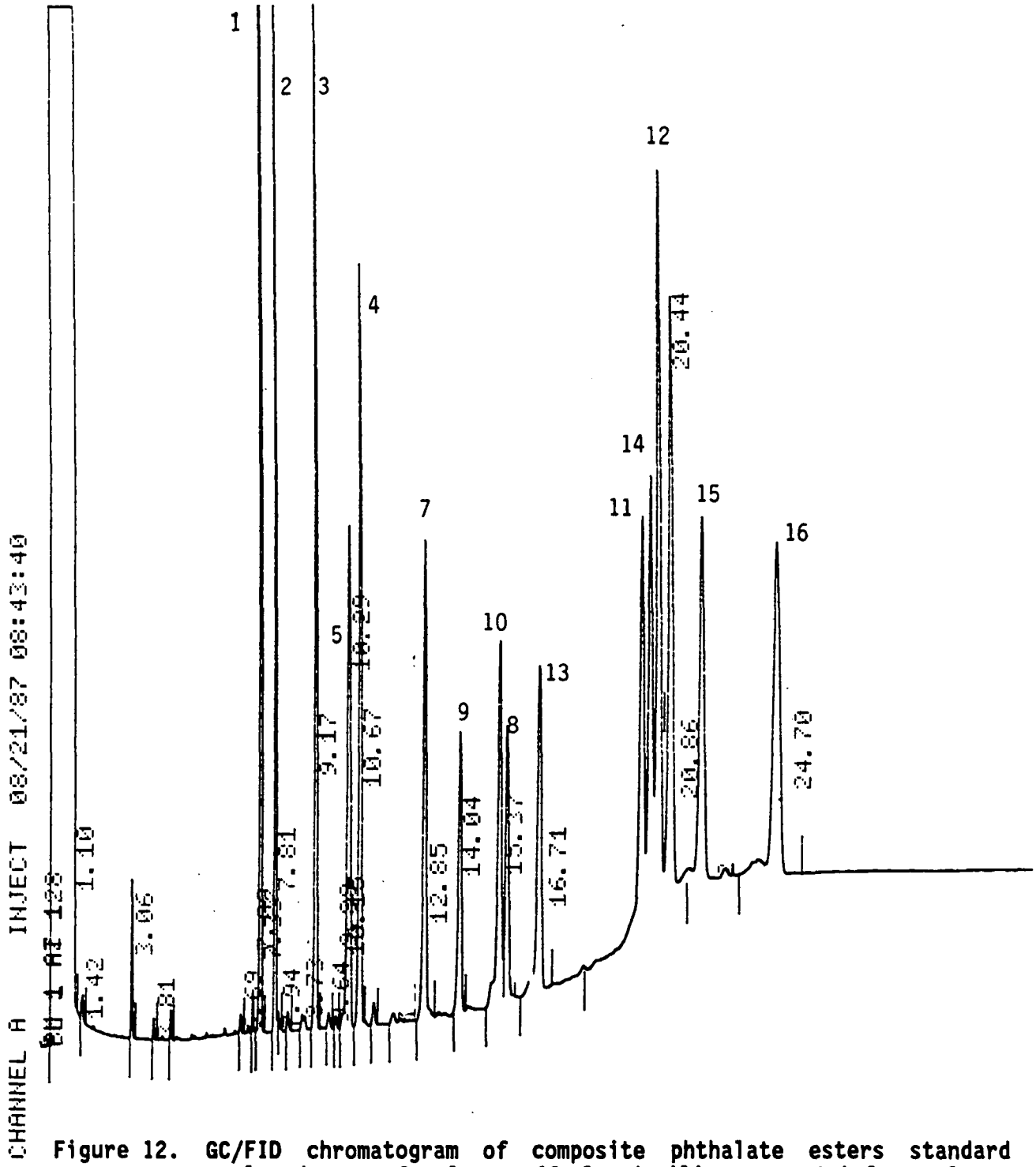


Figure 12. GC/FID chromatogram of composite phthalate esters standard analyzed on a Supelcowax-10 fused-silica open tubular column. Temperature program: 100°C (hold 2 min) to 200°C at 25°C/min, then to 260°C (hold 13 min) at 4°C/min; helium at 20 psi.

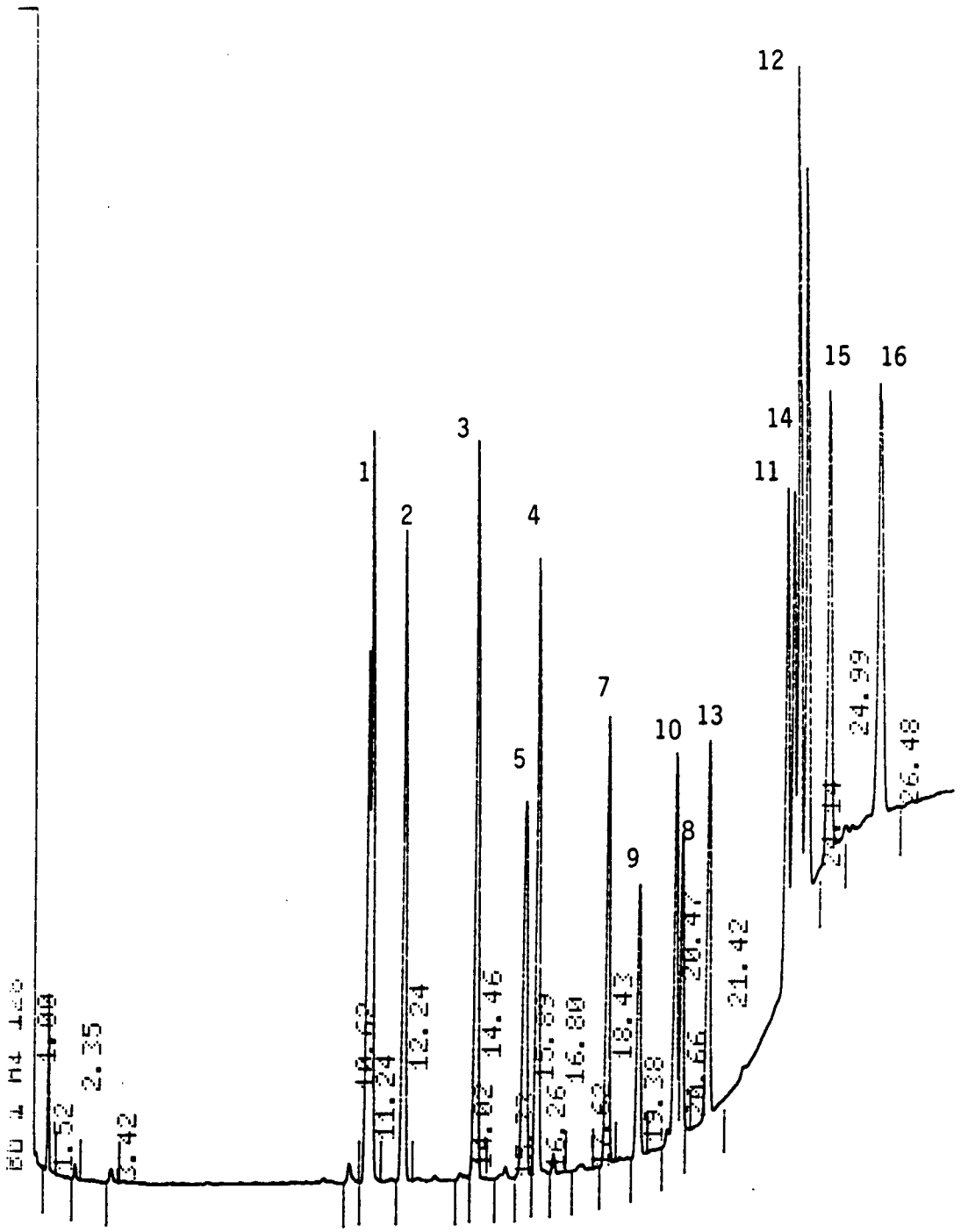


Figure 13. GC/FID chromatogram of composite phthalate esters standard analyzed on a Supelcowax-10 fused-silica open tubular column. Temperature program: 120°C (hold 3 min) to 270°C (hold 10 min) at 7°C/min; helium at 25 psi.

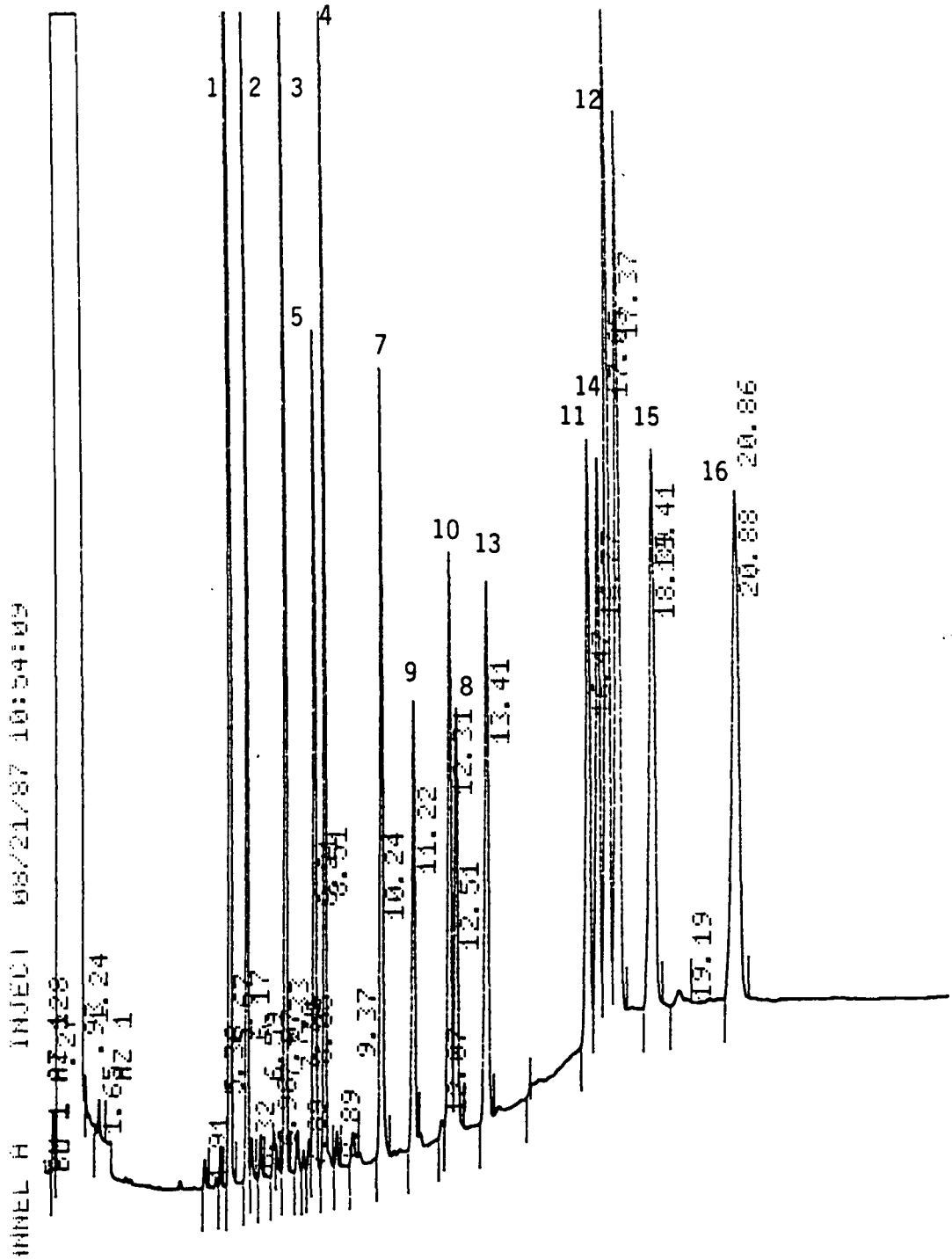


Figure 14. GC/FID chromatogram of composite phthalate esters standard analyzed on a Supelcowax-10 fused-silica open tubular column. Temperature program: 150°C (hold 2 min) to 220°C at 15°C/min, then to 260°C (hold 15 min) at 4°C/min; helium at 33 psi.

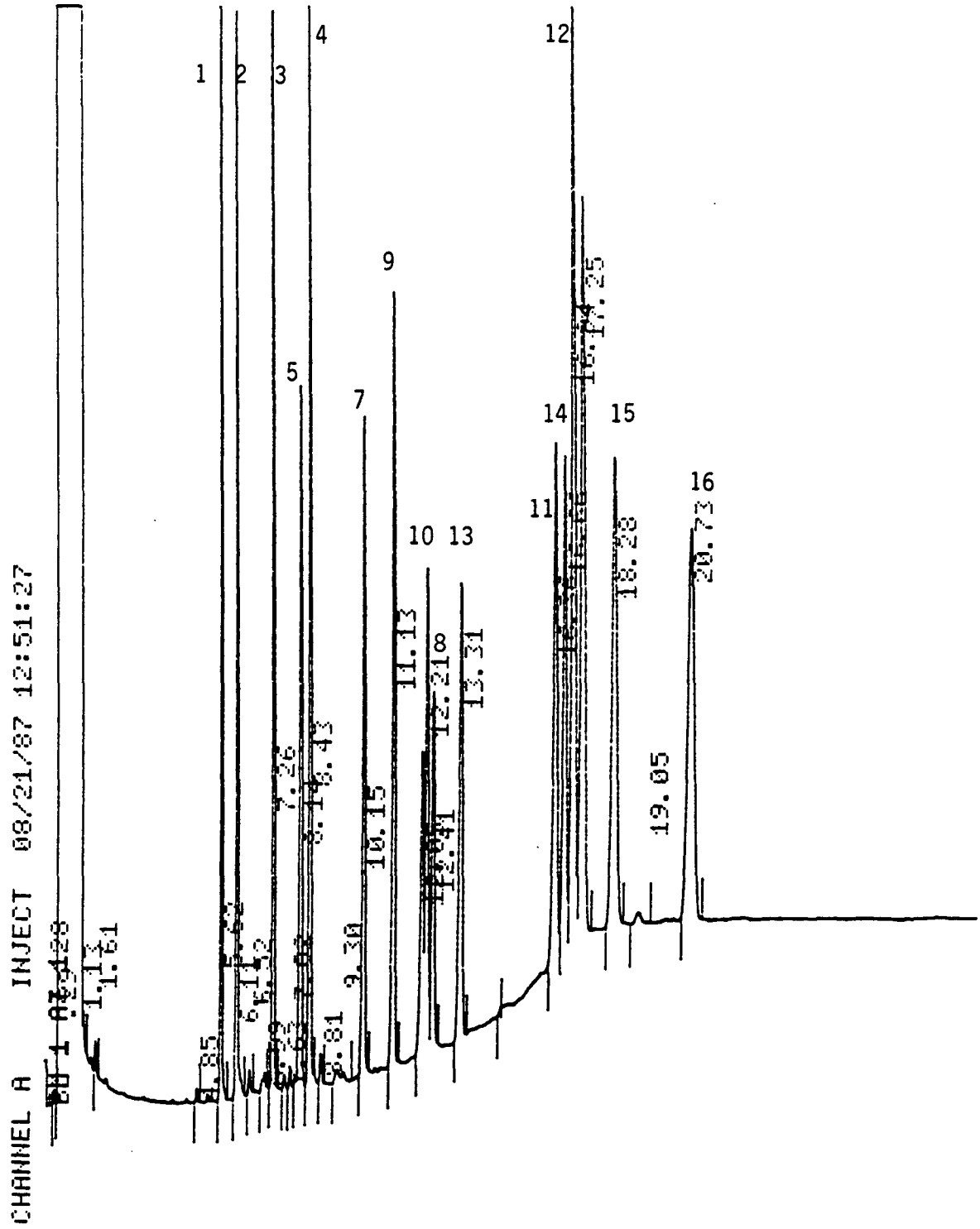


Figure 15. GC/FID chromatogram of composite phthalate esters standard analyzed on a Supelcowax-10 fused-silica open tubular column. Temperature program: 150°C (hold 2 min) to 220°C at 15°C/min, then to 260°C (hold 16 min) at 4°C/min; helium at 20 psi.

TABLE 28. RETENTION TIMES OF THE PHTHALATE ESTER STANDARDS ANALYZED ON A DB-210 FUSED-SILICA OPEN TUBULAR COLUMN

Compound No.	Compound	Retention time[a] (min)
1	DMP	8.38
2	DEP	9.53
3	DIBP	13.29
4	DBP	14.66
7	DAP	17.22
10	DHP	19.64
11	BBP	20.63
13	DEHP	21.56
14	DCP	22.41
15	DOP	24.09
16	DNP	26.62

[a]The GC operating conditions are given in Table 5. A GC/ECD chromatogram of the composite phthalate esters standard is given in Figure 16.

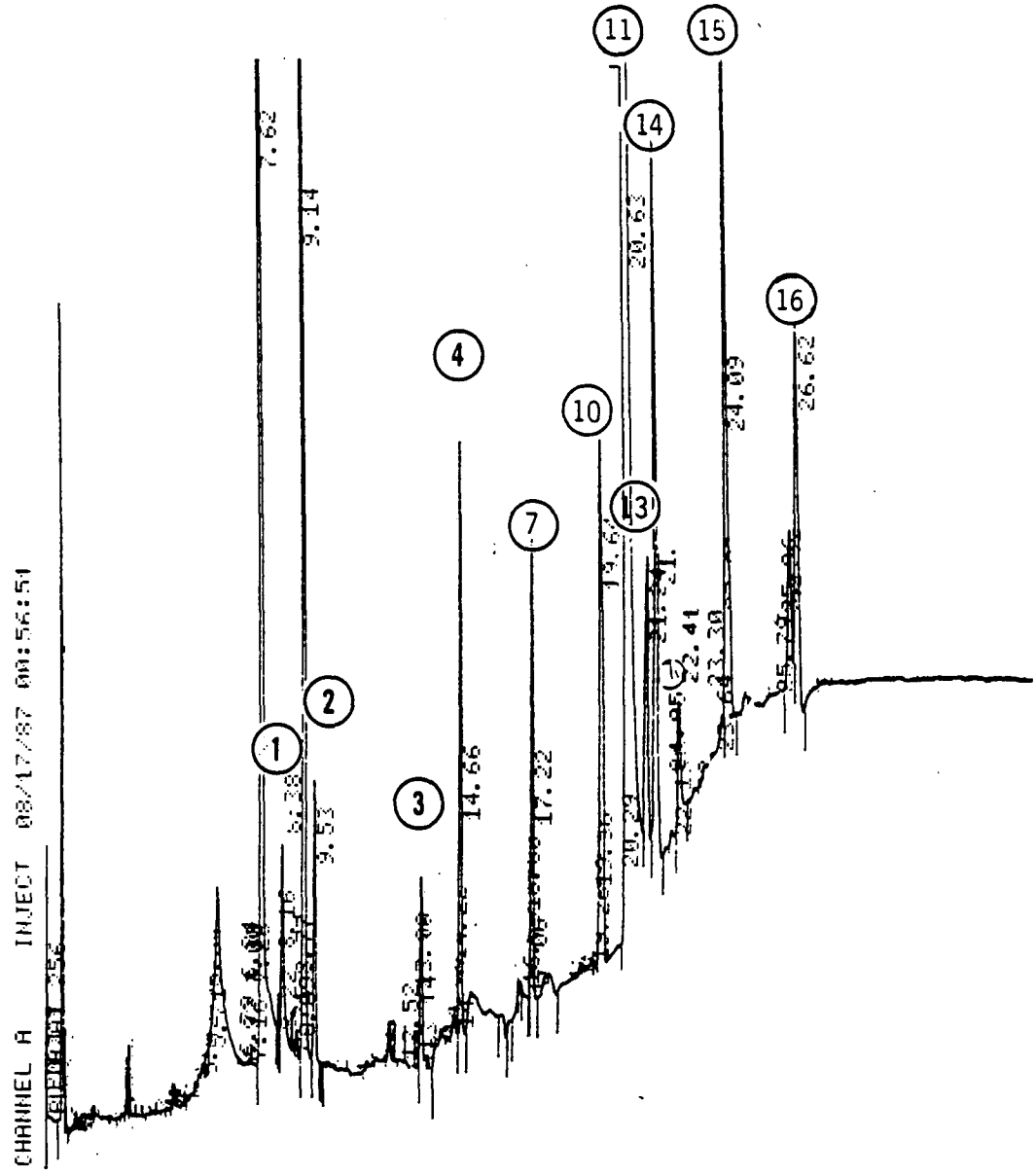


Figure 16. GC/ECD chromatogram of composite phthalate esters standard analyzed on a DB-210 fused-silica open tubular column. The GC operating conditions are given in Table 5. For peak assignments refer to Table 28. Concentration is 25 ppm in hexane.

TABLE 29. RATIO OF EC DETECTOR ABSOLUTE RESPONSE AT 350°C AND 320°C

Compound	Absolute response (percent RSD)				
	320°C[a]		350°C[b]		Ratio[c]
DMP	76,450	(3.1)	82,260	(2.7)	1.08
DEP	55,630	(1.1)	71,370	(2.7)	1.28
DIBP	86,605	(1.7)	122,950	(8.2)	1.42
DBP	75,230	(1.7)	100,800	(6.9)	1.34
BMPP	172,490	(3.0)	330,810	(6.2)	1.92
BMEP	75,860	(10.8)	111,180	(4.8)	1.47
DAP	79,210	(6.3)	109,890	(4.1)	1.39
BEEP	86,820	(2.8)	122,630	(2.8)	1.41
HEHP	111,270	(5.5)	234,660	(5.1)	2.11
DHP	63,040	(8.1)	79,230	(6.7)	1.26
BBP	894,010	(1.7)	1,029,260	(2.0)	1.15
BBEP	75,930	(8.0)	98,100	(10.9)	1.29
DEHP	76,400	(5.3)	102,940	(8.5)	1.35
DCP	177,600	(6.8)	351,900	(8.9)	1.98
DOP	48,670	(9.3)	58,750	(16.1)	1.21
DNP	36,120	(12.5)	47,130	(22.6)	1.30
BB (IS)	85,780	(0.9)	119,540	(1.2)	1.39
DPTP (SU)	124,270	(10.8)	83,730	(14.2)	0.67

[a]The number of determinations was 4.
[b]The number of determinations was 3.
[c]Ratio of absolute response at 350°C to absolute response at 320°C at range 1 and attenuation 32. The GC operating conditions are given in Table 5 under the DB-5 fused-silica capillary column; the temperature program is 120°C to 260°C (hold 15.7 min) at 15°C/min; injector temperature 275°C.

order to ensure satisfactory performance. An attempt made to test the detector at 350°C gave interesting results. Contrary to literature reports (3,4), we found that when the ECD is operated at 350°C, the detector responses are between 1.08 and 2.11 times as high as at 320°C, except for diphenyl terephthalate, for which the response decreased (Table 29). However, because the DB-1701 fused-silica open tubular column could not withstand temperatures above 320°C, all experimental work for the dual-column approach was performed at 320°C (Table 6).

6.2.2 Dual-Column/Dual-Detector Approach

The dual-column/dual-detector approach makes use of the split injection technique in which two fused-silica open tubular columns bonded with dissimilar stationary phases are connected to an injection tee and similar detectors. Four 30 m x 0.53 mm ID columns, DB-5, RT_x-5, DB-608, and DB-1701, of different film thickness (Table 6) were paired as shown in Tables 30 through 33. The best separation of the 16 phthalate esters and three of the surrogates proposed for incorporation in the revised Method 8060 (Method 8061) seems to be achieved with the DB-5/DB-1701 column pair. Retention times and relative retentions of the 16 compounds and 3 surrogates are presented in Tables 30 through 33. GC/ECD chromatograms of a composite phthalate esters standard are presented in Figures 17 through 20. In addition, the reproducibility (percent relative standard deviation) of ECD response using a Supelco 8-in injection tee or a J&W Scientific glass "Y-shape" press fit inlet splitter was determined and is presented in Tables 34, 35, and 36. Method linearity was determined only for the DB-5/DB-1701 column pair and is presented in Table 37. Benzyl benzoate seems to work well as internal standard. The GC method reproducibility was better than 10.9 percent for 16 consecutive injections of calibration standards, method blanks, and actual sample extracts (Table 38).

6.3 SAMPLE EXTRACTION

Several extraction techniques were evaluated for extracting phthalate esters from aqueous and solid matrices. These include the separatory funnel technique (Method 3510) and the continuous liquid-liquid extraction technique (Method 3520) for aqueous samples, and Soxhlet extraction (Method 3540) and sonication (Method 3550) for solid matrices. In addition, two nonconventional techniques, one using a Mixxor device and the other using the preconcentration of the phthalate esters onto a C_{18}-membrane disk followed by elution with acetonitrile were evaluated. Tables 39, 40, and 41 present the results obtained for 12 phthalate esters using the separatory funnel technique, the continuous liquid-liquid extraction technique, and the Mixxor device, respectively. The spiking levels were 50 µg/L for the experiments performed with the separatory funnel and the continuous liquid-liquid extractor, and 1 mg/L for the Mixxor device. The extracting solvent was methylene chloride for the separatory funnel and continuous liquid-liquid extraction, and hexane for the Mixxor extractor. The extracts from the separatory funnel and continuous liquid-liquid extractor were analyzed by both GC/ECD and GC/FID. Recoveries were >70 percent for most compounds and reproducibilities were better than 10 percent for two-thirds of the compounds when the separatory funnel extraction was employed. The continuous liquid-liquid extraction technique gave unacceptable reproducibilities for all compounds; the average

TABLE 30. RETENTION TIMES AND RELATIVE RETENTION TIMES OF PHTHALATE ESTERS ON THE DB-5/DB-608 COLUMN PAIR[a]

Compound No.	Phthalate	DB-5 tr (min)	DB-5 RRT	DB-608 tr (min)	DB-608 RRT
1	DMP	6.49	0.545	6.36	0.555
2	DEP	8.64	0.725	8.25	0.721
3	DIBP	13.67	1.146	12.22	1.067
4	DBP	15.43	1.294	14.13	1.233
5	BMPP	17.84	1.496	15.21	1.328
6	BMEP	16.15	1.355	16.60	1.449
7	DAP	19.29	1.618	17.31	1.511
8	BEEP	18.50	1.552	18.26	1.594
9	HEHP	20.06	1.682	19.01	1.660
10	DHP	23.56	1.976	20.80	1.816
11	BBP	23.81	1.996	23.87	2.084
12	BBEP	26.53	2.225	24.98	2.181
13	DEHP	28.20	2.365	24.23	2.116
14	DCP	27.79	2.331	27.55	2.405
15	DOP	32.48	2.724	28.42	2.481
16	DNP	37.59	3.152	32.27	2.818
	BB(IS)	11.92	1.000	11.45	1.000
	Surrogates:				
	DPTP	32.27	2.707	32.09	2.802
	DPP	28.37	2.380	30.19	2.636
	DBZP	33.19	2.784	35.38	3.089

[a]The GC conditions are given in Table 6.

TABLE 31. RETENTION TIMES AND RELATIVE RETENTION TIMES OF PHTHALATE ESTERS ON THE DB-608/DB-1701 COLUMN PAIR[a]

Compound No.	Phthalate	DB-608 tr (min)	DB-608 RRT	DB-1701 tr (min)	DB-1701 RRT
1	DMP	6.72	0.554	6.73	0.585
2	DEP	8.69	0.716	8.85	0.770
3	DIBP	12.74	1.050	13.36	1.162
4	DBP	14.68	1.210	15.13	1.316
5	BMPP	15.76	1.299	16.73	1.455
6	BMEP	17.24	1.421	16.96	1.475
7	DAP	17.94	1.479	18.64	1.621
8	BEEP	18.93	1.561	18.80	1.635
9	HEHP	19.70	1.624	19.56	1.701
10	DHP	21.50	1.772	22.48	1.955
11	BBP	24.64	2.031	23.76	2.066
12	BBEP	25.71	2.120	25.96	2.257
13	DEHP	24.94	2.056	26.35	2.291
14	DCP	28.33	2.336	27.06	2.353
15	DOP	29.14	2.402	30.57	2.658
16	DNP	32.97	2.718	34.71	3.018
	BB(IS)	12.13	1.000	11.50	1.000
	Surrogates:				
	DPTP	33.99	2.802	32.85	2.856
	DPP	31.97	2.636	29.56	2.570
	DBZP	37.42	3.085	34.34	2.986
	DOIP	31.13	2.566	33.26	2.892
	DPIP	33.79	2.786	32.86	2.857

[a]The GC conditions are given in Table 6.

TABLE 32. RETENTION TIMES AND RELATIVE RETENTION TIMES OF PHTHALATE ESTERS ON THE RT_x-5/DB-608 COLUMN PAIR[a]

Compound No.	Phthalate	RT_x-5 tr (min)	RT_x-5 RRT	DB-608 tr (min)	DB-608 RRT
1	DMP	2.94	0.465	6.33	0.534
2	DEP	4.13	0.653	8.48	0.715
3	DIBP	7.77	1.129	12.49	1.053
4	DBP	9.25	1.464	14.40	1.214
5	BMPP	11.20	1.772	15.50	1.307
6	BMEP	9.93	1.571	16.91	1.426
7	DAP	12.81	2.027	17.30	1.459
8	BEEP	12.33	1.951	18.59	1.567
9	HEHP	13.29	2.103	19.37	1.633
10	DHP	15.53	2.457	21.16	1.784
11	BBP	15.53	2.457	23.45	1.977
12	BBEP	17.75	2.809	25.37	2.139
13	DEHP	18.42	2.915	24.27	2.046
14	DCP	19.00	3.006	27.98	2.359
15	DOP	22.56	3.570	28.81	2.429
16	DNP	26.44	4.184	32.70	2.757
	BB(IS)	6.32	1.000	11.86	1.000
	Surrogates:				
	DPTP	21.96	3.499	32.85	2.770
	DPP	18.81	2.999	30.94	2.609
	DBZP	22.92	3.643	36.27	3.058
	DOIP	24.63	3.916	30.04	2.533
	DPIP	21.90	3.496	32.78	2.764

[a]The GC conditions areas given in Table 6.

TABLE 33. RETENTION TIMES AND RELATIVE RETENTION TIMES OF PHTHALATE ESTERS ON THE DB-5/DB-1701 COLUMN PAIR[a]

Compound No.	Phthalate	DB-5 tr (min)	DB-5 RRT	DB-1701 tr (min)	DB-1701 RRT
1	DMP	7.06	0.555	6.37	0.575
2	DEP	9.30	0.732	8.45	0.763
3	DIBP	14.44	1.136	12.91	1.166
4	DBP	16.26	1.279	14.66	1.324
5	BMPP	18.77	1.477	16.27	1.470
6	BMEP	17.02	1.339	16.41	1.482
7	DAP	20.25	1.593	18.08	1.633
8	BEEP	19.43	1.529	18.21	1.644
9	HEHP	21.07	1.657	18.97	1.714
10	DHP	24.57	1.933	21.85	1.973
11	BBP	24.86	1.955	23.08	2.084
12	BBEP	27.56	2.168	25.24	2.280
13	DEHP	29.23	2.299	25.67	2.318
14	DCP	28.88	2.272	26.35	2.380
15	DOP	33.33	2.622	29.83	2.694
16	DNP	38.80	3.084	33.84	3.056
	BB(IS)	12.71	1.000	11.07	1.000
	Surrogates:				
	DPP(SU-1)	29.46	2.318	28.32	2.558
	DPIP(SU-2)	32.99	2.596	31.37	2.834
	DBZP(SU-3)	34.40	2.707	32.65	2.949

[a]The GC conditions are given in Table 6.

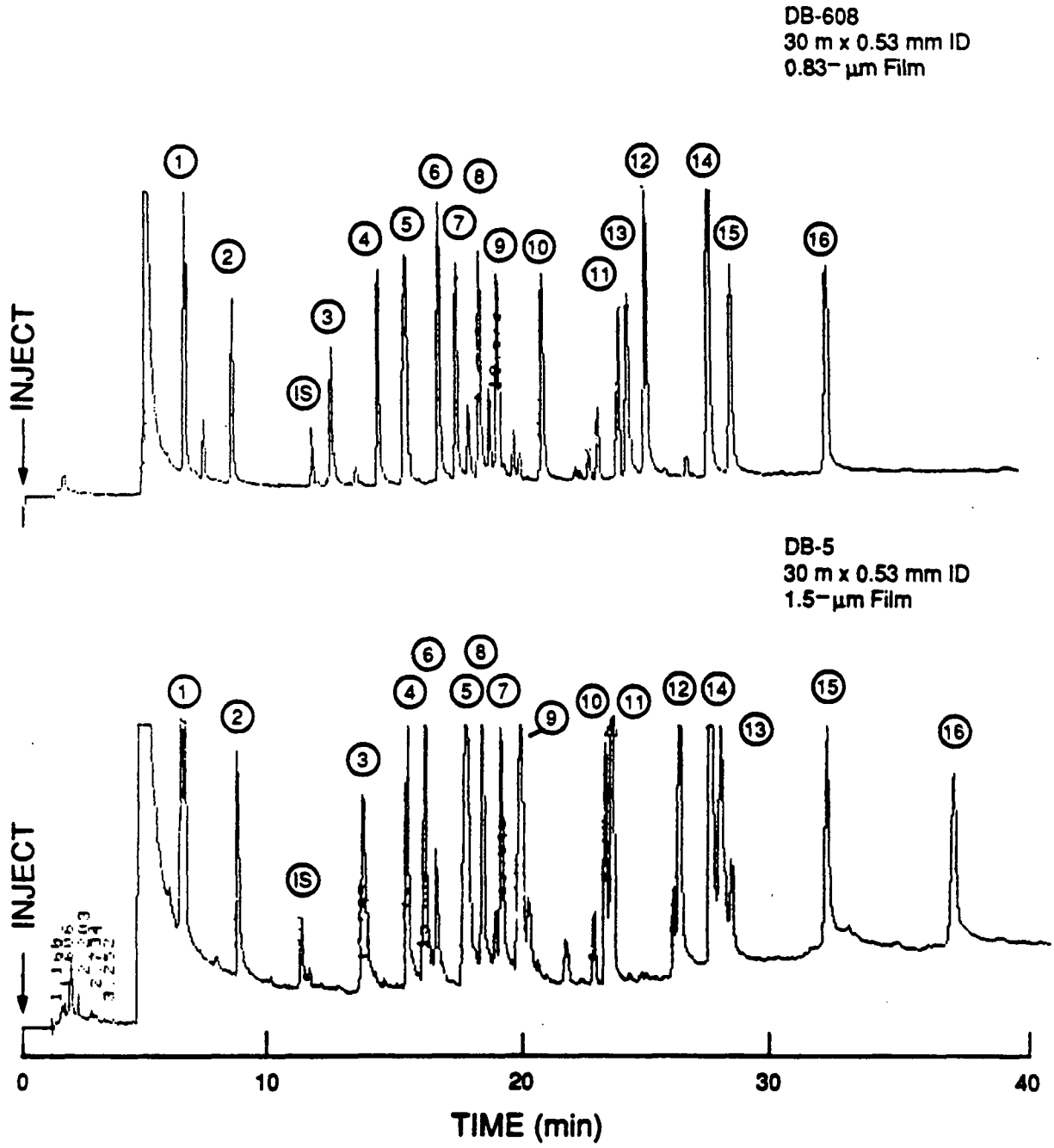


Figure 17. GC/ECD chromatograms of the phthalate esters standard analyzed on the DB-608/DB-5 column pair. The GC operating conditions are given in Table 6. For peak assignments, refer to Table 30.

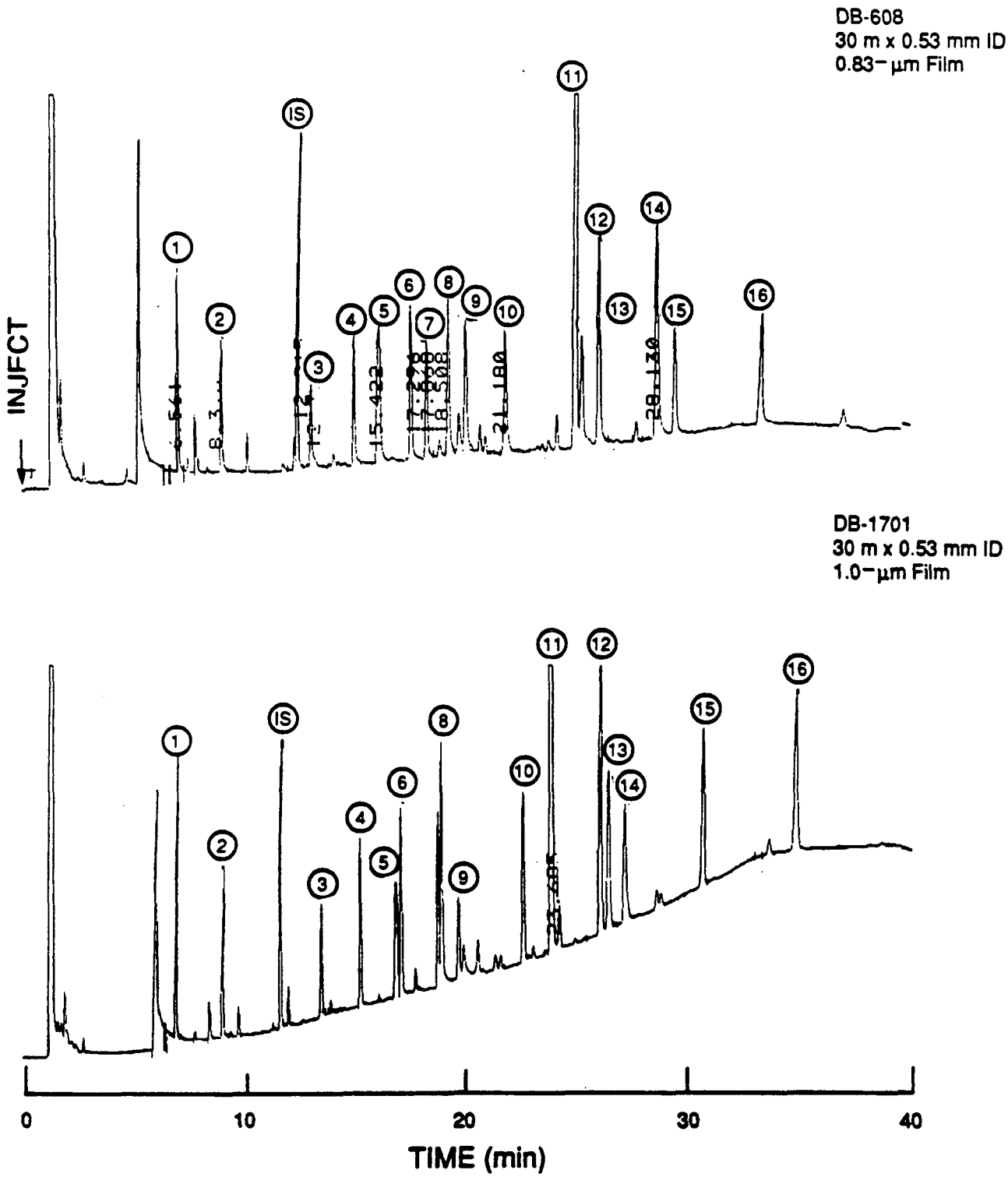


Figure 18. GC/ECD chromatograms of the phthalate esters standard analyzed on the DB-608/DB-1701 column pair. The GC operating conditions are given in Table 6. For peak assignments refer to Table 31.

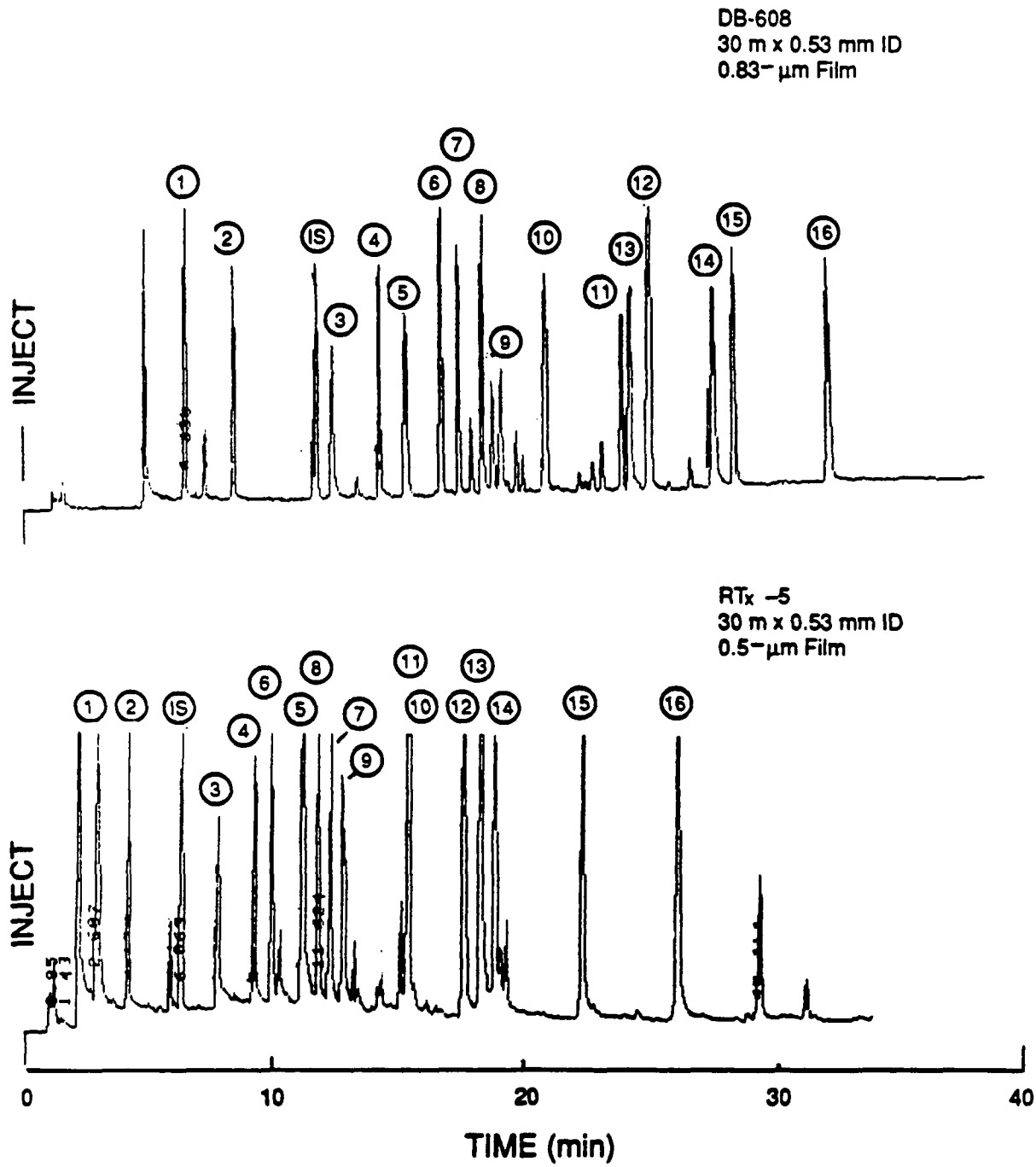


Figure 19. GC/ECD chromatograms of the phthalate esters standard analyzed on the DB-608/RTx-5 column pair. The GC operating conditions are given in Table 6. For peak assignments refer to Table 32.

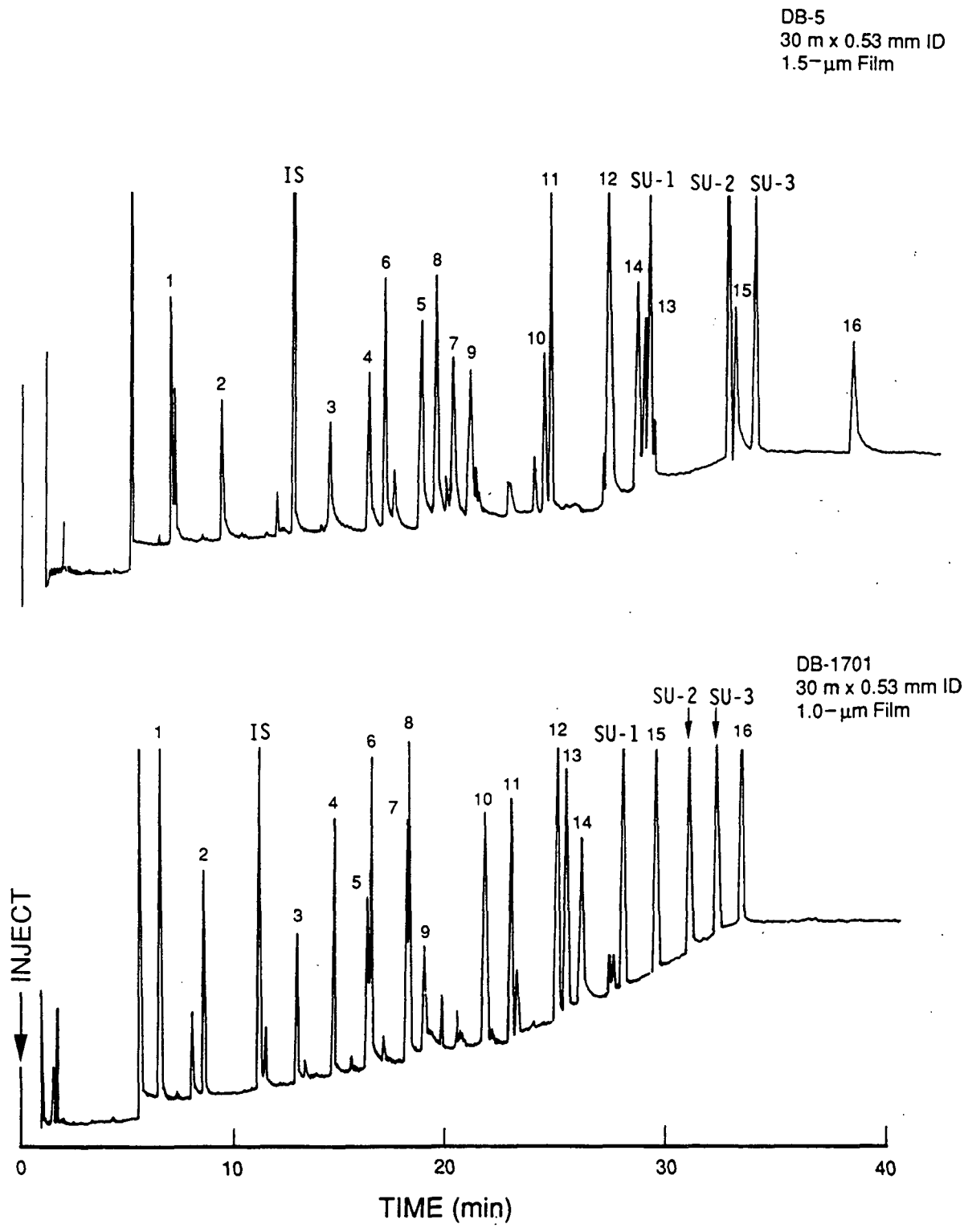


Figure 20. GC/ECD chromatograms of the phthalate esters standard analyzed on the DB-5/DB-1701 column pair. The GC operating conditions are given in Table 6. For peak assignments refer to Table 33.

TABLE 34. REPRODUCIBILITY OF THE DETECTOR RESPONSE USING THE DB-5/DB-608 COLUMN SETUP (J&W SCIENTIFIC INLET SPLITTER)

	Percent RSD[a]	
Phthalate	DB-5 (0.83-μm film)	DB-608 (0.83-μm film)
DMP	3.1	7.6
DEP	2.5	10.5
DIBP	3.8	10.0
DBP	1.9	10.3
BMPP	1.6	8.6
BMEP	2.2	8.7
DAP	1.8	8.7
BEEP	1.9	12.1
HEHP	1.2	8.8
DHP	1.6	9.3
BBP	2.2	10.3
BBEP	2.3	11.1
DEHP	2.4	11.0
DCP	1.5	14.2
DOP	2.9	13.6
DNP	3.0	16.8
BB (IS)	4.8	10.1

[a] The number of determinations was 7. The GC operating conditions are given in Table 6.

TABLE 35. REPRODUCIBILITY OF THE DETECTOR RESPONSE USING THE DB-608/DB-1701 COLUMN SETUP (8-IN INJECTION TEE FROM SUPELCO)

Phthalate	Percent RSD[a]	
	DB-608 (0.83-μm film)	DB-1701 (1.0-μm film)
DMP	1.1	1.1
DEP	1.2	1.2
DIBP	1.4	1.2
DBP	1.4	1.0
BMPP	7.2	1.0
BMEP	1.4	0.9
DAP	1.3	1.3
BEEP	6.9	1.0
HEHP	17.1	[b]
DHP	5.5	1.4
BBP	0.9	1.2
BBEP	5.5	1.1
DEHP	0.9	1.4
DCP	1.3	1.1
DOP	1.9	0.9
DNP	2.8	1.0
BB (IS)	1.0	1.4

[a] The number of determinations was 7. The GC operating conditions are given in Table 6.
[b] Data not available.

TABLE 36. REPRODUCIBILITY OF THE DETECTOR RESPONSE USING THE DB-5/DB-1701 COLUMN SETUP (J&W SCIENTIFIC INLET SPLITTER)

	Percent RSD[a]	
Phthalate	DB-5 (1.5-μm film)	DB-1701 (1.0-μm film)
DMP	5.1	1.7
DEP	4.6	2.2
DIBP	5.8	3.7
DBP	2.7	2.0
BMPP	2.0	3.0
BMEP	3.3	1.9
DAP	3.9	1.7
BEEP	1.5	1.8
HEHP	9.8	[b]
DHP	3.1	2.2
BBP	2.9	2.8
BBEP	3.1	1.6
DEHP	2.2	2.1
DCP	7.1	4.2
DOP	3.5	2.1
DNP	1.8	3.5
BB (IS)	1.8	3.5

[a] The number of determinations was 8. The GC operating conditions are given in Table 6.
[b] Data not available.

TABLE 37. METHOD LINEARITY USING THE DB-5/DB-1701 SETUP

Phthalate	Correlation Coefficient[a] DB-5 (1.5-μm film)	DB-1701 (1.0-μm film)
DMP	0.99284	0.99960
DEP	0.99246	0.99855
DIBP	0.97853	0.99746
DBP	0.99834	0.99890
BMPP	0.99806	0.99900
BMEP	0.99932	0.99900
DAP	0.98967	0.99832
BEEP	0.99595	0.99885
HEHP	0.99281	0.98062
DHP	0.99736	0.98142
BBP	0.99783	0.99555
BBEP	0.99493	0.99897
DEHP	0.99877	0.98771
DCP	0.99885	0.99811
DOP	0.89106	0.99796
DNP	0.93325	0.99563

[a] The concentration range was 20 to 80 ng/μL. The number of data points was 10. The phthalate esters could not be detected at 1 ng/μL. The 5-ng/μg and the 100-ng/μL concentrations did not fit the linear range. The GC operating conditions are given in Table 6.

TABLE 38. GC METHOD EVALUATION—INTERNAL STANDARD SUMMARY

Sample identification[a]	Absolute area	
	DB-5	DB-1701
Calibration Standard	70,835	73,745
8113003-19[b]	51,025	65,399
8113003-1	56,274	74,859
8113003-2	53,898	71,789
8113003-3	56,027	74,392
8113003-7	57,869	74,346
8113003-8	56,401	69,100
8113003-9	60,154	74,342
8113003-20[b]	55,121	71,674
8113003-4	56,961	75,143
8113003-5	59,041	79,203
8113003-6	60,010	78,749
8113003-10	55,184	69,627
8113003-11	54,724	68,981
8113003-12	54,672	70,921
Calibration Standard	76,037	76,105
Average	58,390	73,023
Standard deviation	6,385	3,682
Percent RSD	10.9	5.0

[a]The samples listed here are the acetonitrile extracts of the HPLC-grade water samples and the groundwater samples spiked with the 16 phthalate esters at 25 μg/L and 100 μg/L and extracted using the C_{18}-membrane disk method. The GC operating conditions are given in Table 6 for the DB-5/DB-1701.

[b]Sample 8113002-19 is an HPLC-water blank; Sample 8113003-20 is a groundwater blank.

TABLE 39. AVERAGE RECOVERIES OF METHOD 8060 COMPOUNDS USING SEPARATORY FUNNEL EXTRACTION (METHOD 3510)[a]

Compound	GC/ECD[b] average recovery (percent RSD)	GC/FID[c] average recovery (percent RSD)
DMP	67.6 (18)	80.8 (6.6)
DEP	73.0 (3.2)	80.6 (6.3)
DIBP	75.0 (2.7)	79.7 (5.6)
DBP	70.6 (4.5)	79.2 (5.5)
BMPP	58.8 (8.2)	71.5 (10)
DAP	63.0 (3.5)	75.7 (5.6)
HEHP	76.8 (7.4)	77.9 (5.6)
DHP	60.0 (12)	64.9 (17)
BBP	69.0 (3.1)	72.4 (7.8)
DEHP	63.8 (8.0)	64.0 (17)
DOP	56.6 (24)	59.8 (20)
DNP	54.0 (15)	56.1 (25)

[a]The spiking level was 50 µg/L; the number of determinations was 5. HPLC-grade water (Fisher Scientific Lot No. 873266) was used for this experiment. Extraction was performed with methylene chloride (American Burdick & Jackson Lot No. AQ 352).

[b]The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 µm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; spitless injection.

[c]The GC/FID operating conditions were as follows: 30 m x 0.53 mm ID Supelcowax 10 fused-silica open tubular column (1 µm film thickness); 150°C (hold 2 min) to 220°C at 15°C/min then to 260°C (hold 13.5 min) at 4°C/min; carrier gas: helium at 20 psi; injector and detector temperature: 270°C; spitless injection.

TABLE 40. AVERAGE RECOVERIES OF METHOD 8060 COMPOUNDS USING CONTINUOUS LIQUID-LIQUID EXTRACTION (METHOD 3520)[a]

Compound	GC/ECD[b] average recovery (percent RSD)	GC/FID[c] average recovery (percent RSD)
DMP	67.5 (7.4)	89.7 (9.3)
DEP	72.8 (15)	87.6 (11)
DIBP	71.0 (17)	81.4 (12)
DBP	69.7 (17)	79.2 (14)
BMPP	51.3 (18)	57.1 (17)
DAP	62.5 (20)	68.5 (12)
HEHP	78.0 (22)	71.7 (14)
DHP	44.8 (20)	37.9 (31)
BBP	68.0 (5.6)	15.7 (78)
DEHP	62.7 (29)	24.9 (55)
DOP	32.7 (52)	21.1 (69)
DNP	34.2 (41)	20.3 (53)

[a] The spiking level was 50 µg/L; the number of determinations was 6 for GC/ECD and 3 for GC/FID. HPLC-grade water (Fisher Scientific Lot No. 873266) was used for this experiment. Extraction was performed with methylene chloride (American Burdick & Jackson Lot No. AQ 352).

[b] The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 µm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; spitless injection.

[c] The GC/FID operating conditions were as follows: 30 m x 0.53 mm ID Supelcowax 10 fused-silica open tubular column (1 µm film thickness); 150°C (hold 2 min) to 220°C at 15°C/min then to 260°C (hold 13.5 min) at 4°C/min; carrier gas: helium at 20 psi; injector and detector temperature: 270°C; spitless injection.

TABLE 41. AVERAGE RECOVERIES OF METHOD 8060 COMPOUNDS USING MIXXOR EXTRACTOR AND HEXANE

Compound	Average recovery[a,b] (percent RSD)
DMP	40 (13)
DEP	67 (12)
DIBP	75 (13)
DBP	66 (17)
BMPP	37 (32)
DAP	52 (19)
HEHP	57 (17)
DHP	43 (29)
BBP	65 (11)
DEHP	52 (25)
DOP	36 (14)
DNP	24 (77)

[a]The spiking level was 1 mg/L; the number of determinations was 5. HPLC-grade water (Fisher Scientific Lot No. 873266) was used for this experiment. $V_{extract}$ was 1 mL. Each extract was diluted 500-fold prior to GC/ECD analysis.

[b]The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 µm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; spitless injection.

recoveries for five of the 12 phthalate esters were 20 to 45 percent. Extraction with hexane in the Mixxor device also gave unacceptable recoveries and reproducibilities. Therefore, the separatory funnel extraction method was further evaluated on samples containing 16 phthalate esters at three concentrations: 1 µg/L, 10 µg/L, and 25 µg/L, each in quadruplicate. The results are presented in Tables 42, 43, and 44. Diphenyl terephthalate was used as a surrogate; its average recovery in the 12 samples was 98.2 percent, and the relative standard deviation was 19.2 percent (Table 45). These results indicate that the separatory funnel extraction method is more desirable than the continuous liquid-liquid extraction and the Mixxor device extraction methods.

Three other surrogate compounds were tested for use with Method 3510. Their average recovery and relative standard deviation are also presented in Table 45. Excellent recoveries and reproducibilities were achieved for each surrogate compound.

Tables 46 through 48 present the results of the extraction procedure using the 3M-Empore membrane disks containing either the C_8-silica (Tables 46 and 47) or the C_{18}-silica (Tables 48 and 49). The shorter-chain esters and the alkoxy-substituted esters had recoveries greater than 65 percent when the C_8-membrane disks were used for sample filtration. The longer-chain esters ($>C_5$ alkyl) exhibited recoveries <40 percent, and there seems to be a trend in decreasing recoveries with the increasing number of carbons in the alkyl chain. In the case of relatively clean samples, the membrane disks can be reused, provided that they are cleaned and reconditioned after each sample. The disks were used four consecutive times with HPLC-grade water spiked with 16 target phthalate esters at 24 µg/L. The recovery data for each extraction are presented in Tables 47 for the C_8-membrane disks and 48 for the C_{18}-membrane disks. Since the C_{18}-membrane disks were found to give higher recoveries for the longer-chain esters, they were further evaluated with both HPLC-grade water and groundwater at three concentrations, each in triplicate. Table 49 presents the data for the 25-µg/L and 100-µg/L spike level. The target phthalate esters could not be detected of the 5-µg/L spike level. As expected, method accuracy and precision seem to be a function of concentration (Table 49). The surrogate recoveries for the samples that were preconcentrated on the membrane disks and then extracted with acetonitrile are presented in Table 50.

Extraction of soil samples by sonication with methylene chloride/acetone (1:1) and Soxhlet extraction with hexane/acetone (1:1) was evaluated using a sandy loam soil. Tables 51 and 52 summarize the data. In the case of Method 3550, we prepared two batches of spiked sandy loam soil, and each batch was split into 8 or 9 portions of material. The average recoveries ranged from 31.9 to 112 percent for Batch 1 and 32.1 to 108 percent for Batch 2. The percent relative standard deviations ranged from 4.2 to 24.6 percent for Batch 1 and 8.1 to 25 percent for Batch 2 (Table 51). The average recoveries for Method 3540 were slightly higher, ranging from 53.5 to 135 percent; however, the percent relative standard deviations were much higher than in the case of Method 3550 ranging from 19.8 to 46.9 percent. Method 3550 was subsequently evaluated with other solid matrices including an estuarine sediment and a municipal sludge. The results of these method evaluation

TABLE 42. RESULTS OF METHODS 3510 AND 8060 PERFORMANCE (CONCENTRATION 1)[a]

Compound	Spike level (µg/L)	Concentration (µg/L) Rep.1	Rep.2	Rep.3	Rep.4	Average ± SD (percent RSD)	Average recovery (percent RSD)
DMP	1.0	1.2	1.4	1.3	1.4	1.3 ± 0.1 (7.3)	132 (7.3)
DEP	1.0	0.85	0.99	0.91	0.91	0.92 ± 0.06 (6.2)	91.5 (6.2)
DIBP	1.0	0.97	1.0	0.99	1.0	0.97 ± 0.04 (4.2)	96.7 (4.2)
DBP	1.0	0.81	0.93	0.86	0.85	0.86 ± 0.05 (5.8)	86.2 (5.8)
BMPP	1.0	0.84	0.88	0.87	0.87	0.87 ± 0.02 (2.0)	86.5 (2.0)
BMEP	1.0	0.69	0.73	0.38	0.92	0.68 ± 0.22 (33)	68.0 (33)
DAP	1.0	0.67	0.68	0.66	0.69	0.68 ± 0.01 (1.9)	67.5 (1.9)
BEEP	1.0	0.61	0.74	0.38	0.74	0.62 ± 0.17 (27)	61.7 (27)
HEHP	1.0	0.81	0.74	0.64	0.74	0.73 ± 0.07 (9.6)	73.2 (9.6)
DHP	1.0	0.85	0.93	0.89	0.92	0.90 ± 0.04 (4.0)	89.7 (4.0)
BBP	1.0	1.2	1.7	1.8	1.4	1.5 ± 0.3 (18)	152 (18)
BBEP	1.0	0.55	0.65	0.28	0.65	0.53 ± 0.17 (33)	53.2 (33)
DEHP	1.0	1.0	1.2	1.3	1.0	1.1 ± 0.2 (14)	112 (14)
DCP	1.0	0.75	0.82	0.74	0.79	0.78 ± 0.04 (4.7)	77.5 (4.7)
DOP	1.0	0.88	0.95	0.91	0.93	0.92 ± 0.03 (3.2)	91.7 (3.2)
DNP	1.0	0.74	0.79	0.76	0.77	0.76 ± 0.02 (2.7)	76.5 (2.7)

[a]Each water sample (1 L reagent water, Fisher Scientific Lot No. 873154) was spiked with 100 µL of a 10-ng/µL composite phthalate ester standard (in hexane) and 100 µL of 50 ng/µL diphenyl terephthalate (in hexane). $V_{extract}$ was 10 mL after solvent exchange. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 µm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; spitless injection.

TABLE 43. RESULTS OF METHODS 3510 AND 8060 PERFORMANCE (CONCENTRATION 2)[a]

Compound	Spike level (µg/L)	Concentration (µg/L) Rep.1	Rep.2	Rep.3	Rep.4	Average ± SD (percent RSD)	Average recovery (percent RSD)
DMP	10	7.0	9.8	10.4	10.6	9.5 ± 1.7 (18)	94.5 (18)
DEP	10	9.4	8.9	9.4	9.5	9.3 ± 0.3 (2.9)	93.0 (2.9)
DIBP	10	10.4	11.4	12.5	10.3	11.2 ± 1.0 (9.2)	112 (9.2)
DBP	10	10.3	10.9	11.9	10.1	10.8 ± 0.8 (7.5)	108 (7.5)
BMPP	10	10.1	9.6	10.8	9.2	9.9 ± 0.7 (7.0)	99 (7.0)
BMEP	10	10.7	11.9	12.9	11.3	11.7 ± 0.9 (8.0)	117 (8.0)
DAP	10	9.0	8.4	9.6	7.8	8.7 ± 0.8 (8.9)	87.0 (8.9)
BEEP	10	9.7	10.6	11.7	9.0	10.3 ± 1.2 (11)	103 (11)
HEHP	10	9.8	9.8	11.3	8.8	9.9 ± 1.0 (10)	99.2 (10)
DHP	10	10.1	8.2	9.9	9.3	9.4 ± 0.8 (9.1)	93.7 (9.1)
BBP	10	12.3	9.0	10.9	10.0	10.6 ± 1.4 (13)	106 (13)
BBEP	10	8.4	6.2	7.7	7.8	7.5 ± 0.9 (12)	75.2 (12)
DEHP	10	10.0	8.6	9.0	10.3	9.5 ± 0.8 (8.5)	94.7 (8.5)
DCP	10	9.2	6.4	8.1	8.0	7.9 ± 1.2 (15)	79.2 (15)
DOP	10	10.2	7.4	10.1	10.0	9.4 ± 1.4 (14)	94.2 (14)
DNP	10	8.3	5.5	7.8	7.7	7.3 ± 1.2 (17)	73.2 (17)

[a]Each water sample (1 L reagent water, Fisher Scientific Lot No. 873154) was spiked with 200 µL of a 50-ng/µL composite phthalate ester standard (in hexane) and 100 µL of 50 ng/µL diphenyl terephthalate (in hexane). $V_{extract}$ was 10 mL after solvent exchange. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 µm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas; helium at 21 psi; injector temperature 275°C; detector temperature 320°C; spitless injection.

TABLE 44. RESULTS OF METHODS 3510 AND 8060 PERFORMANCE (CONCENTRATION 3)[a]

Compound	Spike level (µg/L)	Concentration (µg/L) Rep.1	Rep.2	Rep.3	Rep.4	Average ± SD (percent RSD)	Average recovery (percent RSD)
DMP	25	17.3	24.9	25.0	26.3	23.4 ± 4.1 (18)	93.6 (18)
DEP	25	23.2	22.5	23.0	23.9	23.2 ± 0.6 (2.5)	92.8 (2.5)
DIBP	25	26.7	25.4	26.1	26.2	26.1 ± 0.5 (2.1)	104 (2.1)
DBP	25	32.3	26.3	26.9	26.4	28.0 ± 2.9 (1.0)	112 (1.0)
BMPP	25	28.5	25.9	27.1	26.1	26.9 ± 1.2 (4.4)	108 (4.4)
BMEP	25	35.7	30.4	32.4	31.8	32.6 ± 2.2 (6.9)	130 (6.9)
DAP	25	28.7	23.2	24.8	23.8	25.1 ± 2.5 (1.0)	100 (1.0)
BEEP	25	33.0	27.8	30.0	29.2	30.0 ± 2.2 (7.3)	120 (7.3)
HEHP	25	28.2	24.9	26.4	25.2	26.2 ± 1.5 (5.7)	105 (5.7)
DHP	25	28.3	24.1	26.0	26.6	26.3 ± 1.7 (6.6)	105 (6.6)
BBP	25	32.7	29.6	35.2	29.7	31.8 ± 2.7 (8.4)	127 (8.4)
BBEP	25	28.3	22.4	25.5	23.7	25.0 ± 2.6 (10)	100 (10)
DEHP	25	27.6	24.4	26.6	24.2	25.7 ± 1.7 (6.5)	103 (6.5)
DCP	25	25.7	23.6	25.9	23.2	24.6 ± 1.4 (5.7)	98.4 (5.7)
DOP	25	30.2	25.9	29.3	26.2	27.9 ± 2.2 (7.8)	112 (7.8)
DNP	25	24.5	20.6	24.2	20.9	22.6 ± 2.1 (9.2)	90.4 (9.2)

[a]Each water sample (1 L reagent water, Fisher Scientific Lot No. 873154) was spiked with 500 µL of a 50-ng/µL composite phthalate ester standard (in hexane) and 100 µL of 50 ng/µL diphenyl terephthalate (in hexane). $V_{extract}$ was 10 mL after solvent exchange. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 µm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; spitless injection.

TABLE 45. RECOVERY OF SURROGATE COMPOUNDS SPIKED INTO REAGENT WATER SAMPLES (METHOD 3510)

Compound	Spike level (μg/L)	Percent recovery					Average	RSD (percent)
		Rep.1	Rep.2	Rep.3	Rep.4	Rep.5		
DPTP	5						98.2[a]	19.2[a]
DPP	10	81.8	83.8	98.3	100	96.2	92.0	9.3
DPIP	10	78.3	85.9	90.2	94.1	93.1	88.3	7.3
DBZP	10	79.0	75.0	90.2	96.3	94.3	86.9	10.9

[a]The number of determinations was 12.

TABLE 46. EVALUATION OF C_8-MEMBRANE DISKS FOR PRECONCENTRATION OF PHTHALATE ESTERS

Phthalate	Percent Recovery[a] Volume (500 mL)	Volume (1000 mL)
DMP	94.7	101
DEP	91.9	122
DIBP	71.3	101
DBP	64.5	97.5
BMPP	37.3	48.3
BMEP	111	138
DAP	39.7	57.5
BEEP	112	145
HEHP	64.3	102
DHP	35.2	52.5
BBP	63.7	110
BBEP	84.4	121
DEHP	23.8	41.2
DCP	71.9	103
DOP	19.4	34.8
DNP	20.4	33.8

[a] 500 mL or 1000 mL of HPLC-grade water were spiked with the target compounds at 24 µg/L and were passed through a preconditioned 3M-Empore C_8-membrane disk in approximately 26 min. The target compounds were eluted with 10 mL of acetonitrile. A second elution with an additional 10 mL of acetonitrile was performed. No compounds were detected in the second extract. The GC/ECD opera-ting conditions are given in Table 6 under the DB-608/DB-1701 column pair. Single determination.

TABLE 47. EVALUATION OF C_8-MEMBRANE DISKS FOR PRECONCENTRATION OF PHTHALATE ESTERS (MULTIPLE USE OF DISKS)

	Percent Recovery[a]			
Phthalate	1st	2nd	3rd	4th
DMP	92.5	116	103	105
DEP	85.8	106	98.3	91.7
DIBP	69.4	86.7	84.2	78.1
DBP	68.5	92.5	92.5	85.0
BMPP	57.6	99.2	115	136
BMEP	119	123	120	120
DAP	57.2	85.0	57.4	67.8
BEEP	131	136	137	131
HEHP	97.5	115	112	108
DHP	56.6	84.2	56.2	65.3
BBP	90.8	116	102	104
BBEP	97.5	113	123	109
DEHP	50.7	83.3	51.2	62.0
DCP	90.8	104	96.7	92.5
DOP	47.3	78.0	45.4	56.1
DNP	45.3	79.2	47.9	60.5

[a]500 mL of HPLC-grade water were spiked with the target compounds at 24 ug/L and were passed through a preconditioned 3M-Empore C_8-membrane disk in approximately 26 min. The target compounds were eluted with 10 mL of acetonitrile. A second elution with an additional 10 mL of acetonitrile was performed. No compounds were detected in the second extract. The membrane disk was reconditioned with 10 mL of methanol followed by 10 mL of water and reused three consecutive times. The GC operating conditions are given in Table 6 for the DB-608/DB-1701 column pair.

TABLE 48. EVALUATION OF C_{18}-MEMBRANE DISKS FOR PRECONCENTRATION OF PHTHALATE ESTERS (MULTIPLE USE OF DISKS)

	Percent Recovery[a]			
Phthalate	1st	2nd	3rd	4th
DMP	75.5	56.3	58.9	63.6
DEP	73.8	64.9	55.1	66.5
DIBP	76.2	65.1	53.1	63.3
DBP	78.7	65.8	56.3	63.3
BMPP	70.5	63.7	49.3	57.9
BMEP	94.2	68.0	67.2	76.7
DAP	67.1	63.3	46.2	55.3
BEEP	97.6	82.0	75.2	92.4
HEHP	82.7	72.6	63.4	65.7
DHP	73.6	62.9	46.7	57.2
BBP	84.4	80.9	62.9	73.0
BBEP	85.4	84.6	60.8	69.9
DEHP	73.5	70.0	51.9	61.2
DCP	82.4	83.0	60.8	67.5
DOP	75.1	75.9	56.3	55.2
DNP	84.4	84.5	71.3	55.9

[a]500 mL of HPLC-grade water were spiked with the target compounds at 24 ug/L and were passed through a preconditioned 3M-Empore membrane disk in approximately 20 min. The target compounds were eluted with 10 mL of acetonitrile. A second elution with an additional 10 mL of acetonitrile was performed. No compounds were detected in the second extract. The membrane disk was reconditioned with 10 mL of methanol followed by 10 mL of water and reused three consecutive times. The GC/ECD operating conditions are given in Table 6 under the DB-5/DB-608 column pair.

TABLE 49. C_{18}-MEMBRANE DISKS METHOD EVALUATION[a]

	HPLC-Grade Water				Groundwater			
Phthalate	25 μg/L		100 μg/L		25 μg/L[b]		100 μg/L	
DMP	81.7	(5.9)	88.6	(17.7)	67.7	75.6	86.6	(14.3)
DEP	76.6	(1.6)	92.3	(10.3)	71.9	69.3	92.6	(7.2)
DIBP	64.2	(16.7)	87.6	(16.2)	80.0	57.6	89.3	(1.6)
DBP	69.9	(17.2)	90.3	(13.2)	73.5	63.1	95.0	(1.5)
BMPP	62.5	(16.7)	87.2	(9.5)	59.6	58.9	86.7	(4.9)
BMEP	83.3	(3.1)	107	(13.6)	72.3	69.5	113	(2.8)
DAP	54.3	(34.1)	93.6	(21.0)	55.4	54.0	78.9	(5.8)
BEEP	90.9	(9.0)	108	(8.9)	72.5	99.8	102	(4.0)
HEHP	47.7	(40.0)	93.9	(22.4)	92.6	24.0	83.4	(8.8)
DHP	66.5	(26.3)	98.4	(5.0)	73.3	54.5	97.7	(14.8)
BBP	79.1	(17.1)	97.3	(2.6)	[c]	[c]	66.0	(39.3)
BBEP	57.9	(37.2)	91.3	(7.4)	79.4	50.0	96.3	(7.9)
DEHP	78.6	(13.5)	94.8	(6.3)	90.0	72.7	98.7	(6.0)
DCP	47.7	(23.7)	106	(19.9)	75.9	41.4	108	(13.3)
DOP	44.5	(39.6)	84.9	(3.8)	78.1	38.8	90.1	(6.1)
DNP	38.0	(52.4)	96.9	(11.1)	71.2	27.4	95.2	(12.7)

[a] The number of determinations was 3. 500 mL of HPLC-grade water or groundwater were spiked with the target compounds at the levels indicated and were passed through a preconditioned 3M-Empore C_{18}-membrane disk in approximately 20 min. The target compounds were eluted with 10 mL acetonitrile. The GC/ECD operating conditions are given in Table 6 under the DB-5/DB-1701 column pair. Value given is the average recovery; number in parentheses is the relative standard deviation.

[b] One of the replicates was discarded because all of the recoveries were biased low.

[c] Not able to calculate recovery because compound was present in the sample at 28 μg/L.

TABLE 50. C_{18}-MEMBRANE DISKS METHOD EVALUATION—SURROGATE RECOVERIES[a]

Sample identification	Sample description	Percent recovery: Diphenyl phthalate	Diphenyl isophthalate	Dibenzyl phthalate
8113003-1	HPLC-grade water spiked	98.4	99.1	83.8
8113003-2	with phthalate esters	97.6	99.2	85.5
8113003-3	at 5 μg/L	96.8	95.4	84.2
8113003-4	Groundwater sample spiked	103	106	91.9
8113003-5	with phthalate esters	102	103	89.1
8113003-6	at 5 μg/L	115	120	109
8113003-7	HPLC-grade water spiked	63.2	61.1	56.2
8113003-8	with phthalate esters	96.8	99.1	89.1
8113003-9	at 25 μg/L	106	107	99.6
8113003-10	Groundwater sample spiked	99.2	99.5	87.1
8113003-11	with phthalate esters	81.6	82.1	73.0
8113003-12	at 25 μg/L	47.2	49.9	39.1
8113003-13	HPLC-grade water spiked	79.3	82.9	82.8
8113003-14	with phthalate esters	78.9	86.7	83.9
8113003-15	at 100 μg/L	93.8	102	99.3
8113003-16	Groundwater sample spiked	81.7	78.2	80.3
8113003-17	with phthalate esters	81.9	89.8	88.0
8113003-18	at 100 μg/L	83.3	89.7	90.9
8113003-19	HPLC-grade water method blank	101	104	106
8113003-20	Groundwater sample method blank	70.3	70.7	63.2
Average		88.9	91.3	84.1
Standard deviation		16.3	16.8	16.4
Percent RSD		18.3	18.4	19.5

[a]The spike levels of the surrogates were 25 μg/L for Samples -1 through -12, -19, and -20, and 50 μg/L for Samples -13 through -18.

TABLE 51. RESULTS OF METHODS 3550 AND 8060 PERFORMANCE

	Batch 1[a]		Batch 2[b]	
Compound	Average recovery	RSD (percent)	Average recovery	RSD (percent)
DMP	112	17.6	79.4	25.0
DEP	96.0	8.2	73.1	16.9
DIBP	83.4	12.4	65.1	8.1
DBP	89.1	13.3	73.1	13.3
BMPP	31.9	24.6	32.1	16.0
BMEP	93.1	9.3	61.7	21.5
DAP	102	9.9	108	19.7
BEEP	74.9	11.1	68.0	9.4
HEHP	62.9	8.4	58.3	9.3
DHP	103	4.2	87.4	8.7
BBP	94.9	9.1	85.7	8.5
BBEP	103	21.3	74.9	9.7
DEHP	72.0	12.3	98.3	11.9
DCP	69.1	10.6	63.4	10.1
DOP	84.0	7.7	61.7	15.9
DNP	72.0	9.4	65.7	11.4

[a]The number of determinations was 9. Compounds were spiked at 1 ppm.
[b]The number of determinations is 8. Compounds were spiked at 1 ppm.

TABLE 52. RESULTS OF METHODS 3540 AND 8060 PERFORMANCE

Compound	Average Recovery[a]	RSD (percent)
DMP	73.7	19.8
DEP	129	28.0
DIBP	70.3	23.3
DBP	73.7	27.7
BMPP	75.4	34.5
BMEP	74.9	31.8
DAP	87.4	26.2
BEEP	54.3	31.6
HEHP	53.5	25.8
DHP	135	37.2
BBP	95.4	25.5
BBEP	89.7	22.4
DEHP	107	46.9
DCP	66.3	24.0
DOP	58.3	22.1
DNP	62.3	22.4

[a] The number of determinations was 8. Compounds were spiked at 1 ppm.

studies are presented in Section 6.6. Surrogate recoveries for Method 3550 are summarized in Table 53.

6.4 EXTRACT CLEANUP

The current Method 8060 recommends cleanup of sample extracts by either alumina (Method 3610) or Florisil (Method 3620) chromatography. Both methods use large volumes of solvents that may increase the contamination of sample extracts because of impurities present in the eluting solvent. For example, Method 3610 recommends 140 mL of 20 percent diethyl ether in hexane, and Method 3620 recommends 100 mL of 20 percent diethyl ether in hexane. Neither method indicates whether or not the phthalate esters are recovered quantitatively.

We have evaluated both methods with standards in hexane containing 16 phthalate esters. The percent recoveries of the 16 compounds are presented in Table 54.

Alumina cleanup is preferred over the Florisil cleanup since it allows recovery of all target compounds by elution with 20 percent diethyl ether in hexane. Using Florisil cleanup, three of the 16 target compounds could not be recovered at all, and dimethyl and diethyl phthalates gave recoveries of only 40 and 57 percent, respectively.

To improve the recoveries of the five phthalate esters mentioned above, we have taken Florisil and alumina SPE cartridges of 0.5-g, 1.0-g, and 2-g size, charged them with our target compounds and interferents, and eluted them with 10 percent acetone in hexane (for Florisil) and 20 percent acetone in hexane (for alumina). We first attempted the elution of the phthalate esters from the alumina cartridge with 20 percent diethyl ether in hexane. Since none of the phthalate esters was recovered after 10 mL solvent passed through the cartridge, we changed the eluting solvent to 10 percent acetone in hexane and later to 20 percent acetone in hexane to improve the recovery of bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate and bis(2-n-butoxyethyl) phthalate. The results of these experiments are summarized in Tables 55, 56, and 57.

The data shown in Table 55 indicate that all but two phthalate esters can be recovered from a 0.5-g or a 1.0-g Florisil cartridge with 5 mL 10-percent acetone in hexane (Fraction 1) and from a 2.0-g cartridge with 10 mL 10-percent acetone in hexane (no phthalate esters were recovered in Fraction 1, therefore an additional fraction had to be collected). The two phthalate esters that could not be recovered are bis(2-methoxyethyl) phthalate and bis(2-ethoxyethyl) phthalate. When working with the 0.5-g Florisil cartridge, these two phthalate esters were recovered almost quantitatively by eluting the cartridge with an additional 5 mL 10-percent acetone in hexane; however, they could not be recovered from either the 1.0-g or the 2.0-g Florisil cartridge under similar conditions. The alumina cartridge procedure (Table 57) allowed recovery of all 16 phthalate esters except for one compound, bis(2-methoxyethyl) phthalate, from the 2.0-g cartridge.

TABLE 53. RECOVERY OF SURROGATE COMPOUNDS SPIKED INTO SOIL SAMPLES (METHOD 3550)

Compound	Spike level (ng/g)	Percent recovery					Average	RSD (percent)
		Rep.1	Rep.2	Rep.3	Rep.4	Rep.5		
DPTP	330						95.4	12.8
DPP	330	90.2	79.1	90.5	110	86.9	91.3	12.5
DPIP	330	91.5	83.9	97.1	111	87.9	94.3	11.2
DBZP	330	113	85.0	93.9	105	81.4	95.7	13.9

TABLE 54. PERCENT RECOVERIES OF METHOD 8060 COMPOUNDS USING ALUMINA (METHOD 3610) AND FLORISIL (METHOD 3620) COLUMN CHROMATOGRAPHY

	Percent Recovery[a]															
Adsorbent	DMP	DEP	DIBP	DBP	BMPP	BMEP	DAP	BEEP	HEHP	DHP	BBP	BBEP	DEHP	DCP	DOP	DNP
Alumina	63	63	82	73	91	74	77	67	92	73	87	62	76	83	96	73
Alumina	66	62	72	80	88	67	73	67	89	67	87	63	106	86	120	69
Florisil	43	58	83	98	88	0	84	0	110	0	92	0	200	86	120	76
Florisil	37	56	77	72	81	0	79	0	100	0	88	0	64	81	110	69

[a]Alumina and Florisil chromatography were done according to Methods 3610 and 3620, respectively.

TABLE 55. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE METHOD 8060 COMPOUNDS FROM THE FLORISIL CARTRIDGES USING 10 PERCENT ACETONE IN HEXANE[a]

	0.5-g cartridge						1.0-g cartridge						2.0-g cartridge					
Compound	40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1		40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1		40-µg spike Fraction 1		80-µg spike Fraction 1		120-µg spike Fraction 1	
DMP	98.9	101	81.2	80.8	73.9	76.4	91.1	87.6	42.1	57.7	28.5	35.7	70.9	95.3	37.1	39.5	63.6	72.9
DEP	108	113	91.3	93.1	83.7	85.3	99.5	95.1	81.2	87.3	78.6	76.5	111	94.0	100	101	107	107
DIBP	109	106	92.8	91.7	87.8	91.8	94.9	88.6	88.7	92.1	90.6	88.1	114	103	92.2	92.8	86.9	86.0
DBP	104	107	87.4	88.5	80.1	83.1	100	105	89.1	87.4	87.9	85.8	108	108	91.4	92.4	82.5	80.9
BMPP	106	114	98.2	95.9	86.4	90.2	112	99.1	95.4	94.1	92.5	89.2	115	116	94.8	95.8	105	98.5
BMEP[b]	16.0	15.6	11.9	14.8	10.7	15.9	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]	[c]
DAP	107	111	94.8	91.5	82.7	87.9	96.8	92.1	89.4	92.5	88.1	85.6	113	106	91.8	92.3	83.4	82.6
BEEP	96.6	97.6	74.7	69.3	65.8	71.6	96.0	91.1	[d]	[d]	[d]	[d]	[d]	[d]	[d]	[d]	[d]	[d]
HEHP	99.6	98.4	75.6	75.9	65.3	68.9	101	90.8	70.6	70.2	66.1	63.9	83.9	93.8	68.9	84.3	77.8	77.5
DHP	105	109	91.0	87.6	78.6	86.0	99.4	94.1	88.6	87.9	85.1	82.5	106	103	86.4	90.9	80.6	78.3
BBP	108	109	84.1	82.3	67.5	71.3	99.8	97.3	80.4	82.8	70.1	69.5	109	104	83.2	93.9	101	97.2
BBEP	113	117	98.5	94.3	83.2	91.4	105	89.9	95.3	102	97.4	93.5	118	112	98.3	95.9	94.1	87.0
DEHP	111	111	92.1	87.6	76.5	84.5	95.6	87.4	68.0	74.7	47.1	50.2	111	65.8	82.9	84.4	81.5	77.6
DCP	91.4	81.6	62.9	61.7	53.5	57.0	97.0	84.1	62.0	53.7	59.0	48.0	69.6	72.0	59.9	57.3	72.2	59.9
DOP	120	114	102	93.2	83.3	95.4	99.9	94.3	98.1	97.9	98.5	93.0	114	115	103	99.4	97.3	86.9
DNP	118	118	103	92.2	83.1	95.9	111	98.8	98.1	100	98.3	94.8	118	115	101	99.3	92.8	88.5

[a] Each cartridge was preconditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate. Fraction 1 was eluted with 5 mL of 10 percent acetone in hexane; Fraction 2 with 5 mL of 10 percent acetone in hexane. A third fraction was collected from the 2-g cartridge by elution with 5 mL of 10 percent acetone in hexane.

[b] Additional bis(2-methoxyethyl) phthalate was recovered from the 0.5-g Florisil cartridge by eluting the cartridge with an additional 5 mL of 10 percent acetone in hexane. The recoveries in Fraction 2 were 70.3 and 71.3 percent for the 40-µg spike, 55.4 and 54.3 percent for the 80-µg spike, 53.4 and 54.1 percent for the 120-µg spike.

[c] Compound not recovered even when the cartridge was eluted with an additional 5 mL of 10 percent acetone in hexane.

[d] Bis(2-ethoxyethyl) phthalate was recovered by eluting the cartridge with an additional 5 mL of 10 percent acetone in hexane. Total recoveries were 75.1 and 79.3 percent for the 80-µg spike (1.0-g cartridge), 57.3 and 56.5 percent for the 120-µg spike (1.0-g cartridge), 94.6 percent for the 400-µg spike (2-g cartridge), 55.4 and 62.0 percent for the 80-µg spike (2.0-g cartridge), 70.2 and 79.0 percent for the 120-µg spike (2.0-g cartridge).

TABLE 56. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE METHOD 8060 COMPOUNDS USING 10 PERCENT ACETONE IN HEXANE AND 20 PERCENT ACETONE IN HEXANE[a]

	10 Percent acetone in hexane				20 Percent acetone in hexane			
Compound	Fraction 1	(5 mL)	Fraction 2	(5 mL)	Fraction 1	(5 mL)	Fraction 2	(5 mL)
DMP	78.6	65.6	47.9	28.8	101	102	0	0
DEP	101	84.5	0	0	103	103	0	0
DIBP	94.0	75.8	0	0	105	104	0	0
DBP	101	88.1	0	0	109	107	0	0
BMPP	86.4	37.0	0	0	104	102	0	0
BMEP	0	0	31.5	40.3	66.6	61.6	38.8	34.8
DAP	63.6	57.3	0	0	106	100	0	0
BEEP	16.6	19.6	109	102	121	102	0	0
HEHP	68.5	56.9	0	0	103	99.3	0	0
DHP	99.9	89.3	0	0	112	105	0	0
BBP	93.8	89.6	10.3	5.4	106	100	0	0
BBEP	75.4	66.3	50.2	47.6	114	103	0	0
DEHP	99.1	88.3	0	0	102	83.1	0	0
DCP	73.3	67.0	0	0	99.0	90.5	0	0
DOP	97.9	120	0	0	118	107	0	0
DNP	89.5	113	0	0	93.5	101	0	0

[a] 1-g Alumina cartridges (Supelco, lot SP 0214) were used; each cartridge was preconditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate; amount spiked was 40 μg per component per cartridge (2 mL of 20 μg/mL in hexane).

TABLE 57. ELUTION PATTERNS AND PERCENT RECOVERIES OF THE METHOD 8060 COMPOUNDS FROM ALUMINA CARTRIDGES OF VARIOUS SIZES BY ELUTION WITH 20 PERCENT ACETONE IN HEXANE[a]

	0.5-g cartridge						1.0-g cartridge						2.0-g cartridge					
Compound	40-μg spike Fraction 1		80-μg spike Fraction 1		120-μg spike Fraction 1		40-μg spike Fraction 1		80-μg spike Fraction 1		120-μg spike Fraction 1		40-μg spike Fraction 1		80-μg spike Fraction 1		120-μg spike Fraction 1	
DMP	106	108	67.8	72.6	69.5	71.3	108	117	100	92.1	115	113	98.6	93.8	92.3	73.2	84.1	93.0
DEP	111	112	76.2	78.9	73.1	75.3	139	148	106	125	126	127	106	108	105	102	112	104
DIBP	92.5	94.3	79.8	80.6	116	115	77.5	85.4	93.8	108	96.9	94.0	84.6	86.5	119	110	99.8	100
DBP	101	103	83.8	86.7	91.3	89.6	101	109	109	121	103	101	95.4	94.6	108	103	98.2	92.8
BMPP	98	96.4	81.4	82.6	100	109	75.1	90.4	92.3	107	83.3	81.5	81.8	80.3	101	98.1	81.5	78.8
BMEP	98.8	104	76.0	79.4	87.7	88.8	87.1	93.8	92.2	101	90.3	88.5	[b]	[b]	[b]	[b]	[b]	[b]
DAP	103	104	83.6	83.2	99.3	98.7	92.4	101	103	116	95.0	93.0	82.4	84.4	98.6	94.9	87.7	83.3
BEEP	107	110	80.9	84.6	95.2	94.5	96.5	105	97.7	109	103	96.6	81.6[c]	67.9[c]	76.9[c]	55.8[c]	45.6[c]	70.3[c]
HEHP	102	104	68.3	72.0	78.1	69.8	81.1	104	90.3	110	87.4	86.2	74.9	78.8	94.1	87.9	78.5	74.2
DHP	101	100	81.5	87.4	101	85.4	116	126	94.9	106	118	116	95.5	97.8	87.8	81.6	101	93.7
BBP	113	116	59.2	61.9	62.0	60.5	103	110	99.1	106	104	103	89.3	91.0	96.8	92.8	94.5	88.4
BBEP	86.4	78.5	83.0	91.1	117	113	88.1	92.5	99.4	110	104	103	73.3	73.9	101	96.5	87.3	79.5
DEHP	112	112	77.3	87.8	96.6	91.3	99.4	107	100	113	93.5	92.0	85.6	87.0	99.1	93.1	90.2	85.6
DCP	100	102	63.9	62.3	73.5	72.6	99.3	105	92.4	106	90.5	89.9	57.4	59.1	82.1	71.1	60.7	57.5
DOP	84.3	74.3	79.6	90.5	103	101	93.3	108	101	113	103	102	85.6	86.5	101	97.1	93.1	85.9
DNP	77.1	66.2	80.7	89.5	96.4	94.7	106	114	103	114	113	110	88.9	91.5	100	96.1	102	92.9

[a]Each cartridge was preconditioned with 4 mL hexane prior to use. Each experiment was performed in duplicate. Fraction 1 was eluted with 5 mL of 20 percent acetone in hexane; Fraction 2 with 5 mL of 20 percent acetone in hexane. A third fraction was collected from the 2-g cartridge by elution with 5 mL of 20 percent acetone in hexane.

[b]BMEP was recovered from the 2.0-g alumina cartridge by eluting the cartridge with two additional 5-mL portions of 20 percent acetone in hexane (Fractions 2 and 3). The recoveries in Fraction 2 were 77.6 and 50.9 percent (40-μg spike), 57.8 and 46.2 percent (80-μg spike), 26.3 and 61.5 percent (120-μg spike). The recoveries in Fraction 3 were 38.1 percent (40-μg spike), 37.9 and 31.9 percent (120-μg spike).

[c]Additional BEEP was recovered from the 2.0-g alumina cartridge by eluting the cartridge with an additional 5 mL of 20 percent acetone in hexane. The recoveries in Fraction 2 were 13.3 and 30.9 percent (40-μg spike), 28.6 and 55.9 percent (80-μg spike), 62.7 and 28.9 percent (120-μg spike).

Matrix interferents such as corn oil, diesel hydrocarbons, elemental sulfur, and the organochlorine pesticides listed in SW-846 Method 8081 were added to hexane solutions containing the target analytes at known concentrations, and the hexane solutions were then subjected to the Florisil or alumina cartridge procedure to establish if there are any changes in the compound elution pattern and in the target analyte recovery when matrix interferents are present (Table 58). Such interferents were selected because they mimic typical background contamination in certain environmental sample matrices that could also be contaminated with the target compounds. For example, corn oil would be representative of fatty acid triglycerides, diesel hydrocarbons of petroleum hydrocarbons, and organochlorine pesticides of compounds of environmental significance that would be expected to behave in the same way as the target analytes investigated in this study. The data presented in Table 58 indicate that neither the corn oil nor the diesel hydrocarbons affected the elution patterns of the 16 phthalate esters. Corn oil was also removed from the Florisil cartridge with 10 percent acetone in hexane. Fortunately, its presence does not seem to affect the determination of the 16 phthalate esters. This statement is true only for corn oil concentrations below 0.2 mg/mL of solvent (or 1 mg per cartridge) because this is the maximum concentration we used. Diesel hydrocarbons do not seem to cause problems with the quantification of the phthalate esters because the detector is transparent to aliphatic hydrocarbons. Elemental sulfur, if present, is eluted from the Florisil cartridge with 10 percent acetone in hexane. Therefore, extracts that are known to contain elemental sulfur should be subject to sulfur cleanup (Method 3660) prior to Florisil cartridge cleanup.

The effect of interferents when the Florisil cartridges were eluted with hexane/diethyl ether (1:1) is presented in Table 59.

Corn oil was also removed from the Florisil cartridge by hexane/diethyl ether; however, it did not seem to affect the determination of the 16 phthalate esters if the corn oil levels did not exceed 1 mg/cartridge (Table 59).

Recoveries of the test compounds in the presence of diesel hydrocarbons were quantitative except for DAP which could not be quantified because of interference from the diesel fuel hydrocarbons (Table 59).

The organochlorine pesticides overlapped with the phthalate esters when the GC analysis was performed on the DB-5 fused-silica capillary column and had to be separated prior to the gas chromatographic analysis. The hexane/diethyl ether (1:1) combination did not give adequate recoveries for half of the target compounds (Table 59) but use of 20 percent methylene chloride in hexane followed by elution with hexane/acetone (9:1) was found to remove most of the organochlorine pesticides and gave quantitative recoveries for 14 of the 16 phthalate esters (Table 60).

Additional experiments were performed in order to develop a procedure that will allow the determination of the phthalate esters in the presence of the organochlorine pesticides. The experimental design is presented in Table 61. Tables 62 and 63 present the recovery data and elution patterns of the 16 target phthalate esters when the cartridges were eluted with methylene

TABLE 58. PERCENT RECOVERIES OF METHOD 8060 COMPOUNDS FROM FLORISIL AND ALUMINA CARTRIDGES WHEN INTERFERENTS ARE PRESENT[a]

Compound	Florisil cartridge				Alumina cartridge			
	Corn oil (1000 μg per cartridge)		Diesel hydrocarbons (2000 μg per cartridge)		Corn oil (1000 μg per cartridge)		Diesel hydrocarbons (2000 μg per cartridge)	
DMP	119	123	106	111	105	104	92.5	94.4
DEP	133	133	123	129	120	119	92.5	94.4
DIBP	101	104	111	107	88.8	87.7	82.8	85.8
DBP	111	111	110	114	92.4	91.1	88.7	90.4
BMP	104	104	93.2	95.7	61.2	63.1	69.8	71.0
BMEP[b]	b	b	b	b	81.4	81.8	74.1	75.8
DAP	96.6	96.8	98.8	98.8	82.7	83.1	74.9	76.9
BEEP[c]	53.3	64.6	43.7	32.3	70.9	71.8	66.0	67.9
HEHP	89.8	91.2	87.1	86.6	74.3	82.9	71.1	73.1
DHP	108	106	103	104	99.8	98.9	90.3	91.5
BBP	106	107	102	104	93.8	92.6	84.6	87.3
BBEP	104	104	98.8	100	87.8	87.8	88.3	81.6
DEHP	99.9	99.4	92.1	94.6	83.3	83.1	72.6	74.6
DCP	81.4	81.2	68.2	68.2	81.8	81.3	72.0	73.8
DOP	109	108	102	103	93.1	92.7	80.9	82.7
DNP	114	114	107	111	98.5	99.2	86.4	88.3

[a] 1-g cartridges were used for these experiments. Each cartridge was preconditioned with 4 mL hexane. Each experiment was performed in duplicate. The Florisil cartridge was eluted with 5 mL of 10 percent acetone in hexane. The alumina cartridge was eluted with 5 mL of 20 percent acetone in hexane.

[b] BMEP was recovered from the Florisil cartridge by eluting the cartridge with an additional 5 mL of 10 percent acetone in hexane. The recoveries were 81.9 and 95.6 percent when corn oil was present as interferent and 71.5 and 62.3 percent when diesel hydrocarbons were the interferents.

[c] Additional BEEP was recovered from the Florisil cartridge by eluting the cartridge with an additional 5 mL of 10 percent acetone in hexane. The recoveries in Fraction 2 were 41.6 and 31.7 percent when corn oil was present as interferent, and 56.8 and 63.4 percent when diesel hydrocarbons were the interferents.

TABLE 59. ELUTION PATTERNS AND PERCENT RECOVERIES OF METHOD 8060 COMPOUNDS FROM FLORISIL CARTRIDGES WITH HEXANE/DIETHYL ETHER (1:1)[a]

Compound	Fraction 1 (5 mL of hexane/diethyl ether 1:1)								Fraction 2 (5 mL of hexane/diethyl ether (1:1)							
	No interferents		With corn oil		With diesel hydrocarbons		With organochlorine pesticides		No interferents		With corn oil		With diesel hydrocarbons		With organochlorine pesticides	
DMP	94	94	78	82	116	108	93	91	<5	<5	<5	<5	<5	<5	<5	<5
DEP	96	95	84	93	74	70	103	98	<5	<5	10	<5	7.6	<5	6.2	6.4
DIBP	122	119	122	115	105	97	118	111	<5	<5	<5	<5	<5	<5	19	22
DBP	116	114	[b]	105	124	113	[b]	[b]	<5	<5	<5	<5	<5	<5	<5	<5
BMPP	108	109	103	87	109	96	[b]	[b]	<5	<5	<5	<5	<5	<5	60	72
BMEP	2.6	96	38	19	128	109	[b]	[b]	32	<5	<5	20	32	22	103	128
DAP	95	101	[b]	103	[b]	[b]	[b]	[b]	<5	<5	<5	<5	6.1	7.2	74	87
BEEP	8.9	99	7.8	44	55	48	14	58	51	<5	66	54	62	58	53	54
HEHP	112	104	127	116	88	81	86	83	<5	<5	11	8.2	8.2	6.0	<5	<5
DHP	98	98	128	106	107	103	[b]	[b]	<5	<5	6.0	<5	<5	<5	17	20
BBP	111	117	122	117	118	112	[b]	[b]	<5	<5	<5	<5	<5	<5	6.8	7.4
BBEP	65	97	78	90	103	112	b	b	27	<5	25	10	9.6	10	58	69
DEHP	95	103	89	83	85	78	91	86	<5	<5	<5	<5	<5	<5	<5	<5
DCP	98	101	118	86	114	104	100	96	<5	<5	<5	<5	<5	<5	<5	<5
DOP	106	109	114	80	114	107	108	102	<5	<5	<5	<5	<5	<5	<5	<5
DNP	90	91	80	72	104	95	94	90	<5	<5	<5	<5	<5	<5	<5	<5

[a]Florisil cartridges (1 g) were used. Fraction 1 was eluted with 5 mL hexane/diethyl ether (1:1) and Fraction 2 with an additional 5 mL hexane/diethyl ether (1:1). Final volume of each fraction was 5 mL. Method 8060 compounds were spiked at 2,500 ng per Florisil cartridge.

[b]Not able to determine because of interference from organochlorine pesticides.

TABLE 60. RESULTS OF THE FLORISIL CARTRIDGE CLEANUP EVALUATION STUDY (PHTHALATE ESTER STANDARDS ONLY; ELUTION WITH 20 PERCENT METHYLENE CHLORIDE IN HEXANE, AND HEXANE/ACETONE (9:1))

	Percent recovery					
	8712-013-10 Fraction		8712-013-11 Fraction		8712-013-12 Fraction	
Compound	I	II	I	II	I	II
DMP	0	68.0	0	121	0	201
DEP	0	87.7	0	90.7	0	86.3
DIBP	0	107	0	140	0	108
DBP	0	103	23.5	129	0	131
BMPP	0	116	0	123	0	130
BMEP	0	36.0	0	39.1	0	20.7
DAP	0	75.0	0	130	6.6	76.0
BEEP	0	78.3	0	99.0	0	69.0
HEHP	0	118	0	134	0	127
DHP	0	72.0	0	61.0	0	53.0
BBP	0	91.0	0	102	0	102
BBEP	0	113	0	188	0	103
DEHP	0	107[a]	0	113[a]	0	110[a]
DCP	0	106	0	109	0	102
DOP	0	125	0	131	0	114
DNP	0	100	0	112	0	94.7

[a]The value not corrected for method blank; if corrected, recovery becomes 0.

TABLE 61. EXPERIMENTAL DESIGN FOR FLORISIL CARTRIDGE CLEANUP METHOD DEVELOPMENT[a]

Sample identification	Amount spiked (ng)		Fraction I (5 mL)	Fraction II (5 mL)
	Phthalate esters	OCPs		
8712-013-1	500	500	Hexane	Hexane/diethyl ether (1:1)
8712-013-2	500	500	Hexane	Hexane/diethyl ether (1:1)
8712-013-3	500	500	Hexane	Hexane/diethyl ether (1:1)
8712-013-4	500	500	Hexane	Hexane/acetone (9:1)
8712-013-5	500	500	Hexane	Hexane/acetone (9:1)
8712-013-6	500	500	Hexane	Hexane/acetone (9:1)
8712-013-7	500	500	20% methylene chloride in hexane	20% methylene chloride in hexane
8712-013-8	500	500	20% methylene chloride in hexane	20% methylene chloride in hexane
8712-013-9	500	500	20% methylene chloride in hexane	20% methylene chloride in hexane
8712-013-10	500	0	20% methylene chloride in hexane	Hexane/acetone (9:1)
8712-013-11	500	0	20% methylene chloride in hexane	Hexane/acetone (9:1)
8712-013-12	500	0	20% methylene chloride in hexane	Hexane/acetone (9:1)
8712-013-13	0	500	20% methylene chloride in hexane	Hexane/acetone (9:1)
8712-013-14	0	500	20% methylene chloride in hexane	Hexane/acetone (9:1)
8712-013-15	0	500	20% methylene chloride in hexane	Hexane/acetone (9:1)
8712-013-16	500	500	20% methylene chloride in hexane	Hexane/acetone (9:1)
8712-013-17	500	500	20% methylene chloride in hexane	Hexane/acetone (9:1)
8712-013-18	500	500	20% methylene chloride in hexane	Hexane/acetone (9:1)
8712-013-22	0	0	20% methylene chloride in hexane	Hexane/acetone (9:1)

(continued)

TABLE 61 (continued)

Sample identification	Amount spiked (ng) Phthalate esters	OCPs	Fraction I (5 mL)	Fraction II (5 mL)
8712-013-23	0	0	20% methylene chloride in hexane	Hexane/acetone (9:1)
8712-013-24	500	0	15% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-25	500	0	15% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-26	500	0	15% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-27	500	0	25% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-28	500	0	25% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-29	500	0	25% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-30	500	0	30% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-31	500	0	30% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-32	500	0	30% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-33	0	500	15% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-34	0	500	25% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-35	0	500	30% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-36	500	500	15% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-37	500	500	15% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-38	500	500	15% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-39	500	500	25% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-40	500	500	25% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-41	500	500	25% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-42	500	500	30% methylene chloride in hexane	10% ethyl acetate in hexane

(continued)

TABLE 61 (concluded)

Sample identification	Amount spiked (ng) Phthalate esters	OCPs	Fraction I (5 mL)	Fraction II (5 mL)
8712-013-43	500	500	30% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-44	500	500	30% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-45	0	0	15% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-46	0	0	25% methylene chloride in hexane	10% ethyl acetate in hexane
8712-013-47	0	0	30% methylene chloride in hexane	10% ethyl acetate in hexane

[a] 1-g Florisil cartridges were used. The 16 phthalate esters were spiked at 500 ng per component. The organochlorine pesticides (OCPs) were also spiked at 500 ng per component.

TABLE 62. RECOVERY OF PHTHALATE ESTERS FROM THE 1-G FLORISIL CARTRIDGE BY ELUTION WITH 15 PERCENT, 25 PERCENT, AND 30 PERCENT METHYLENE CHLORIDE IN HEXANE (FRACTION I) AND 10 PERCENT ETHYL ACETATE IN HEXANE (FRACTION II)[a]

	Percent recovery																	
	8712-013-24 Fraction		8712-013-25 Fraction		8712-013-26 Fraction		8712-013-27 Fraction		8712-013-28 Fraction		8712-013-29 Fraction		8712-013-30 Fraction		8712-013-31 Fraction		8712-013-32 Fraction	
Compound	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II
DMP	7.5	7.0	5.7	6.6	4.1	0	0	13.0	12.3	0	12.6	2.2	4.4	4.3	13.6	13.2	12.8	12.4
DEP	0	34.5	0	37.9	0	40.1	0	65.8	0	27.3	12.9	38.6	0	26.6	0	27.2	0	24.8
DIBP	0	98.0	0	60.4	0	64.2	0	64.6	0	60.7	0	89.8	0	58.6	0	53.6	0	56.1
DBP	13.1	65.0	13.5	80.0	0	85.0	0	112	0	83.7	0	69.8	0	49.8	0	52.4	0	51.9
BMPP	0	101	0	102	0	105	0	102	0	90.7	0	96.6	0	79.4	0	78.7	0	79.4
BMEP	0	0	0	21.0	0	32.8	0	23.4	0	24.2	0	24.2	0	0	0	18.9	0	18.2
DAP	0	156	0	161	0	166	0	143	0	179	0	184	0	159	0	108		103
BEEP	0	6.0	0	6.2	0	5.0	0	6.8	0	0	0	17.6	0	0	0	0	0	0
HEHP	13.7	91.0	0	90.0	0	101	0	110	0	120	14.7	89.3	0	115	0	120	0	101
DHP	49.0	40.1	40.2	42.5	43.3	44.3	46.2	50.9	46.2	44.9	80.5	51.3	0	50.7	0	47.2	0	49.2
BBP	4.0	73.0	0	81.0	0	89.0	27.3	95.4	24.7	84.4	29.2	93.4	3.7	101	6.5	106	1.5	103
BBEP	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DEHP	0	54.0	0	46.0	0	56.0	0	31.3	0	36.2	0	36.0	0	50.0	0	43.9	0	44.9
DCP	0	125	0	97.5	0	110	0	110	0	100	0	108	0	142	0	142	0	148
DOP	0	94.2	0	95.3	0	107	0	108	0	99.8	0	108	0	104	0	100	0	106
DNP	0	80.3	0	75.4	0	82.9	0	93.4	0	81.1	0	78.8	0	105	0	115	0	94.3

[a]The spiking level was 500 ng of each phthalate ester per cartridge.

TABLE 63. RECOVERY OF PHTHALATE ESTERS FROM THE 1-G FLORISIL CARTRIDGE IN THE PRESENCE OF THE OCPs BY ELUTION WITH 15 PERCENT, 20 PERCENT, AND 30 PERCENT METHYLENE CHLORIDE IN HEXANE (FRACTION I) AND 10 PERCENT ETHYL ACETATE IN HEXANE (FRACTION II)[a]

	Percent Recovery								
Compound	8712-013-36 Fraction II	8712-013-37 Fraction II	8712-013-38 Fraction II	8712-013-39 Fraction II	8712-013-40 Fraction II	8712-013-41 Fraction II	8712-013-42 Fraction II	8712-013-43 Fraction II	8712-013-44 Fraction II
DMP	160[b]	172[b]	174[b]	118	112	101	120	113	114
DEP	49.5	57.5	60.0	63.2	56.3	56.7	40.2	51.1	34.9
DIBP	150[b]	105	108	98.2	108	99.0	92.5	95.8	97.6
DBP	123	121	115	118	121	108	109	106	102
BMPP	1560[b]	74.9	72.7	78.8	116	110	109	102	102
BMEP	138[b]	645[b]	224[b]	456[b]	162[b]	185[b]	124	210[b]	367[b]
DAP	5,550[b]	5,620[b]	5,530[b]	1,420[b]	1,410[b]	850[b]	1,640[b]	454[b]	881[b]
BEEP	ND	ND	ND	28.3	26.3	29.2	29.0	24.2	25.7
HEHP	112	102	103	108	113	110	110	88.6	99.7
DHP	137[b]	123	129[b]	146[b]	120	113	126[b]	92.7	110
BBP	123	124	117	127[b]	125	129[b]	117	106	121
BBEP	560[b]	520[b]	530[b]	338[b]	362[b]	274[b]	335[b]	171[b]	227[b]
DEHP	135[b]	119	112	151[b]	128[b]	119	220[b]	181[b]	249[b]
DCP	112	104	97.8	110	110	112	103	94.3	107
DOP	117	118	109	126[b]	123	126[b]	112	90.7	111
DNP	43.0	40.6	38.4	42.0	43.6	43.8	45.2	38.3	44.3

[a] The spiking level was 500 ng of phthalate ester per cartridge. The OCPs were also spiked at 500 ng per component per cartridge.

[b] High recovery due to interferents eluted from the cartridge by 10 percent ethyl acetate in hexane and/or contaminants in ethyl acetate.

chloride/hexane and then ethyl acetate/hexane. Interferences in the determination of phthalate esters caused by organochlorine pesticides (OCPs) and method blank analyses are presented in Tables 64 and 65.

The Florisil procedure was further evaluated using extracts of environmental samples spiked with 16 phthalate esters at known concentration. The results presented in Table 66 indicate that recoveries were greater than 74 percent except for bis(2-ethoxyethyl) phthalate (recovery ranges from 24 to 62 percent) and bis(methoxyethyl) phthalate which could not be recovered in Fraction 2.

6.5 PRESERVATION STUDY

This section summarizes the results of the preservation studies for reagent water samples and soil samples spiked with the test compounds at 5 µg/L and 1 µg/g, respectively. Tables 67, 68, and 69 summarize results for the water samples. Table 70 summarizes results for the soil samples. The same results given in Tables 67 through 69 are presented in Figures 21, 22, and 23.

Spiked water samples preserved at neutral and acidic pH and 4°C give comparable recoveries which are above 60 percent for most compounds, even after 21 days of storage. Preservation of water samples at pH 9 and 4°C should be avoided since most compounds show a significant decrease in concentration after 14 days of storage.

The recovery data presented in Table 70 and Figures 24 and 25 indicate that the average recoveries of the phthalate esters except BMPP from soil are >60 percent. Storage of spiked soil samples at -10°C is preferred over refrigeration at 4°C, since it allows higher recoveries of the lower-molecular-weight esters, which are more easily degradable, to be recovered.

6.6 REVISED METHOD 8060

The revised Method 8060 was evaluated in terms of reproducibility of the injection technique, the linearity of response over several orders of magnitude in concentration, how precise the identification and the measurement of the gas chromatographic technique is, and in terms of what the minimum detectable levels for the phthalate esters are. Subsequent sections address the reproducibility of the injection technique, the instrument calibration, the method accuracy, and the method detection limit.

6.6.1 Reproducibility of the GC Technique

To establish the reproducibility of the GC technique, 11 consecutive injections of hexane blanks spiked with 10 µL of a benzyl benzoate solution at 50 µg/µL (nominal concentration of benzyl benzoate that was analyzed is 500 ng/µL) were performed by an autosampler.

The results are presented in Table 71 as the average retention time of the 11 replicates and the RSD, and the average detector response and the RSD. The reproducibility of the retention time was 0.072 percent and the reproducibility of the detector response was 2.3 percent. When actual samples

TABLE 64. INTERFERENCES IN THE DETERMINATION OF PHTHALATE ESTERS CAUSED BY OCPs

	Concentration (ng/mL)[a]											
	8712-013-13 Fraction		8712-013-14 Fraction		8712-014-15 Fraction		8712-013-33 Fraction		8712-013-34 Fraction		8712-013-35 Fraction	
Compound	I	II	I	II	I	II	I	II	I[b]	II	I[b]	II
DMP	ND[c]	260	ND	227	45.2	205	ND	208		137		143
DEP	ND	ND	ND	ND	ND	37.7	ND	ND		ND		ND
DIBP	23.2	24.5	57.3	70.4	50.9	66.6	45.6	20.4		30.3		36.3
DBP	64.1	34.0	26.2	30.0	27.8	26.7	28.6	20.8		ND		ND
BMPP	1,810	660	2,250	386	2,020	19.8	1,260	18.0		130		ND
BMEP	6,160	23.8	6,420	325	6,274	544	7,510	585		313		293
DAP	370	4,220	2,070	2,870	857	3,960	557	6,200		1,110		491
BEEP	ND	ND	ND	32.7	38.2	32.1	60.4	22.1		21.7		22.1
HEHP	3,070	30.9	3,270	69.9	3,120	251	3,540	21.7		19.9		150
DHP	42.2	122	52.6	103	63.8	89.4	65.1	107		87.2		63.0
BBP	33.2	36.3	37.2	31.7	34.5	30.5	35.8	36.5		33.2		28.5
BBEP	ND	586	31.6	583	ND	606	ND	629		346		99.1
DEHP	48.4	70.4	53.0	129	69.3	112	65.9	219		124		76.6
DCP	ND	ND	ND	ND	ND	ND	ND	ND		ND		ND
DOP	ND	ND	ND	ND	ND	ND	ND	ND		ND		ND
DNP	ND	ND	ND	ND	ND	ND	ND	ND		ND		ND

[a] The Florisil cartridges were charged only with OCPs. The various peaks detected in these fractions as phthalate esters are not contaminants in the OCP standards but rather OCP peaks eluting at the same retention times as the target analytes. If the OCPs would not interfere with the quantification of the phthalate esters, the sum of the concentrations in Fractions I and II should be 100.
[b] Analysis did not pass QC criteria, results are therefore not reported.
[c] Not detected; detection limit was approximately 10 ng/mL.

TABLE 65. RESULTS OF METHOD BLANK ANALYSES FOR THE FLORISIL CARTRIDGE

	Concentration (ng/mL)[a]									
	8712-013-22 Fraction		8712-013-23 Fraction		8712-013-45 Fraction		8712-013-46 Fraction		8712-013-47 Fraction	
Compound	I	II	I	II	I	II	I	II	I	II
DMP	40.7	151	51.9	200	12.4	55.4	17.0	33.2	24.2	32.4
DEP	ND[b]	ND	ND	ND	ND	ND	ND	ND	ND	ND
DIBP	ND	ND	22.8	22.1	ND	ND	ND	ND	ND	ND
DBP	ND	26.8	ND	30.1	ND	36.8	36.6	13.9	ND	33.1
BMPP	ND	ND	ND	ND	ND	ND	ND	ND	ND	16.4
BMEP	ND	ND	ND	ND	ND	18.5	ND	ND	ND	17.9
DAP	63.9	137	ND	139	ND	ND	46.8	ND	61.8	ND
BEEP	ND	16.3	18.8	18.2	ND	14.9	ND	14.8	ND	20.7
HEHP	33.9	18.6	18.3	ND	ND	16.7	ND	ND	ND	ND
DHP	50.6	49.8	ND	54.4	ND	40.0	ND	38.2	49.0	35.1
BBP	24.9	30.2	35.9	37.5	35.7	35.9	ND	35.6	27.1	24.7
BBEP	ND	ND	ND	ND	ND	ND	59.1	ND	ND	56.7
DEHP	68.8	121	100	114	60.2	56.1	81.1	61.1	58.2	58.1
DCP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DOP	52.2	ND	64.1	ND	ND	ND	ND	ND	ND	ND
DNP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a]The Florisil cartridge (1 g) was eluted with 5 mL of 20 percent methylene chloride in hexane and 5 mL of hexane/acetone (9:1) in the case of samples 8712-013-22, -23, and 5 mL of 15 percent, 25 percent, and 30 percent methylene chloride in hexane for samples -45, -46, and -47. Fraction II for samples -45, -46, -47 was eluted with 5 mL of 10 percent ethyl acetate in hexane. Final volume of each fraction was 5 mL.
[b]Not detected; detection limit was approximately 10 ng/mL.

TABLE 66. 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]

Compound	Sandy loam soil[b]	Sediment of unknown origin	NBS SRM-1572	NBS SRM-1632a	NBS SRM-1633a
DMP	78	75	80	76	82
DEP	79	79	89	79	84
DIBP	79	82	90	108	86
DBP	74	78	84	83	83
BMPP	77	84	102	91	86
BMEP	0	0	0	0	0
DAP	82	86	100	76	89
BEEP	37	24	62	32	33
HEHP	80	88	95	93	81
DHP	78	88	86	92	80
BBP	82	99	114	102	98
BBEP	86	94	98	106	98
DEHP	74	85	108	88	112
DCP	91	96	106	98	95
DOP	80	92	104	95	88
DNP	84	96	106	111	92

[a] The spiking level was 50 ng/mL of extract for each compound. Data shown are for Fraction 2 which was eluted with 5 mL hexane/acetone (9:1).
[b] Sandy loam soil from Puyallup, Washington, with the following physicochemical characteristics: pH 5.9 to 6.0; 89 percent sand, 7 percent silt, 4 percent clay; cation exchange capacity 7 meg/100 g; total organic carbon content 1,290 ± 185 mg/Kg.

TABLE 67. CONCENTRATION OF THE 16 PHTHALATE ESTERS AS A FUNCTION OF TIME AT pH 6.8 TO 6.9

Compound	Concentration (pg/μL of extract)[a]													
	t=0		t=1 day		t=3 days		t=7 days		t=10 days		t=14 days		t=21 days	
DMP	3,180	2,790	2,180	1,930	3,100	3,690	2,900	2,970	2,750	2,580	2,760	2,710	3,870	3,440
DEP	3,970	3,100	3,010	2,910	2,620	3,700	3,560	3,430	3,350	3,080	3,330	3,280	3,840	3,550
DIBP	4,620	3,970	3,920	3,840	3,170	4,100	4,420	4,390	4,110	3,660	3,880	3,340	3,790	3,700
DBP	4,840	4,190	4,100	3,790	3,030	4,010	4,400	4,440	3,960	3,450	4,190	3,190	3,230	3,300
BMPP	b	b	b	b	b	b	b	b	b	b	b	b	b	b
BMEP	4,460	4,530	4,540	4,140	5,220	5,910	4,970	5,770	4,610	4,200	4,240	4,600	4,480	5,370
DAP	4,100	3,490	3,520	2,990	2,340	3,310	3,230	3,960	2,770	2,350	3,180	2,570	3,080	2,870
BEEP	4,420	3,970	3,460	3,350	2,300	3,410	4,020	3,580	3,610	3,090	2,990	2,200	2,470	1,370
HEHP	5,210	4,220	3,830	3,810	2,990	4,240	3,970	3,950	3,640	3,060	3,080	2,460	2,800	2,670
DHP	4,680	3,780	3,110	2,980	2,560	3,240	4,280	3,890	3,600	3,200	3,000	2,720	3,060	2,730
BBP	6,470	5,610	5,450	5,590	4,440	5,920	4,590	4,880	4,720	4,220	4,190	3,220	3,590	3,350
BBEP	4,860	4,540	3,970	3,750	3,510	4,580	4,240	4,200	3,990	3,330	4,060	4,060	3,700	3,570
DEHP	4,590	4,040	3,910	3,750	3,240	3,780	3,800	3,760	3,450	2,980	2,630	2,240	2,990	2,860
DCP	4,660	4,010	3,930	3,830	2,730	3,880	3,810	3,810	3,470	3,000	2,890	2,120	2,970	2,830
DOP	5,240	4,170	4,150	4,150	2,870	4,140	4,290	4,130	3,630	3,130	2,520	2,050	2,920	3,510
DNP	4,100	3,350	3,180	3,180	1,800	3,140	3,430	3,360	2,890	2,580	1,820	1,450	2,390	2,180
DPTP[c]	135	106	112	118	115	138	78.5	87.5	76.2	72.7	74.8	72.6	77.6	76.9

[a] The spike level was equivalent to 5,000 pg/μL of extract or 5 μg/L of water (1 L reagent water was spiked with 5 μg of each phthalate ester; extraction by Method 3510; $V_{extract}$ was 1 mL). Duplicate determinations were performed at each time event.
[b] Not able to quantitate because of interference.
[c] The value given is the percent recovery for the extraction step.

TABLE 68. CONCENTRATION OF THE 16 PHTHALATE ESTERS AS A FUNCTION OF TIME AT pH 9

Compound	Concentration (pg/μL of extract)[a]					
	t=0		t=7 days		t=14 days	
DMP	2,320	1,910	3,180	750	380[c]	380[c]
DEP	2,870	2,730	3,850	1,070	450[c]	450[c]
DIBP	3,790	3,130	4,390	3,760	1,810	1,870
DBP	4,090	3,100	4,240	2,980	1,500	1,290
BMPP	[b]	[b]	[b]	[b]	[b]	[b]
BMEP	4,950	4,480	5,440	1,430	756	819
DAP	3,650	2,860	4,080	3,070	1,270	1,180
BEEP	3,870	3,030	3,770	3,220	1,930	2,430
HEHP	4,400	3,250	3,860	2,690	1,560	1,420
DHP	3,560	2,990	4,020	3,360	2,000	1,960
BBP	7,080	5,860	5,140	1,510	226	265
BBEP	4,980	4,170	4,250	1,390	[d]	[d]
DEHP	4,120	3,440	3,670	3,660	2,670	2,600
DCP	4,250	3,390	3,660	3,040	1,890	1,720
DOP	4,370	3,500	3,650	3,030	2,290	2,200
DNP	3,230	2,660	2,990	2,480	1,290	1,410
DPTP[e]	155	124	90.1	94.8	70.9	73.1

[a]The spike level was equivalent to 5,000 pg/μL of extract or 5 μg/L of water (1 L reagent water was spiked with 5 μg of each phthalate ester, adjusted to pH 9 with 6N NaOH; extraction by Method 3510; $V_{extract}$ was 1 mL). Duplicate determinations were performed at each time event.
[b]Not able to quantitate because of interference.
[c]Manual quantitation of the peak.
[d]Not detected.
[e]The value given for the DPTP surrogate is the percent recovery for the extraction step.

TABLE 69. CONCENTRATION OF THE 16 PHTHALATE ESTERS AS A FUNCTION OF TIME AT pH 2

Compound	Concentration (pg/μL of extract)[a]					
	t=0		t=7 days		t=14 days	
DMP	2,690	2,920	3,150	3,050	2,780	2,900
DEP	5,710	5,920	3,350	3,500	3,100	3,270
DIBP	3,600	3,740	3,890	3,720	3,550	3,390
DBP	3,450	3,700	4,070	3,850	4,060	3,680
BMPP	[b]	[b]	[b]	[b]	[b]	[b]
BMEP	4,610	5,180	5,000	5,150	4,320	3,830
DAP	3,110	3,510	4,490	3,380	3,520	3,360
BEEP	3,240	3,370	3,490	3,130	2,730	2,770
HEHP	3,900	4,150	3,660	3,470	3,080	2,700
DHP	3,130	3,540	3,950	3,550	2,900	2,720
BBP	5,510	6,220	4,400	4,480	4,240	4,060
BBEP	3,990	5,040	4,520	3,680	3,640	3,400
DEHP	3,330	4,160	3,680	2,990	2,760	2,600
DCP	3,350	3,870	3,380	3,080	2,790	2,540
DOP	3,220	3,660	3,600	3,130	2,540	2,620
DNP	2,630	2,960	2,940	2,660	1,840	1,900
DPTP[c]	105	128	84.5	83.3	74.3	72.1

[a] The spike level was equivalent to 5,000 pg/μL of extract or 5 μg/L of water (1 L reagent water was spiked with 5 μg of each phthalate ester, adjusted to pH 2 with 6N H_2SO_4 (3 mL); extraction by Method 3510; $V_{extract}$ was 1 mL). Duplicate determinations were performed at each time event.
[b] Not able to quantitate because of interference.
[c] The value given for the DPTP surrogate is the percent recovery for the extraction step.

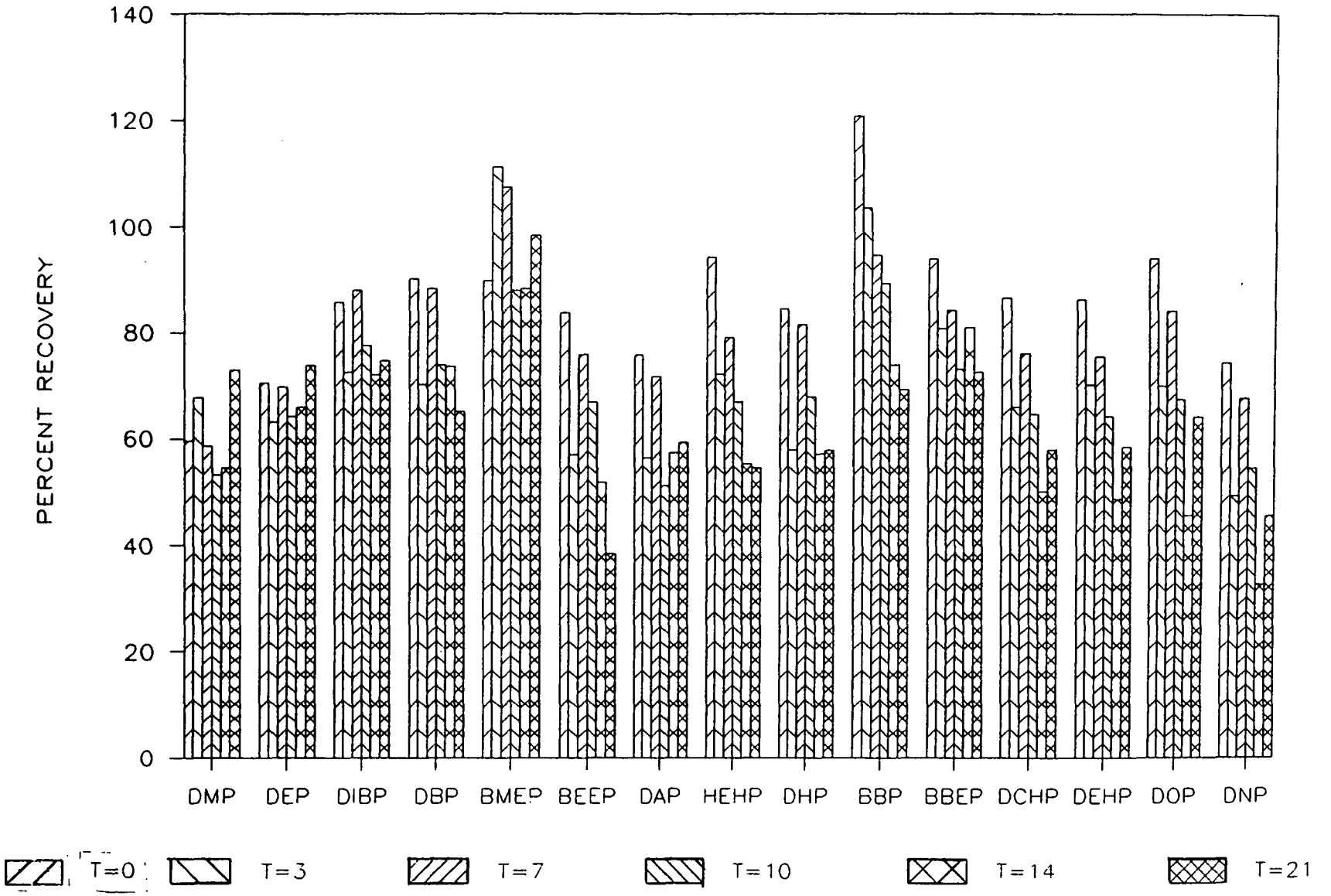


Figure 21. Average recovery of Method 8060 compounds from HPLC-grade water as a function of time at pH 7.

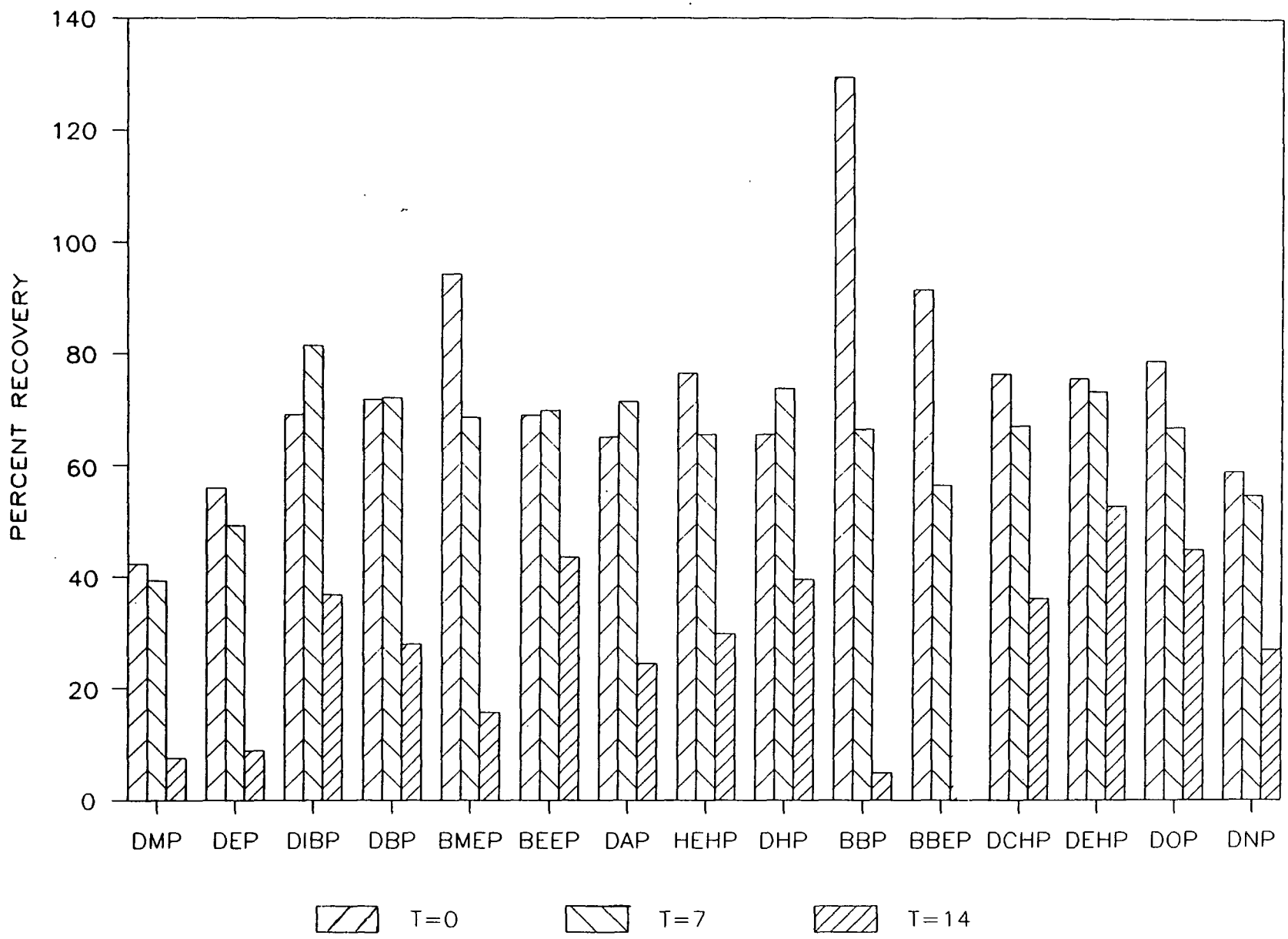


Figure 22. Average recovery of Method 8060 compounds from HPLC-grade water as a function of time at pH 9.

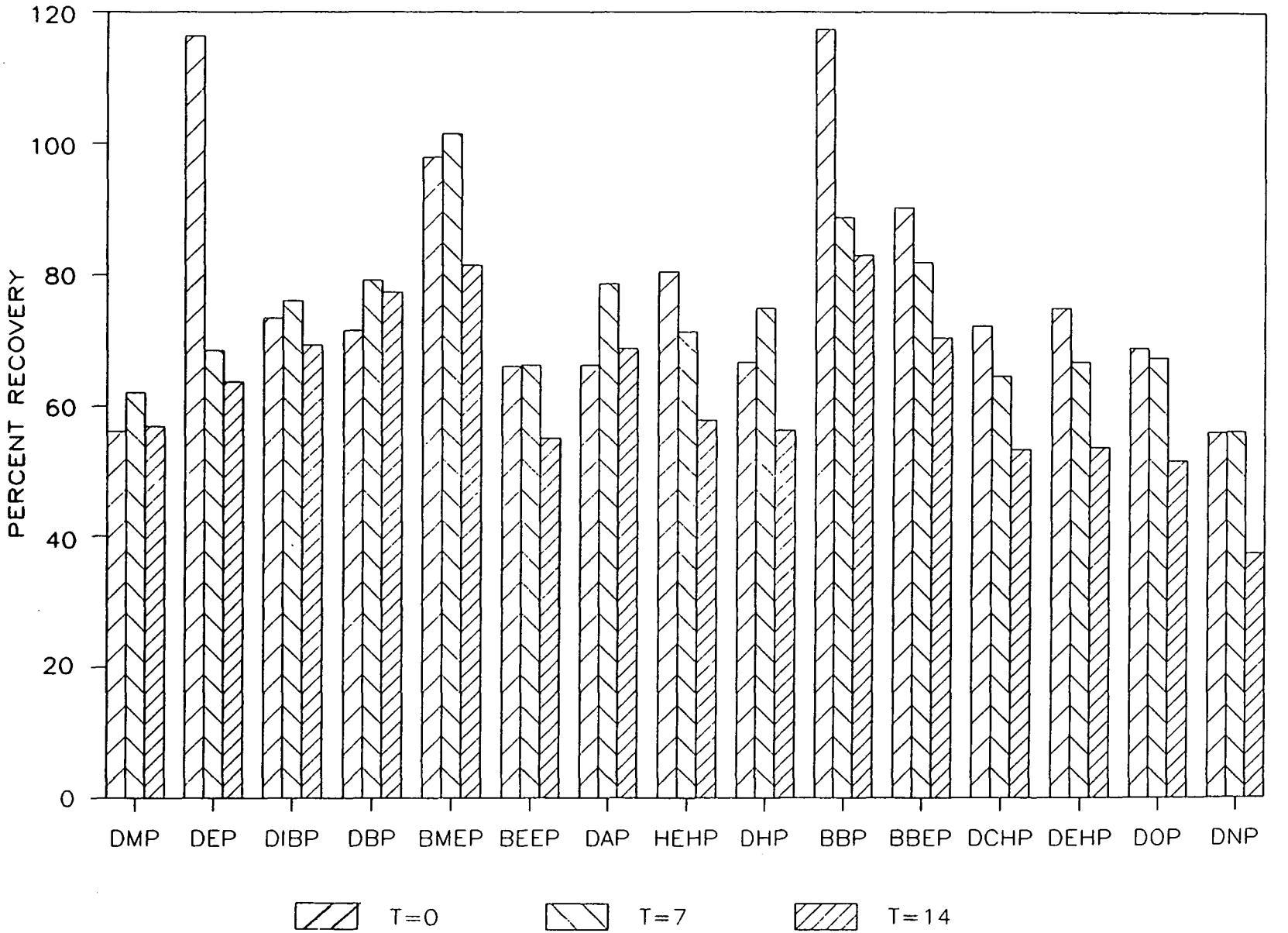


Figure 23. Average recovery of Method 8060 compounds from HPLC-grade water as a function of time at pH 2.

TABLE 70. RECOVERY OF THE 16 PHTHALATE ESTERS AS A FUNCTION OF TIME AT -10°C (SOIL MATRIX)

	Percent Recovery[a]				
Compound	t=0	t=3 days	t=7 days	t=14 days	t=28 days
DMP	77.3	60.8	51.4	47.4	59.0
DEP	61.3	69.2	52.1	58.2	60.7
DIBP	75.8	110	60.4	108	102
DBP	111	91.1	70.2	87.4	99.1
BMPP	83.8	145	74.9	20.5	29.9
BMEP	68.4	25.9	59.2	57.4	52.4
DAP	76.2	73.6	56.1	63.7	71.3
BEEP	41.4	11.9	26.8	0	0
HEHP	68.2	82.4	49.2	23.8	19.6
DHP	191	90.4	79.8	110	105
BBP	96.7	73.3	80.9	75.4	95.4
BBEP	77.7	47.9	65.4	62.9	75.8
DEHP	94.4	159	106	91.4	89.2
DCP	73.2	66.7	73.4	48.0	48.0
DOP	86.9	85.1	87.1	95.4	109
DNP	112	94.9	128	124	164

[a]The spike level was 1,000 ng/g; samples were extacted by Method 3550; volume of extract was 3 mL; 2 mL were subjected to Florisil chromatography. GC analyses were performed on the DB-5/DB-1701 column pair (Table 6).

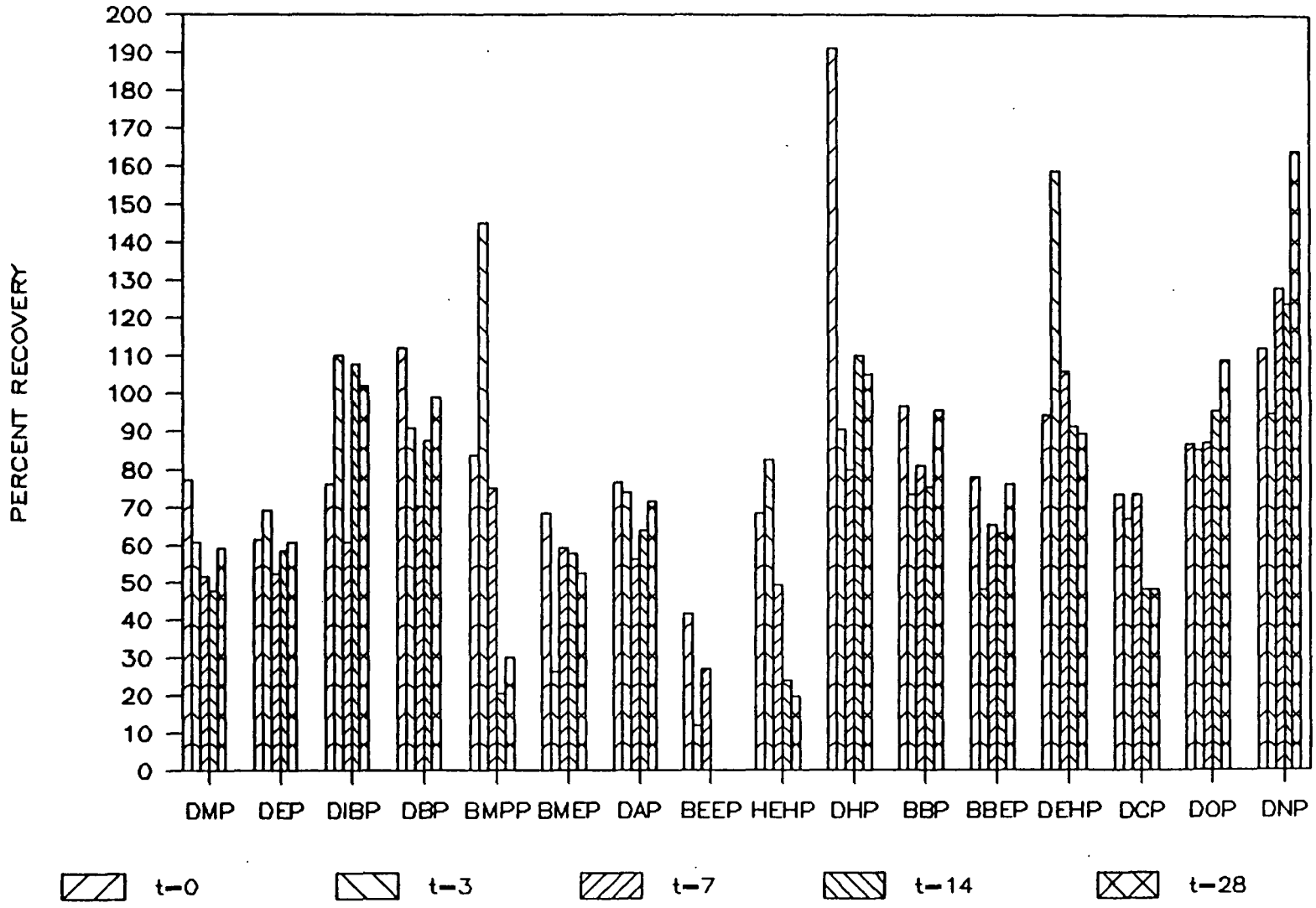


Figure 24. Recovery of Method 8060 compounds from sandy loam soil as a function of time at -10°C.

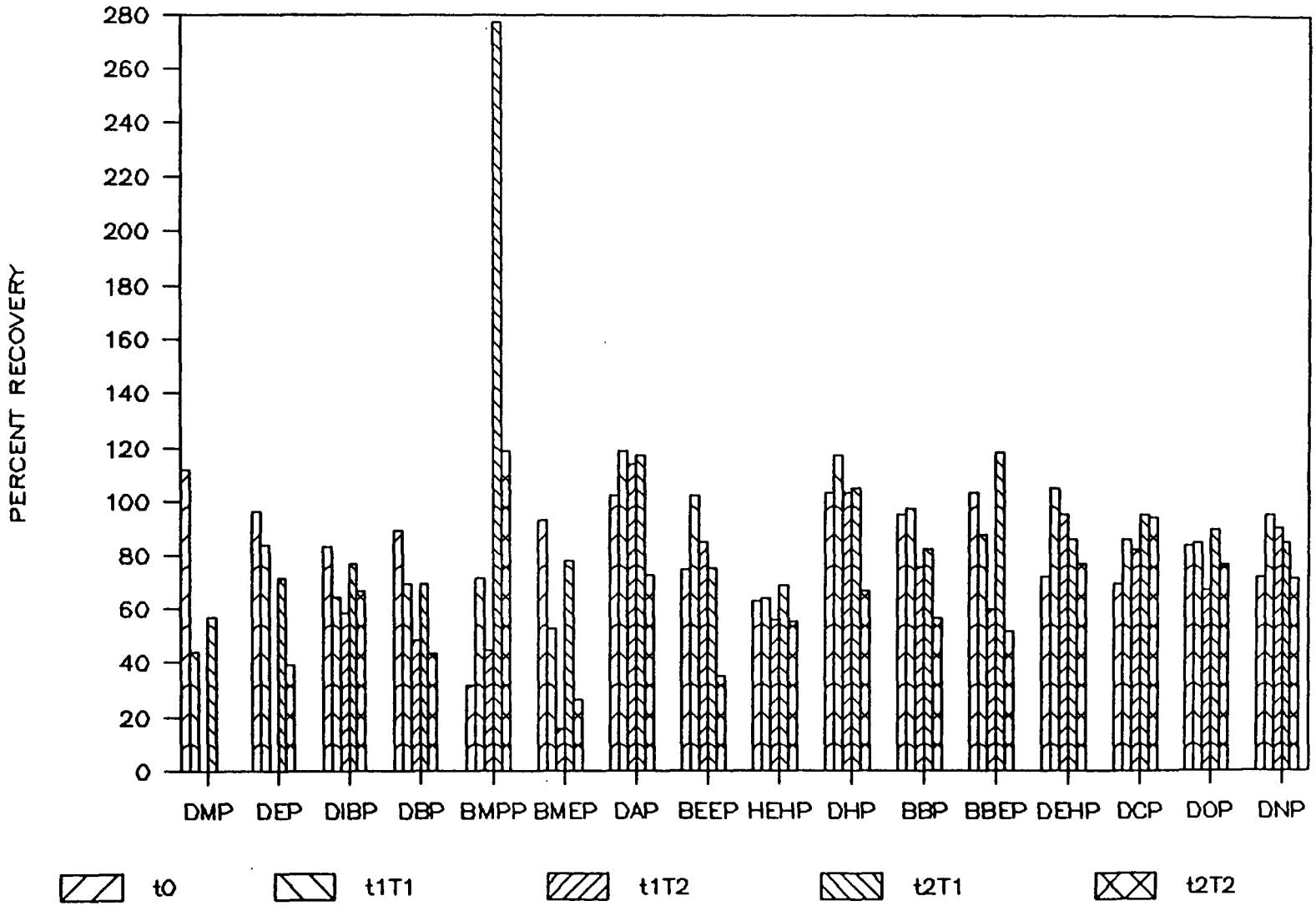


Figure 25. Recovery of Method 8060 compounds from sandy loam soil as a function of time at -10°C and +4°C (t_0 - initial times; t_1 - 1 month; t_2 - 1.5 months; T_1 - temperature of -10°; T_2 - temperature of +4°C).

TABLE 71. REPRODUCIBILITY OF THE ABSOLUTE AREA AND RETENTION TIME OF BENZYL BENZOATE[a]

Experiment No.	Retention time (min)	Absolute area
1	5.821	59,682
2	5.808	58,450
3	5.807	58,429
4	5.808	58,897
5	5.809	58,331
6	5.806	60,242
7	5.809	61,203
8	5.808	57,292
9	5.806	56,784
10	5.807	57,912
11	5.810	57,132
Average	5.809	58,578
SD	0.004	1,360
RSD (percent)	0.072	2.3

[a]The reproducibility was determined for 11 consecutive injections. The nominal spike level of benzyl benzoate was 500 pg/μL. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; spitless injection.

were analyzed over a 24-hr period, the reproducibility of detector response was 6.2 percent (Table 72); nonetheless, this value is quite acceptable. Reproducibility of detector response for each of the 16 phthalate esters is given in Table 73. The data indicate that excellent reproducibilities were achieved at concentrations of 100 pg/μL.

6.6.2 Instrument Calibration

Quantification of compounds is typically performed using two types of calibration: external standard calibration and internal standard calibration. In the former case, working solutions containing the test compound are analyzed prior to samples to determine the linear dynamic range of the instrument. Quantification of compounds in an unknown sample is performed by comparing the detector response obtained for the unknown sample to that measured for a calibration standard within the linear range of the instrument. In the latter case, the linear dynamic range of the instrument needs to be established in the same way. In addition, an internal standard is spiked into every calibration standard and unknown sample, and the ratio of detector responses of the test compound to the internal standard for the calibration standard and the unknown sample are compared.

During the course of this project we have performed five sets of multilevel calibrations using the DB-5 fused-silica capillary column. Initially, we analyzed standards ranging in concentration from 50 to 5,000 pg/μL. From these data, we concluded that the linear range extends from 50 to 3,000 pg. The data presented in Tables 74 through 76 give the average response factors (RF), slopes, intercepts, and correlation coefficients for the five sets of multilevel calibrations. It can be seen that the RFs were for the most part low for the first two calibrations, reached a maximum for the November 17, 1987, calibration, and began decreasing for the last two calibrations. The explanation is that the detector was so contaminated in August, 1987, that we had to send it to the manufacturer for cleaning. When the cleaned detector was in operation, the response increased and then began decreasing steadily with use. To exemplify that, the daily response factors, measured at three concentrations over a period of 5 days, are shown in Tables 77 through 85. It is quite obvious, from comparing the percent differences between the daily response and the average response, that the instrument performance changes significantly from day to day.

One way to compensate for that change is to use an internal standard. Table 86 presents the average relative response factors (RRFs), slopes, intercepts, and correlation coefficients for two multilevel calibrations performed with benzyl benzoate as internal standard. It can be seen now that the values for the slopes of the calibration lines are much closer (ideally they should be identical).

The following comments are made based on observations gathered during the course of this project:

- Establishment of the instrument dynamic range should be considered; however, because the ECD is such a sensitive detector and its performance changes so drastically even during the course of the day, we recommend that a three-level calibration bracketing the sample

TABLE 72. ABSOLUTE AREAS OF THE INTERNAL STANDARD

Sample identification	Absolute area[a]
Phthalate std (2,500 pg/μL)	50,512
Phthalate std (2,500 pg/μL)	59,728
Phthalate std (2,000 pg/μL)	54,883
Phthalate std (1,500 pg/μL)	53,074
8711-049-9 (Rep.1)	55,670
8711-049-10 (Rep.2)	48,495
8711-049-11 (Rep.3)	48,342
8711-049-12 (Rep.4)	45,572
8711-049-15 (spiking solution)	52,162
Phthalate std (2,500 pg/μL)	52,900
Phthalate std (1,000 pg/μL)	53,481
Phthalate std (1,000 pg/μL)	57,261
Phthalate std (500 pg/μL)	53,231
8711-049-5 (Rep.1)	51,325
8711-049-6 (Rep.2)	45,797
8711-049-7 (Rep.3)	51,206
8711-049-8 (Rep.4)	51,323
8711-049-14 (spiking solution)	53,405
Phthalate std (1,000 pg/μL)	53,200
Phthalate std (500 pg/μL)	50,911
Phthalate std (100 pg/μL)	48,125
Phthalate std (50 pg/μL)	51,826
8711-049-1 (Rep.1)	50,359
8711-049-2 (Rep.2)	50,951
8711-049-3 (Rep.3)	50,159
8711-049-4 (Rep.4)	48,668
8711-049-13 (spiking solution)	51,436
Phthalate std (50 pg/μL)	47,477
Average	51,481
SD	3,193
RSD (percent)	6.2
n	28

[a]The internal standard was benzyl benzoate; nominal spike level was 500 pg/μL. The analyses are listed in the order in which they were performed over a 24-hr period. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

TABLE 73. REPRODUCIBILITY OF THE GC/ECD RESPONSE FACTORS USED IN QUANTITATION[a]

Compound	Average response factor[b]	RSD[b] (percent)	Average response factor[c]	RSD[c] (percent)
DMP	395	2.3	322	6.2
DEP	418	1.3	351	5.9
DIBP	376	1.1	373	4.7
DBP	423	5.0	370	5.1
BMPP	443	2.9	441	1.7
BMEP	253	1.3	244	6.7
DAP	404	2.4	385	9.3
BEEP	376	3.1	371	7.3
HEHP	355	2.8	310	11
DHP	358	2.6	346	2.5
BBP	1,080	3.7	1,140	4.3
BBEP	348	4.2	378	8.5
DEHP	499	3.0	470	2.0
DCP	564	3.3	582	2.6
DOP	394	3.0	393	2.0
DNP	397	1.9	369	7.3

[a]The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

[b]Date: November 10, 1987, and November 11, 1987; time of analysis for the three calibration standards was: 3:59 p.m.; 10:04 p.m.; 2:06 a.m. Concentration was 100 pg/μL.

[c]Date: November 12, 1987; time of analysis for the three calibration standards was: 10:36 a.m.; 11:09 a.m.; and 8:21 p.m. Concentration was 100 pg/μL.

TABLE 74. COMPARISON OF THE MULTILEVEL CALIBRATIONS PERFORMED ON AUGUST 18, 1987, AND AUGUST 28, 1987

	August 18, 1987				August 28, 1987			
Compound	Average RF[a]	Slope	Intercept	CC[b]	Average RF[a]	Slope	Intercept	CC[b]
DMP	64.7	52.5	8,552	0.9986	32.9	45.4	-8,566	0.9921
DEP	78.2	56.8	13,917	0.9962	46.4	44.6	1,980	0.9990
DIBP	90.6	54.5	24,921	0.9911	65.7	45.7	10,130	0.9954
DBP	129	57.4	71,079	0.9822	79.9	52.4	25,300	0.9853
BMPP	c	c	c	c	c	c	c	c
BMEP	c	c	c	c	c	c	c	c
DAP	143	86.3	23,064	0.9423	84.3	60.8	8,254	0.9911
BEEP	c	c	c	c	c	c	c	c
HEHP	c	c	c	c	c	c	c	c
DHP	c	c	c	c	68.3	30.4	14,170	0.9892
BBP	1,180	797	269,700	0.9904	1,000	726	137,500	0.9969
BBEP	c	c	c	c	c	c	c	c
DEHP	328	186	105,200	0.9803	218	154	31,720	0.9905
DCP	338	246	70,350	0.9931	308	199	47,950	0.9958
DOP	169	97.6	56,680	0.9817	112	72.8	22,170	0.9861
DNP	183	126	39,520	0.9927	121	86.0	16,700	0.9880

[a]Number of determinations was 10 for August 18, 1987, and 11 for August 28, 1987. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.
[b]CC - Linear regression correlation coefficient.
[c]Compound was not available for testing.

TABLE 75. COMPARISON OF THE MULTILEVEL CALIBRATIONS PERFORMED ON NOVEMBER 17, 1987, AND NOVEMBER 25, 1987

	November 17, 1987				November 25, 1987			
Compound	Average RF[a]	Slope	Intercept	CC[b]	Average RF[a]	Slope	Intercept	CC[b]
DMP	229	183.6	24,418	0.9954	157	110.3	29,685	0.9829
DEP	239	171.4	30,299	0.9950	172	97.0	37,012	0.9800
DIBP	244	162.2	37,851	0.9924	193	98.7	45,580	0.9755
DBP	250	176.9	35,716	0.9931	198	104.7	45,414	0.9743
BMPP	351	304.6	22,387	0.9985	335	228.6	57,890	0.9878
BMEP	198	151.0	27,730	0.9933	174	96.0	39,003	0.9731
DAP	260	178.0	40,534	0.9920	214	104.1	55,675	0.9621
BEEP	265	185.1	40,415	0.9920	233	111.3	61,906	0.9591
HEHP	266	225.7	22,535	0.9973	244	164.8	46,205	0.9837
DHP	215	138.5	33,899	0.9918	179	75.2	47,015	0.9600
BBP	844	661.9	91,943	0.9963	861	566.4	15,344	0.9854
BBEP	285	202.6	43,765	0.9898	240	127.3	57,774	0.9688
DEHP	309	198.6	59,356	0.9739	250	131.6	57,217	0.9727
DCP	505	398.9	49,510	0.9976	472	307.4	85,690	0.9858
DOP	253	196.5	30,271	0.9951	215	126.9	48,591	0.9718
DNP	251	195.9	31,541	0.9933	233	144.5	49,159	0.9770

[a]The number of determinations was 11. The GC/ECD operating conditions were as specified in Table 74.
[b]CC - Linear regression correlation coefficient.

TABLE 76. MULTILEVEL CALIBRATION PERFORMED ON DECEMBER 8, 1987

Compound	Average RF[a]	Slope	Intercept	CC[b]
DMP	162	134.2	17,331	0.9974
DEP	164	116.1	23,203	0.9954
DIBP	178	110.5	27,970	0.9950
DBP	163	106.0	25,875	0.9946
BMPP	289	227.2	27,798	0.9956
BMEP	119	89.99	18,582	0.9961
DAP	159	105.9	27,207	0.9902
BEEP	173	106.2	32,387	0.9874
HEHP	206	160.3	21,293	0.9947
DHP	132	71.08	23,445	0.9920
BBP	656	487.6	63,386	0.9933
BBEP	141	103.2	17,575	0.9924
DEHP	190	112.5	26,970	0.9931
DCP	357	272.9	37,954	0.9927
DOP	131	94.17	15,630	0.9917
DNP	151	110.7	16,825	0.9915

[a]The number of determinations was 11. The GC/ECD operating conditions were as specified in Table 74.
[b]CC - Linear regression correlation coefficient.

TABLE 77. DAILY RESPONSE FACTOR AT 500 pg/μL

Compound	Average response factor[a] November 17, 1987	RF_{500}[b] November 18, 1987	Percent D[c]
DMP	229	188	-18
DEP	239	184	-23
DIBP	244	210	-14
DBP	250	210	-16
BMPP	351	310	-12
BMEP	198	181	-8.6
DAP	260	233	-10
BEEP	265	240	-9.4
HEHP	266	243	-8.7
DHP	215	191	-11
BBP	844	815	-3.4
BBEP	285	271	-4.9
DCP	505	461	-8.7
DEHP	309	328	+6.1
DOP	253	239	-5.5
DNP	251	244	-2.8

[a] Multilevel calibration; 11 data points at concentrations between 50 pg/μL and 3,000 pg/μL. The GC/ECD conditions were as specified in Table 74.
[b] RF_{500} is the compound's response factor.
[c] Percent difference.

TABLE 78. DAILY RESPONSE FACTOR AT 1,000 pg/μL

Compound	Average response factor[a] November 17, 1987	RF_{1000}[b] November 18, 1987	Percent D[c]
DMP	229	184	-20
DEP	239	182	-24
DIBP	244	187	-23
DBP	250	204	-18
BMPP	351	307	-13
BMEP	198	168	-15
DAP	260	215	-17
BEEP	265	222	-16
HEHP	266	233	-12
DHP	215	168	-22
BBP	844	769	-8.9
BBEP	285	241	-15
DEHP	309	231	-25
DCP	505	423	-16
DOP	253	224	-12
DNP	251	230	-8.4

[a]Multilevel calibration; 11 data points at concentrations between 50 pg/μL and 3,000 pg/μL. The GC/ECD conditions were as specified in Table 74.
[b]RF_{1000} is the compound's response factor.
[c]Percent difference.

TABLE 79. DAILY RESPONSE FACTOR AT 1,500 pg/μL

Compound	Average response factor[a] November 17, 1987	RF_{1500}[b] November 18, 1987	Percent D[c]
DMP	229	188	-18
DEP	239	181	-24
DIBP	244	178	-27
DBP	250	191	-24
BMPP	351	293	-16
BMEP	198	159	-20
DAP	260	201	-23
BEEP	265	207	-22
HEHP	266	221	-17
DHP	215	160	-26
BBP	844	716	-15
BBEP	285	229	-18
DEHP	309	224	-28
DCP	505	402	-20
DOP	253	209	-17
DNP	251	204	-19

[a]Multilevel calibration; 11 data points at concentrations between 50 pg/μL and 3,000 pg/μL. The GC/ECD conditions were as specified in Table 74.
[b]RF_{1500} is the compound's response factor.
[c]Percent difference.

TABLE 80. DAILY RESPONSE FACTOR AT 500 pg/μL

Compound	Average response factor[a] November 17, 1987	RF_{500}[b] November 19, 1987	Percent D[c]
DMP	229	185	-19
DEP	239	173	-28
DIBP	244	201	-18
DBP	250	210	-16
BMPP	351	337	-4.0
BMEP	198	187	-5.6
DAP	260	245	-5.8
BEEP	265	253	-4.5
HEHP	266	262	-1.5
DHP	215	190	-12
BBP	844	870	+3.1
BBEP	285	290	+1.8
DEHP	309	278	-10
DCP	505	488	-3.4
DOP	253	248	-2.0
DNP	251	250	-0.4

[a]Multilevel calibration; 11 data points at concentrations between 50 pg/μL and 3,000 pg/μL. The GC/ECD conditions were as specified in Table 74.
[b]RF_{500} is the compound's response factor.
[c]Percent difference.

TABLE 81. DAILY RESPONSE FACTOR AT 1,000 pg/μL

Compound	Average response factor[a] November 17, 1987	RF_{1000}[b] November 19, 1987	Percent D[c]
DMP	229	186	-19
DEP	239	183	-23
DIBP	244	185	-24
DBP	250	206	-18
BMPP	351	323	-8.0
BMEP	198	175	-12
DAP	260	222	-15
BEEP	265	229	-14
HEHP	266	245	-7.9
DHP	215	170	-21
BBP	844	780	-7.6
BBEP	285	286	+0.4
DEHP	309	256	-17
DCP	505	440	-13
DOP	253	245	-3.2
DNP	251	228	-9.2

[a]Multilevel calibration; 11 data points at concentrations between 50 pg/μL and 3,000 pg/μL. The GC/ECD conditions were as specified in Table 74.
[b]RF_{1000} is the compound's response factor.
[c]Percent difference.

TABLE 82. DAILY RESPONSE FACTOR AT 1,500 pg/μL

Compound	Average response factor[a] November 17, 1987	RF_{1500}[b] November 19, 1987	Percent D[c]
DMP	229	202	-12
DEP	239	198	-17
DIBP	244	184	-25
DBP	250	207	-17
BMPP	351	320	-8.8
BMEP	198	170	-14
DAP	260	217	-17
BEEP	265	223	-16
HEHP	266	240	-9.8
DHP	215	166	-23
BBP	844	744	-12
BBEP	285	264	-7.4
DEHP	309	239	-23
DCP	505	425	-16
DOP	253	216	-15
DNP	251	198	-21

[a]Multilevel calibration; 11 data points at concentrations between 50 pg/μL and 3,000 pg/μL. The GC/ECD conditions were as specified in Table 74.
[b]RF_{1500} is the compound's response factor.
[c]Percent difference.

TABLE 83. DAILY RESPONSE FACTOR AT 500 pg/μL

Compound	Average response factor[a] November 17, 1987	RF_{500}[b] November 23, 1987	Percent D[c]
DMP	229	206	-10
DEP	239	201	-16
DIBP	244	225	-7.8
DBP	250	235	-6.0
BMPP	351	339	-3.4
BMEP	198	209	+5.6
DAP	260	269	+3.5
BEEP	265	274	+3.4
HEHP	266	269	+1.1
DHP	215	220	+2.3
BBP	844	892	+5.7
BBEP	285	294	+3.2
DEHP	309	283	-8.4
DCP	505	490	+3.0
DOP	253	244	-3.6
DNP	251	214	-15

[a]Multilevel calibration; 11 data points at concentrations between 50 pg/μL and 3,000 pg/μL. The GC/ECD conditions were as specified in Table 74.
[b]RF_{500} is the compound's response factor.
[c]Percent difference.

TABLE 84. DAILY RESPONSE FACTOR AT 1,000 pg/μL

Compound	Average response factor[a] November 17, 1987	RF_{1000}[b] November 23, 1987	Percent D[c]
DMP	229	150	-35
DEP	239	144	-40
DIBP	244	157	-36
DBP	250	172	-31
BMPP	351	291	-17
BMEP	198	153	-23
DAP	260	185	-29
BEEP	265	193	-28
HEHP	266	216	-19
DHP	215	147	-32
BBP	844	746	-12
BBEP	285	217	-24
DEHP	309	207	-33
DCP	505	391	-23
DOP	253	185	-27
DNP	251	163	-35

[a]Multilevel calibration; 11 data points at concentrations between 50 pg/μL and 3,000 pg/μL. The GC/ECD conditions were as specified in Table 74.
[b]RF_{1000} is the compound's response factor.
[c]Percent difference.

TABLE 85. DAILY RESPONSE FACTOR AT 1,500 pg/μL

Compound	Average response factor[a] November 17, 1987	RF_{1500}[b] November 23, 1987	Percent D[c]
DMP	229	161	-30
DEP	239	151	-37
DIBP	244	155	-37
DBP	250	173	-31
BMPP	351	287	-18
BMEP	198	147	-26
DAP	260	184	-29
BEEP	265	189	-29
HEHP	266	215	-19
DHP	215	149	-31
BBP	844	737	-13
BBEP	285	217	-24
DEHP	309	208	-33
DCP	505	394	-22
DOP	253	190	-25
DNP	251	170	-32

[a]Multilevel calibration; 11 data points at concentrations between 50 pg/μL and 3,000 pg/μL. The GC/ECD conditions were as specified in Table 74.
[b]RF_{1500} is the compound's response factor.
[c]Percent difference.

TABLE 86. COMPARISON OF THE MULTILEVEL CALCULATIONS PERFORMED ON NOVEMBER 25, 1987, AND DECEMBER 8, 1987

	November 25, 1987				December 8, 1987			
Compound	Average RRF[a]	Slope	Intercept	CC[b]	Average RRF[a]	Slope	Intercept	CC[b]
DMP	0.0028	0.0040	0.5511	0.9806	0.0036	0.0022	0.5197	0.9877
DEP	0.0031	0.0017	0.6823	0.9770	0.0031	0.0019	0.6122	0.9850
DIBP	0.0035	0.0017	0.7834	0.9720	0.0034	0.0018	0.7024	0.9848
DBP	0.0036	0.0018	0.8543	0.9701	0.0031	0.0017	0.6556	0.9853
BMPP	0.0060	0.0040	1.0793	0.9872	0.0055	0.0038	0.8597	0.9938
BMEP	0.0032	0.0017	0.7178	0.9696	0.0025	0.0015	0.4943	0.9879
DAP	0.0039	0.0018	1.0174	0.9594	0.0030	0.0017	0.6718	0.9804
BEEP	0.0042	0.0019	1.1302	0.9561	0.0033	0.0017	0.7775	0.9954
HEHP	0.0044	0.0029	0.8572	0.9711	0.0039	0.0027	0.6386	0.9926
DHP	0.0032	0.0013	0.8585	0.9570	0.0026	0.0012	0.5631	0.9856
BBP	0.0154	0.0099	2.8515	0.9848	0.0125	0.0080	1.9222	0.9938
BBEP	0.0043	0.0022	1.0587	0.9658	0.0027	0.0017	0.4880	0.9899
DEHP	0.0045	0.0023	1.0494	0.9711	0.0037	0.0018	0.6899	0.9904
DCP	0.0085	0.0053	1.5932	0.9852	0.0066	0.0045	1.1257	0.9929
DOP	0.0039	0.0022	0.8934	0.9697	0.0025	0.0016	0.4930	0.9913
DNP	0.0042	0.0025	0.9077	0.9731	0.0029	0.0018	0.4874	0.9423

[a] The number of determinations was 4. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection. RRF is the compound's response factor relative to benzyl benzoate (internal standard).

[b] CC - Linear regression correlation coefficient.

concentration be performed at least at 8- to 10-hour intervals or every 10 samples. If the expected sample concentrations are, for example, 100 pg/μL of extract, then the three levels should be 50, 100, and 150 pg/μL. If the expected concentrations are not known, then the sample should be analyzed twice, before and after the calibration standards that bracket the unknown sample were analyzed. It may appear that such an approach would double the effort required in the analysis; however, if the analyses are performed with an autosampler, then such an effort will not be so burdensome.

- Whenever routine analyses are performed with an autosampler it may be necessary to begin the daily analysis sequence with four or five calibration standards of the same concentration. We observed that the instrument response usually stabilizes after the fourth injection.

- After changing the septum in the injector, we have observed that the detector requires as much as 48 hrs to stabilize. Therefore, septa should always be preheated in the oven at 250°C prior to use and they should be replaced at the end of the working day, or preferably before the weekend, thus allowing the detector enough time to stabilize and without affecting the sample throughput during the working day.

6.6.3 Method Accuracy

Method performance data are presented in this report as method accuracy, method precision, and method detection limits. Table 87 and 88 and Figures 26 through 29 summarized the method accuracy and precision for the aqueous and solid samples, respectively. In the case of aqueous samples, method accuracy, given as percent recovery of the 16 phthalate esters spiked into estuarine water, leachate, and groundwater, at two concentrations (20 μg/L and 60 μg/L) (Figure 26) ranged from 59.5 to 117. In the case of solid samples, the percent recoveries were distributed over a much wider range (Figure 28), demonstrating that method accuracy is indeed a function of both matrix and analyte concentration. Method precision for aqueous samples (Figure 27) was better than 27.5 percent. Method precision for solid samples (Figure 29) varied from matrix to matrix.

In addition to the real samples, which were used during the entire method protocol evaluation, we also analyzed six EPA performance evaluation samples on a DB-5 fused-silica capillary column. Four of these samples contained phthalate esters and two did not. The results of the GC/ECD analyses are presented in Tables 89 through 94 and in Figures 30 through 33. Percent biases range from -26.2 and +15.5. All phthalate esters that were reported by EPA to be present in those samples were identified correctly. Because these samples contained many other compounds and the analyses were carried out only on one capillary column, we reported false positives. Confirmation of the target phthalate esters on another capillary column probably would have eliminated the false positives.

6.6.4 Method Detection Limits

The determination of the method detection limits was performed according to the following procedure:

TABLE 87. ACCURACY AND PRECISION DATA FOR METHOD 3510 AND METHOD 8061[a]

Compound	Spike level (20 μg/L)			Spike level (60 μg/L)		
	Estuarine water	Leachate	Groundwater	Estuarine water	Leachate	Groundwater
DMP	84.0 (4.1)	98.9 (19.6)	87.1 (8.1)	87.1 (7.5)	112 (17.5)	90.9 (4.5)
DEP	71.2 (3.8)	82.8 (19.3)	88.5 (15.3)	71.0 (7.7)	88.5 (17.9)	75.3 (3.5)
DIBP	76.0 (6.5)	95.3 (16.9)	92.7 (17.1)	99.1 (19.0)	100 (9.6)	83.2 (3.3)
DBP	83.2 (6.5)	97.5 (22.3)	91.0 (10.7)	87.0 (8.0)	106 (17.4)	87.7 (2.7)
BMPP	78.6 (2.6)	87.3 (18.2)	92.6 (13.7)	97.4 (15.0)	107 (13.3)	87.6 (2.9)
BMEP	73.8 (1.0)	87.2 (21.7)	82.4 (4.4)	82.5 (5.5)	99.0 (13.7)	76.9 (6.6)
DAP	78.2 (7.3)	92.1 (21.5)	88.8 (7.5)	89.2 (2.8)	112 (14.2)	92.5 (1.8)
BEEP	75.6 (3.3)	90.8 (22.4)	86.4 (5.8)	88.7 (4.9)	109 (14.6)	84.8 (5.9)
HEHP	84.7 (5.3)	91.1 (27.5)	81.4 (17.6)	107 (16.8)	117 (11.4)	80.1 (4.1)
DHP	79.8 (7.2)	102 (21.5)	90.9 (7.6)	90.1 (2.4)	109 (20.7)	88.9 (2.4)
BBP	84.1 (6.4)	105 (20.5)	89.6 (6.1)	92.7 (5.6)	117 (24.7)	93.0 (2.0)
BBEP	78.5 (3.5)	92.3 (16.1)	89.3 (3.6)	86.1 (6.2)	107 (15.3)	92.4 (0.6)
DEHP	81.4 (4.1)	93.0 (15.0)	90.5 (4.9)	86.5 (6.9)	108 (15.1)	91.1 (3.0)
DCP	77.4 (6.5)	88.2 (13.2)	91.7 (15.2)	87.7 (9.6)	102 (14.3)	71.9 (2.4)
DOP	74.9 (4.9)	87.5 (18.7)	87.2 (3.7)	85.1 (8.3)	105 (17.7)	90.4 (2.0)
DNP	59.5 (6.1)	77.3 (4.2)	67.2 (8.0)	97.2 (7.0)	108 (17.9)	90.1 (1.1)
Surrogates:						
DPP	98.5 (2.6)	113 (14.9)	110 (3.3)	110 (12.4)	95.1 (7.2)	107 (2.4)
DPIP	95.8 (1.9)	112 (11.7)	109 (3.3)	104 (5.9)	97.1 (7.1)	106 (2.8)
DBZP	93.9 (4.4)	112 (14.0)	106 (3.8)	111 (5.9)	93.3 (9.5)	105 (2.4)

[a] The number of determinations was 3. Values given in parentheses are the percent relative standard deviations of the average recoveries. The sample extracts were not subjected to Florisil cleanup.

TABLE 88. ACCURACY AND PRECISION DATA FOR METHOD 3550 AND METHOD 8061[a]

Compound	Spike level (1 μg/g)			Spike level (3 μg/g)		
	Estuarine sediment[b]	Municipal sludge	Sandy loam soil	Estuarine sediment[b]	Municipal sludge	Sandy loam soil
DMP	77.9 (42.8)	52.1 (35.5)	[c]	136 (9.6)	64.8 (11.5)	70.2 (2.0)
DEP	68.4 (1.7)	68.6 (9.1)	54.7 (6.2)	60.2 (12.5)	72.8 (10.0)	67.0 (15.1)
DIBP	103 (3.1)	106 (5.3)	70.3 (3.7)	74.8 (6.0)	84.0 (4.6)	79.2 (0.1)
DBP	121 (25.8)	86.3 (17.7)	72.6 (3.7)	74.6 (3.9)	113 (5.8)	70.9 (5.5)
BMPP	108 (57.4)	97.3 (7.4)	[c]	104 (1.5)	150 (6.1)	83.9 (11.8)
BMEP	26.6 (26.8)	72.7 (8.3)	0	19.5 (14.8)	59.9 (5.4)	0
DAP	95.0 (10.2)	81.9 (7.1)	81.9 (15.9)	77.3 (4.0)	116 (3.7)	82.1 (15.5)
BEEP	[c]	66.6 (4.9)	[c]	21.7 (22.8)	57.5 (9.2)	84.7 (8.5)
HEHP	[c]	114 (10.5)	57.7 (2.8)	72.7 (11.3)	26.6 (47.6)	28.4 (4.3)
DHP	103 (3.6)	96.4 (10.7)	77.9 (2.4)	75.5 (6.8)	80.3 (4.7)	79.5 (2.7)
BBP	113 (12.8)	82.8 (7.8)	56.5 (5.1)	72.9 (3.4)	76.8 (10.3)	67.3 (3.8)
BBEP	114 (21.1)	74.0 (15.6)	[c]	38.3 (25.1)	98.0 (6.4)	62.0 (3.4)
DEHP	[c]	76.6 (10.6)	99.2 (25.3)	59.5 (18.3)	85.8 (6.4)	65.4 (2.8)
DCP	36.6 (48.8)	65.8 (15.7)	92.8 (35.9)	33.9 (66.1)	68.5 (9.6)	62.2 (19.1)
DOP	[c]	93.3 (14.6)	84.7 (9.3)	36.8 (16.4)	88.4 (7.4)	115 (29.2)
DNP	[c]	80.0 (41.1)	64.2 (17.2)	[c]	156 (8.6)	115 (13.2)

[a] The number of determinations was 3. Values given in parentheses are the percent relative standard deviations of the average recoveries. All samples were subjected to Florisil cartridge cleanup.
[b] The estuarine sediment extract (Florisil, Fraction 1) was subjected to sulfur cleanup (Method 3660 with tetrabutylammonium sulfite reagent).
[c] Not able to determine because of matrix interferent.

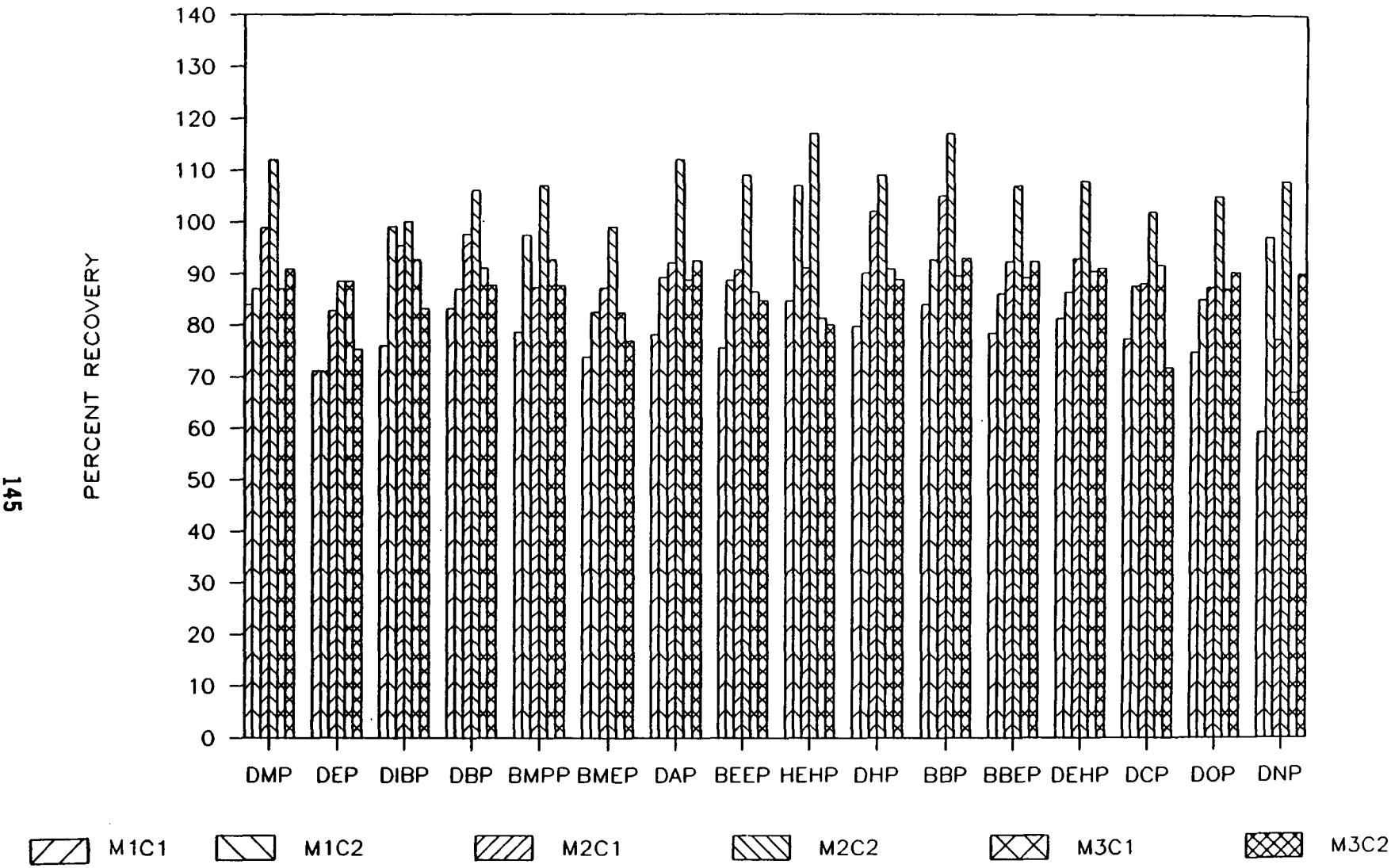


Figure 26. Method accuracy for aqueous matrices (M_1 - estuarine water; M_2 - leachate; M_3 - groundwater; C_1 - concentration at 20 μg/L per component; C_2 - concentration at 60 μg/L per component).

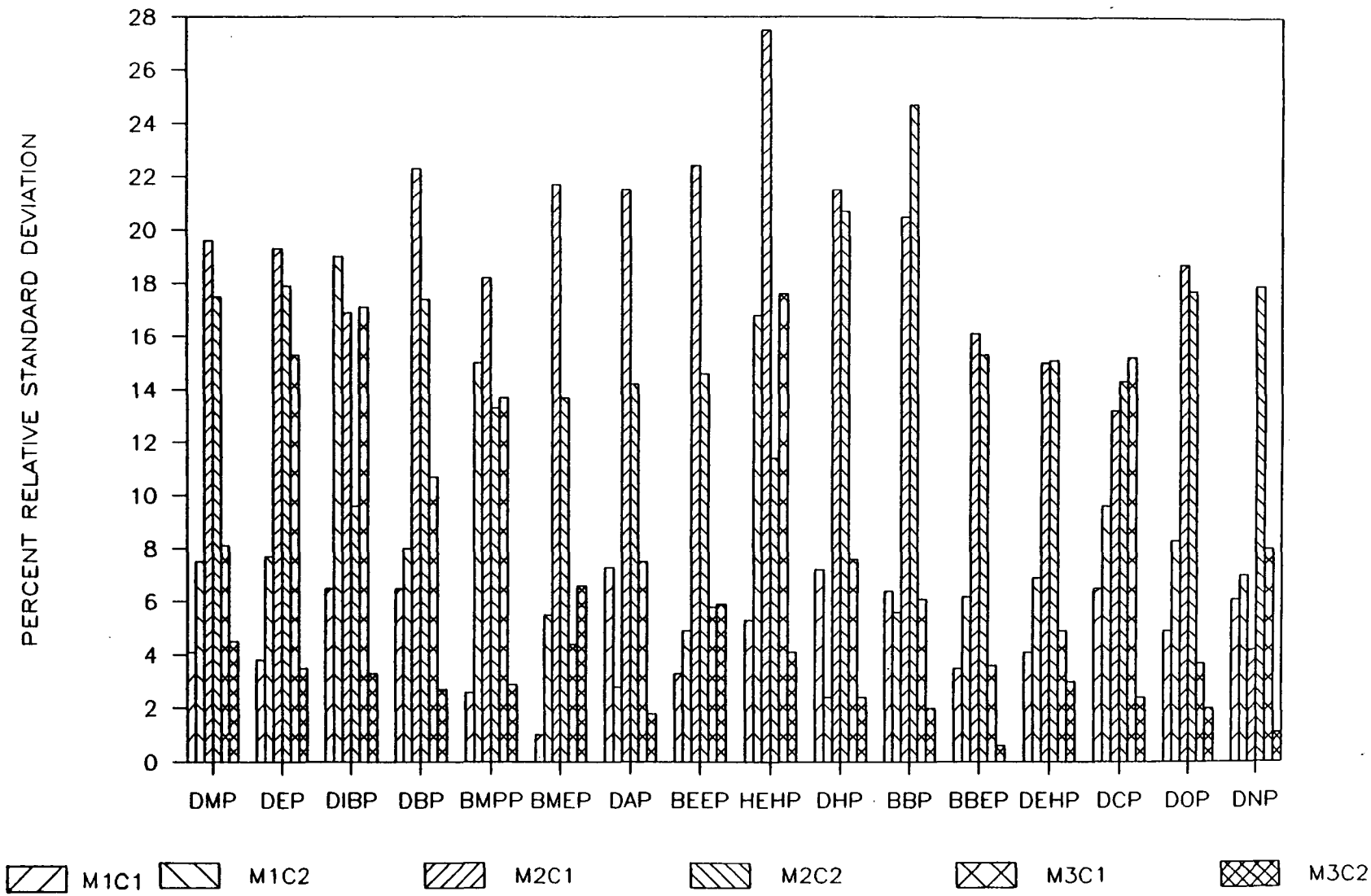


Figure 27. Method precision for aqueous matrices (M_1 - estuarine water; M_2 - leachate; M_3 - groundwater; C_1 - concentration at 20 μg/L per component; C_2 - concentration at 60 μg/L per component).

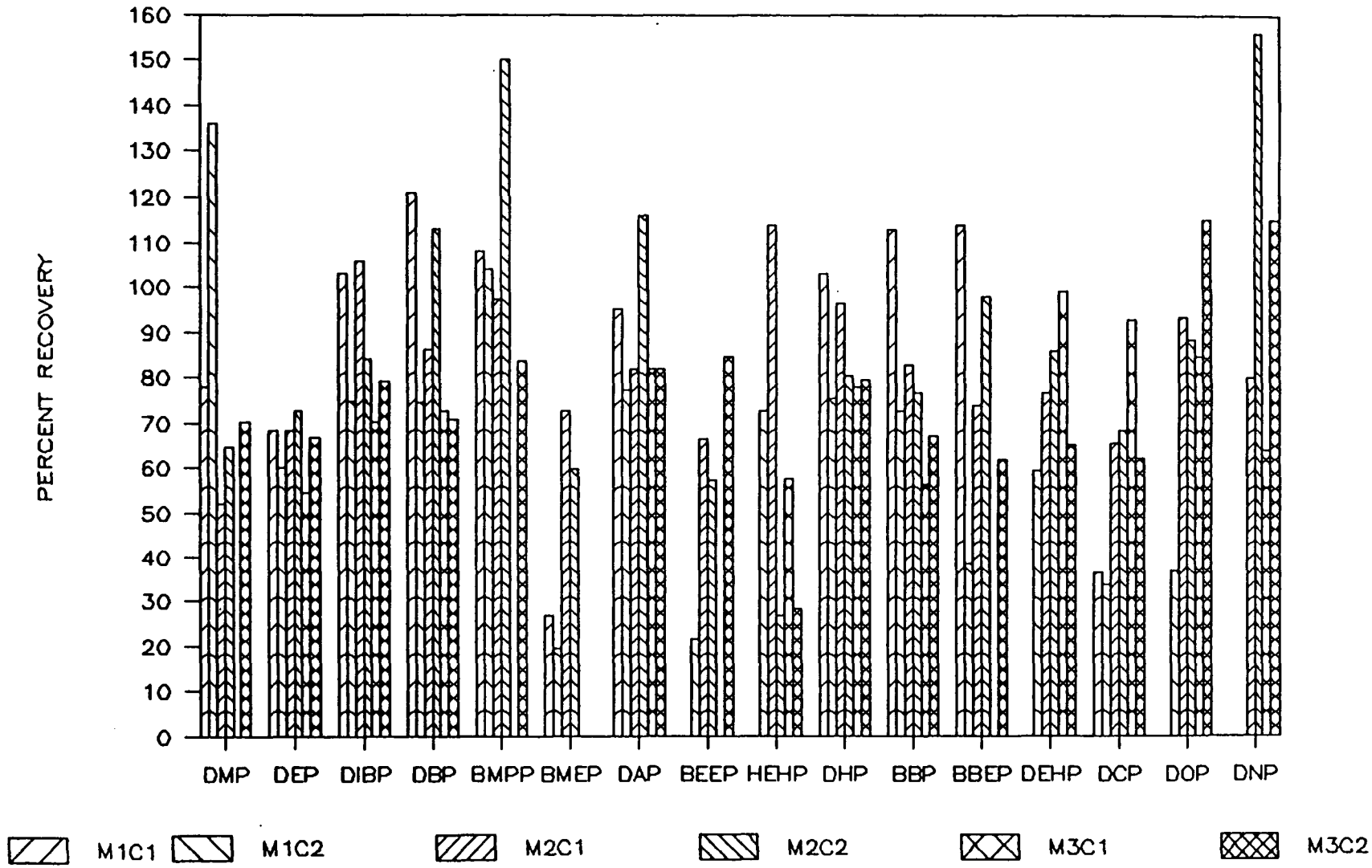


Figure 28. Method accuracy for solid matrices (M_1 - estuarine sediment; M_2 - municipal sludge; M_3 - sandy loam soil; C_1 - concentration at 1 $\mu g/g$ per component; C_2 - concentration at 3 $\mu g/g$ per component)

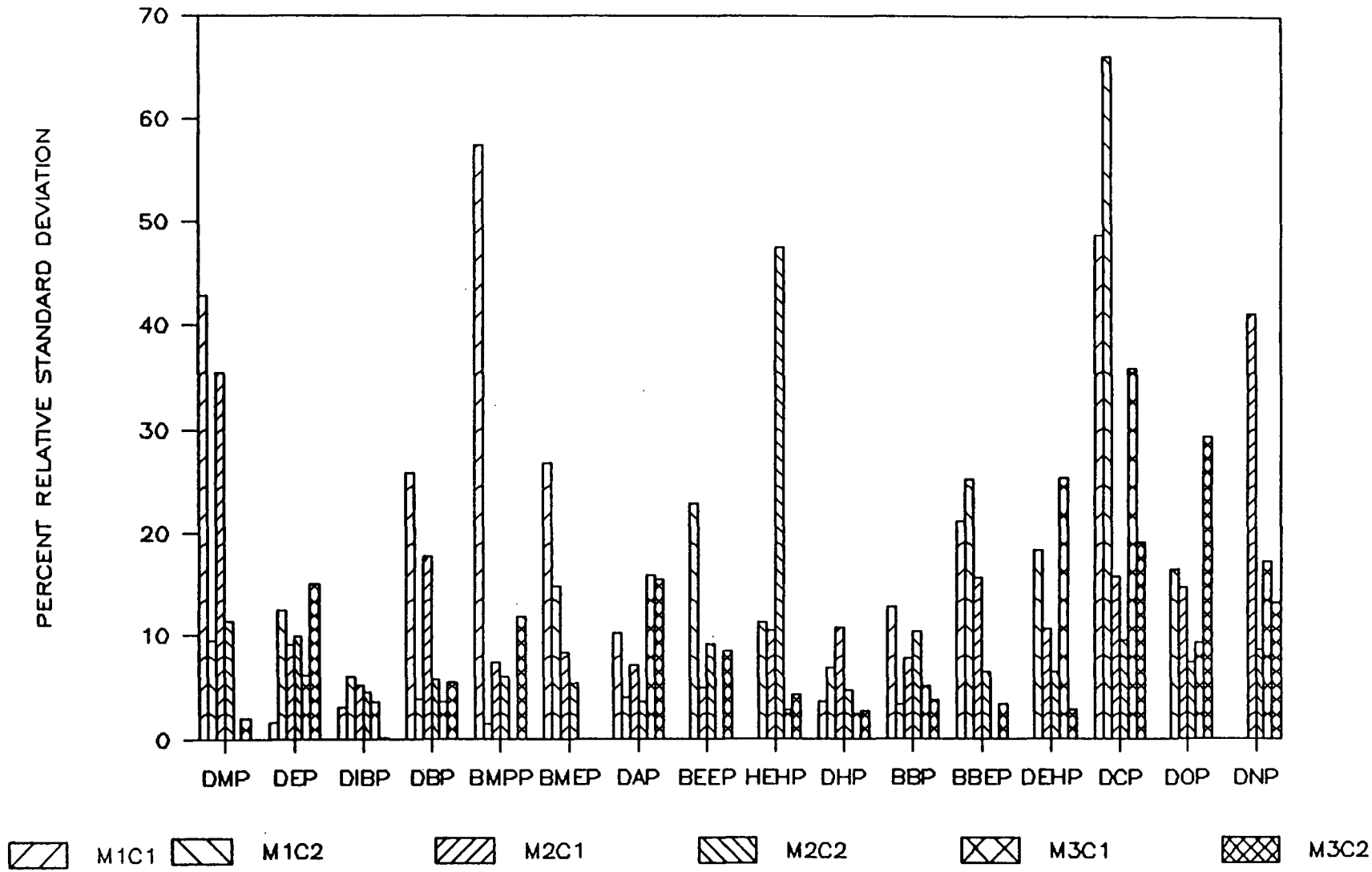


Figure 29. Method precision for solid matrices (M_1 - estuarine sediment; M_2 - municipal sludge; M_3 - sandy loam soil; C_1 - concentration at 1 $\mu g/g$ per component; C - concentration at 3 $\mu g/g$ per component)

TABLE 89. RESULTS OF METHOD 8060 ANALYSIS FOR EPA WP-482 SAMPLE 4

Compounds known to be present in WP-482 sample 4 at µg/L		Phthalates found by the revised EPA Method 8060 at µg/L		Percent bias
1,4-Dichlorobenzene	251			
Bis(2-chloroisopropyl)ether	204			
Hexachloroethane	303			
Nitrobenzene	373			
Naphthalene	250			
DMP	404	DMP	298	-26.8
Acenaphthene	197			
Fluorene	250			
4-Chlorophenyl phenyl ether	374			
4-Bromophenyl phenyl ether	373			
Anthracene	200			
Fluoranthene	301			
BBP	250	BBP	227	-9.2
Chrysene	209			
Ethyl hexyl phthalate	153			
Benzo(b)fluoranthene	203			
Benzo(a)pyrene	224			
Dibenzo(a,h)anthracene	204			
Benzo(g,h,i)perylene	300			
		False Positives:		
		DBP	8.8	
		BMEP	10.2	
		BEEP	20.8	
		DHP	27.6	
		DEHP	78.6	

[a] The concentrations reported are based on spiking 1 mL of the stock solution WP-482 into 1 L HPLC-grade water. 100 µL of the stock solution WP-482 were spiked into 1 L HPLC-grade water and extracted with methylene chloride using EPA Method 3510 for Florisil cleanup. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 µm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection. Since we used only 100 µL of the stock solution to spike, our results have been multiplied by a factor of 10 in order to compare them with the true values reported by EPA.

TABLE 90. RESULTS OF METHOD 8060 ANALYSIS FOR EPA WP-482 SAMPLE 1

Compounds known to be present in WP-482 sample 1 at ng/μL		Compounds found by EPA Method 8060[a] at ng/μL[a]		Percent bias
Bis(2-chloroethyl)ether	48.2			
1,3-Dichlorobenzene	52.0			
1,2-Dichlorobenzene	24.7			
Nitrosodipropylamine	34.8			
Isophorone	76.6			
Bis(2-chloroethoxy)methane	48.5			
1,2,4-Trichlorobenzene	25.3			
Hexachlorobutadiene	49.6			
2-Chloronaphthalene	25.4			
2,6-Dinitrotoluene	76.5			
2,4-Dinitrotoluene	73.8			
DEP	25.1	DEP	29.0	+15.5
Hexachlorobenzene	35.7			
Phenanthrene	40.2			
DBP	24.9	DBP	23.6	- 5.2
Pyrene	60.2			
Benzo(a)anthracene	73.9			
DOP	43.9	DOP	39.2	-10.7
Benzo(k)fluoranthene	45.7			
		False Positives:		
		BMEP	2.8	
		BMPP	0.35	
		BEEP	2.9	
		DAP	1.9	
		HEHP	0.94	
		DHP	0.50	
		BBP	1.2	
		DCP	0.74	
		DEHP	3.2	

[a] The EPA spiking solution WP-482 was diluted with hexane and analyzed by GC/ECD. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

TABLE 91. RESULTS OF METHOD 8060 ANALYSIS FOR EPA WP-482 SAMPLE 2

Compounds known to be present in EPA Method WP-482 sample 2 at ng/μL		Compounds found by EPA Method 8060 at ng/μL[a]		Percent bias
Bis(2-chloroethyl)ether	253			
1,3-Dichlorobenzene	148			
1,2-Dichlorobenzene	250			
Nitrosodipropylamine	352			
Isophorone	149			
Bis(2-chloroethoxy)methane	255			
1,2,4-Trichlorobenzene	256			
Hexachlorobutadiene	157			
2-Chloronaphthalene	251			
2,6-Dinitrotoluene	229			
2,4-Dinitrotoluene	277			
DEP	254	DEP	216	-15.0
Hexachlorobenzene	350			
Phenanthrene	202			
DBP	252	DBP	192	-23.8
Pyrene	298			
Benzo(a)anthracene	315			
DOP	230	DOP	200	-13.0
Benzo(k)fluoranthene	246			
		False Positives:		
		DMP	10.7	
		DIBP	6.6	
		BMEP	29.4	
		BEEP	19.5	
		DAP	15.8	
		HEHP	11.3	
		DHP	46.4	
		BBP	9.2	
		BBEP	7.7	
		DCP	4.6	
		DEHP	29.9	

[a]A GC/ECD chromatogram is shown in Figure 30. The EPA spiking solution was diluted with hexane and analyzed by GC/ECD. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

TABLE 92. RESULTS OF METHOD 8060 ANALYSIS FOR EPA WP-482 SAMPLE 3

Compound known to be present in WP-482 sample 3 at ng/μL		Compounds found by EPA Method 8060 at ng/μL[a]		Percent bias
1,4-Dichlorobenzene	24.8			
Bis(2-chloroisopropyl)ether	38.8			
Hexachloroethane	30.0			
Nitrobenzene	76.5			
Naphthalene	24.8			
DMP	40.0	DMP	33.5	-16.3
Acenaphthene	19.5			
Fluorene	51.2			
4-Chlorophenyl phenyl ether	76.7			
4-Bromophenyl phenyl ether	41.5			
Anthracene	40.0			
Fluoranthene	29.8			
BBP	51.3	BBP	43.4	-15.4
Chrysene	69.9			
Ethyl hexyl phthalate	29.1			
Benzo(b)fluoranthene	40.0			
Benzo(a)pyrene	24.9			
Dibenzo(a,h)anthracene	40.7			
Benzo(g,h,i)perylene	80.4			
		False positives:		
		DEP	16.2	
		BMPP	0.35	
		DHP	3.4	
		BBEP	0.94	
		DCP	0.20	
		DEHP	24.3	

[a] A GC/ECD chromatogram is shown in Figure 31. The EPA spiking solution was diluted with hexane and analyzed by GC/ECD. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

TABLE 93. RESULTS OF METHOD 8060 ANALYSIS FOR EPA WP-485

Compounds known to be present in the sample at ng/μL		Compounds found by EPA Method 8060 at ng/μL[a] (false positives)	
Acenaphthylene	100	DMP	3.6
Phenanthrene	100	BMPP	0.14
Fluoranthene	10.0	DAP	0.09
Benzo(a)anthracene	10.0	DHP	6.4
Benzo(a)pyrene	10.0		
Benzo(b)fluoranthene	10.0		
Dibenzo(a,n)anthracene	10.0		
Benzo(g,h,i)perylene	10.0		

[a] A GC/ECD chromatogram is shown in Figure 32. The EPA spiking solution was diluted with hexane and analyzed by GC/ECD. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

TABLE 94. RESULTS OF METHOD 8060 ANALYSIS FOR WP-281 SAMPLE 2

Compounds known to be present in WP-281 sample 2 at ng/μL		Compounds found by EPA Method 8060 at ng/μL[a] (false positives)	
Phenol	15.0	DMP	5.2
2,4-Dimethylphenol	12.5	BMPP	0.50
2-Chlorophenol	8.3	DAP	0.90
2-Chloro-3-methylphenol	20.0	DHP	1.6
2,4-Dichlorophenol	10.0	BBP	0.36
2,4,6-Trichlorophenol	12.5	DEHP	2.4
Pentachlorphenol	10.0		
2-Nitrophenol	20.0		
4-Nitrophenol	15.0		

[a] A GC/ECD chromatogram is shown in Figure 33. The EPA spiking solution was diluted with hexane and analyzed by GC/ECD. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

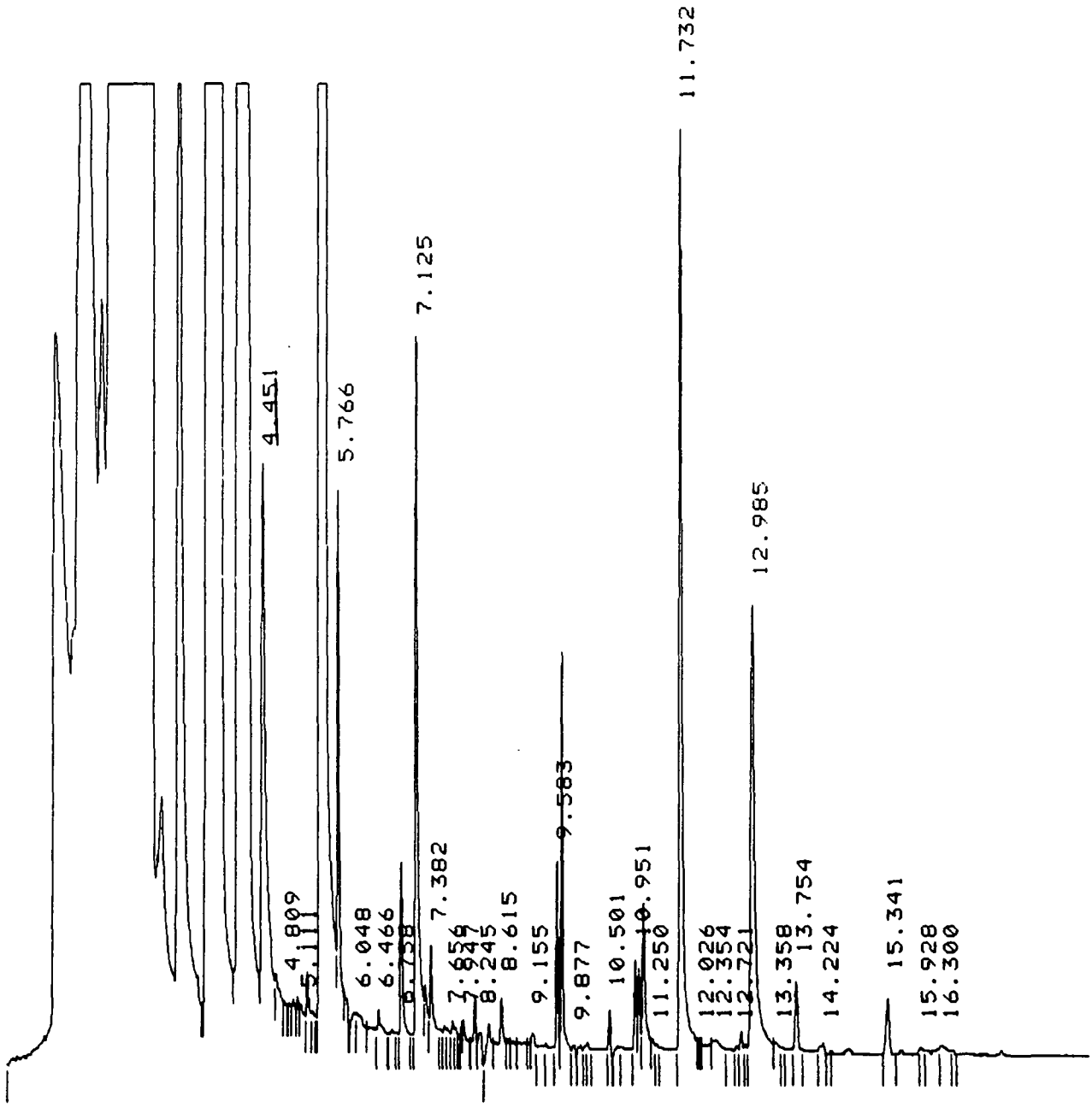


Figure 30. GC/ECD chromatogram of WP-482 Sample 2.

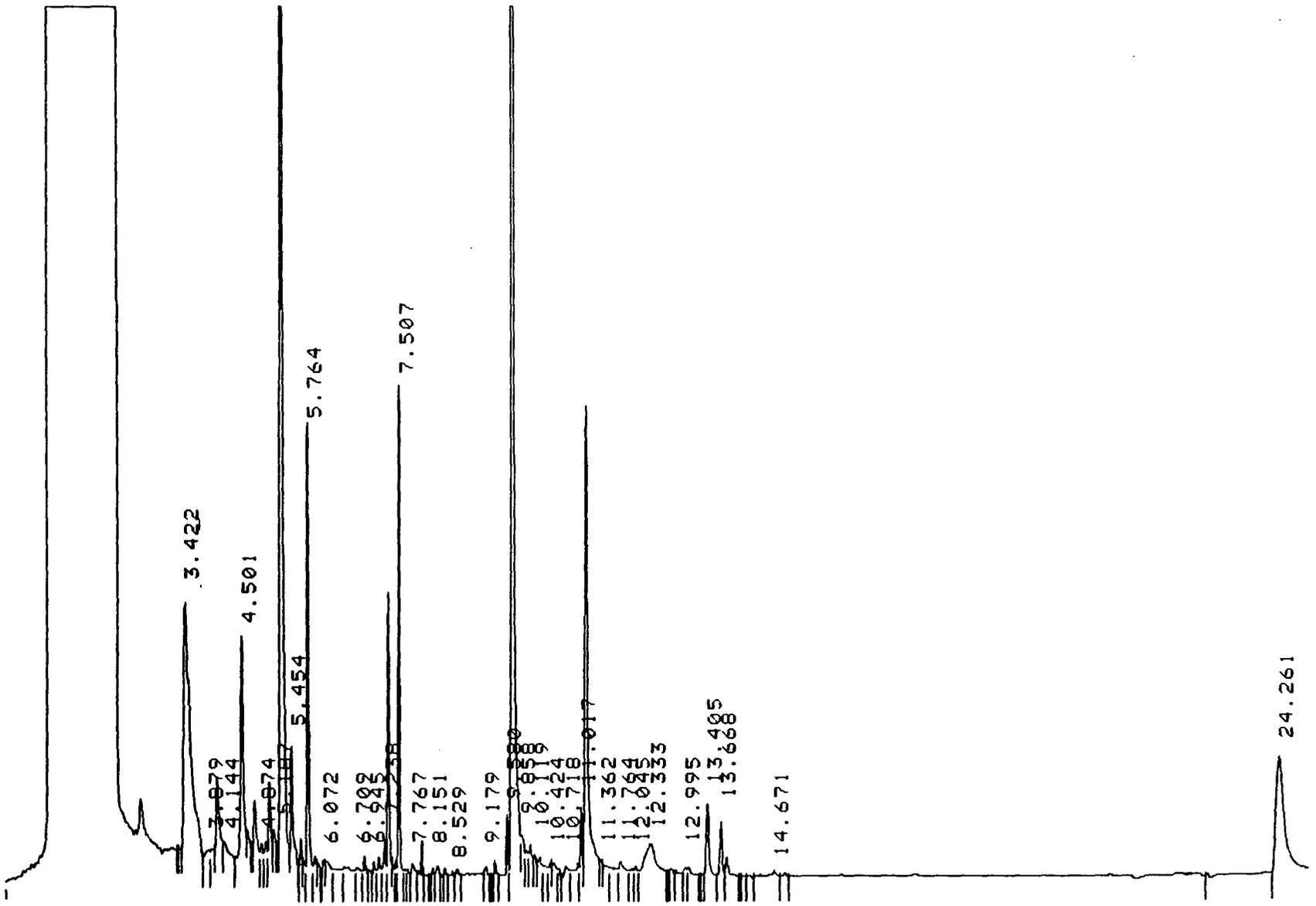


Figure 31. GC/ECD chromatogram of WP-482 Sample 3.

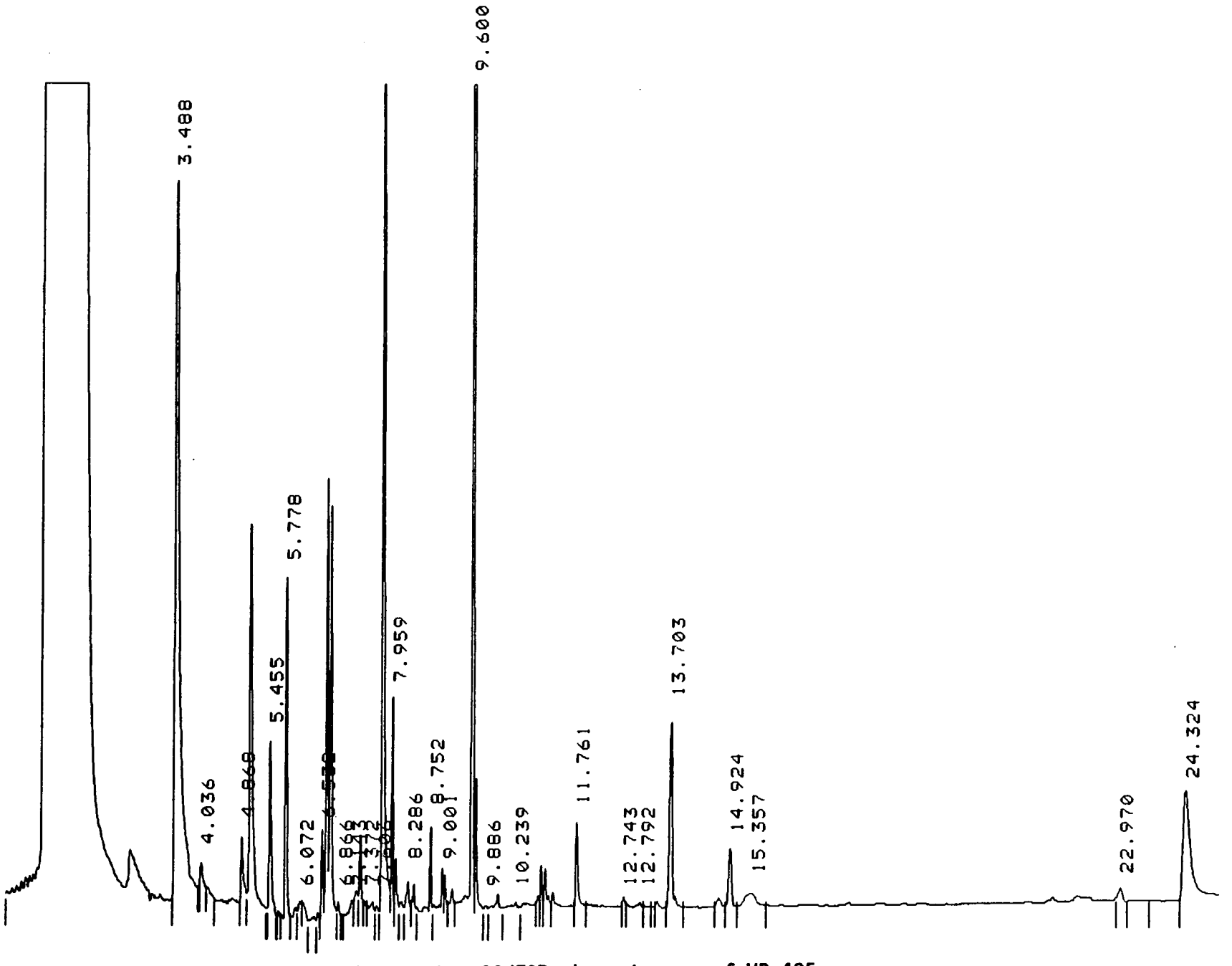


Figure 32. GC/ECD chromatogram of WP-485.

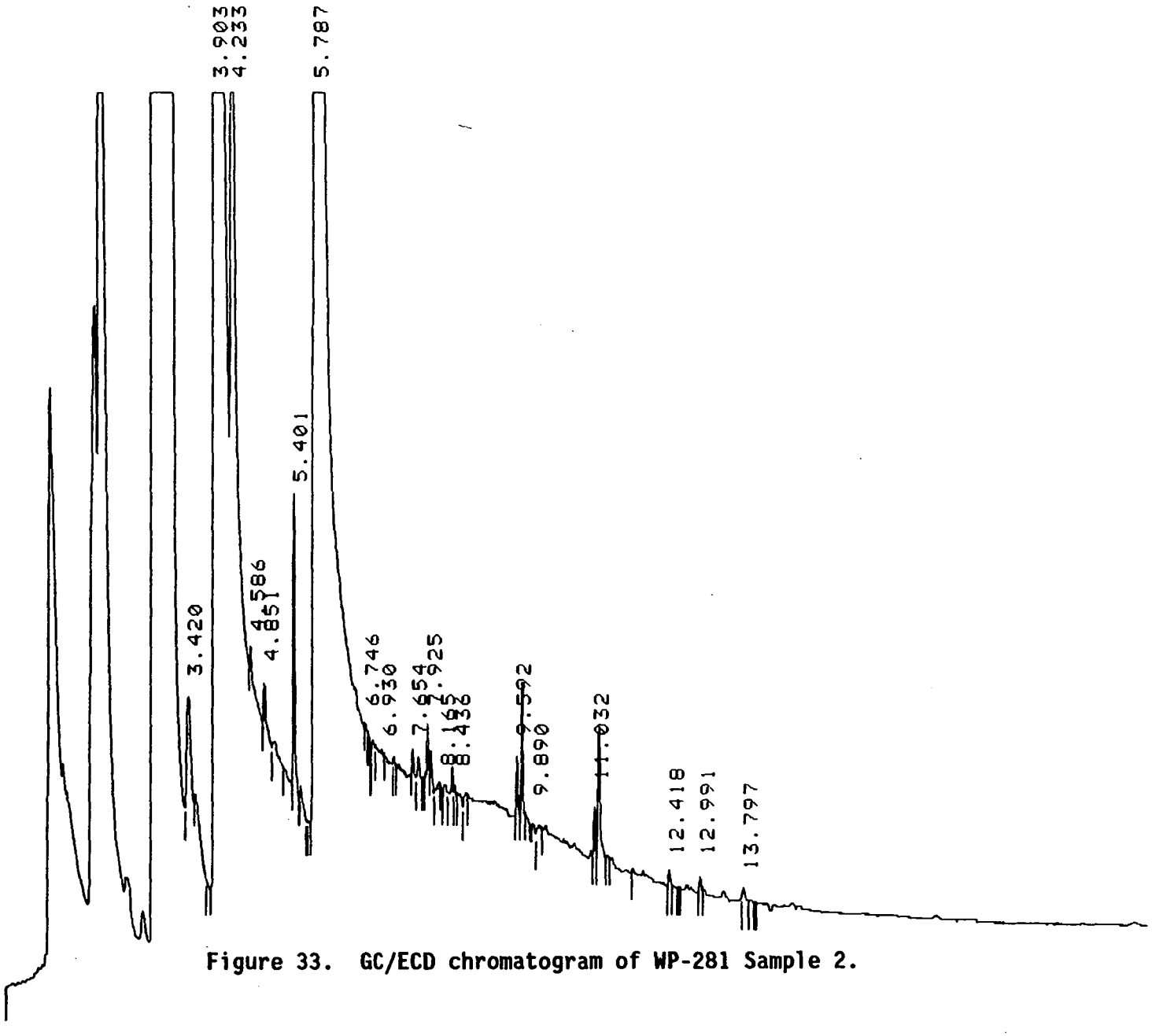


Figure 33. GC/ECD chromatogram of WP-281 Sample 2.

- Make an estimate of the detection limit from the concentration value that corresponds to an instrument signal-to-noise ratio in the range of 5 to 10. The data in Table 95 indicate that all 16 phthalate esters are detected in the 25-pg/µL standard. The GC/ECD chromatogram in Figure 39 indicates that BBP is significantly larger than the other phthalate esters. Consequently, this compound should be spiked at 10 times lower levels for MDL determination. Furthermore, DMP and DEP should be spiked at higher concentrations because the detector response to these compounds is low compared to DBP or DAP.

- Spike reagent water at a concentration that is in the same concentration range as the estimated method detection limit; in this case, the concentration is 200 ng/L for all compounds except BBP at 20 and DMP and DEP at 1,000 ng/L.

- Take seven aliquots of the spiked matrix and process each aliquot through the entire analytical process. Make all computations according to the protocol written for the revised Method 8060. Seven blank measurements are also performed to determine the concentrations of the 16 phthalate esters in the sample matrix (these values are then subtracted from the respective sample measurements).

- Calculate the standard deviation of the seven replicate measurements and compute the MDL as follows:

$$MDL = t_{(n-1,\ 0.99)} \times SD$$

where $t_{(n-1,\ 0.99)}$ is the student's t value appropriate for a 99 percent confidence level and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements. The value of t for 6 degrees of freedom is 3.143.

Table 95 presents the values found for each of the 16 phthalate esters in a hexane blank and six calibration standards at 0.5, 1.0, 5.0, 10, 25, and 50 pg/µL. The GC/ECD chromatograms of these analyses are shown in Figures 34 through 40. The results of method blank analyses with and without Florisil cleanup are shown in Tables 96 and 97, and the MDL data for water samples are summarized in Tables 98 and 99.

Approximate MDLs for soil samples can be derived from these data assuming that a 30 g soil sample is taken for extraction and the final extract volume is 10 mL.

6.6.5 Ruggedness Testing

A ruggedness test was performed for Method 8060 to determine how sensitive the method is to changes of the seven conditions identified in Table 100. They include: injector temperature, detector temperature, injection volume, time set up for the injector during which all sample is transferred to the fused-silica capillary column (splitless time), type of solvent, and matrix interferences from diesel hydrocarbons and chlorinated organochlorine pesticides. The seven conditions are assigned the letters A through G, and the altered values are assigned the same letters in the lower

TABLE 95. ESTIMATION OF THE INSTRUMENT DETECTION LIMIT

Compound	Retention time (min)	Concentration (pg/μL)[a]						
		Hexane blank	Std 0.5	Std 1.0	Std 5.0	Std 10	Std 25	Std 50
DMP	3.422	--	--	--	--	--	54	137
DEP	4.465	--	--	--	--	20	54	84
DIBP	6.496	--	--	--	2.3	22	22	69
DBP	7.161	--	4.2	13	10	29	29	58
BMPP	7.980	--	--	9.2	8.1	20	12	52
BMEP	7.417	--	--	19	7.8	30	28	59
DAP	8.433	--	--	--	15	15	20	41
BEEP	8.195	35	33	50	38	42	40	48
HEHP	8.656	--	--	--	8.1	21	30	47
DHP	9.638	22	25	39	31	30	43	53
BBP	9.715	7.0	8.6	10.3	14	19	32	53
BBEP	10.560	--	--	--	8.8	15	40	61
DEHP	11.157	6.2	9.6	14	14	24	35	60
DCP	11.011	3.4	4.4	16	10	18	30	53
DOP	13.067	--	--	--	--	26	31	67
DNP	16.049	--	--	--	--	--	23	75

[a] The value given was obtained by calibrating against a 50 pg/μL standard analyzed prior to the seven analyses shown in this table. Reproducibility of the injection technique is 2.87 percent as determined from the absolute response of the internal standard. The five standards (1 to 50 pg/μL) were obtained from a 100-pg/μL standard by appropriate dilutions; the 0.5-pg/μL standard was obtained from the 50-pg/μL standard. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

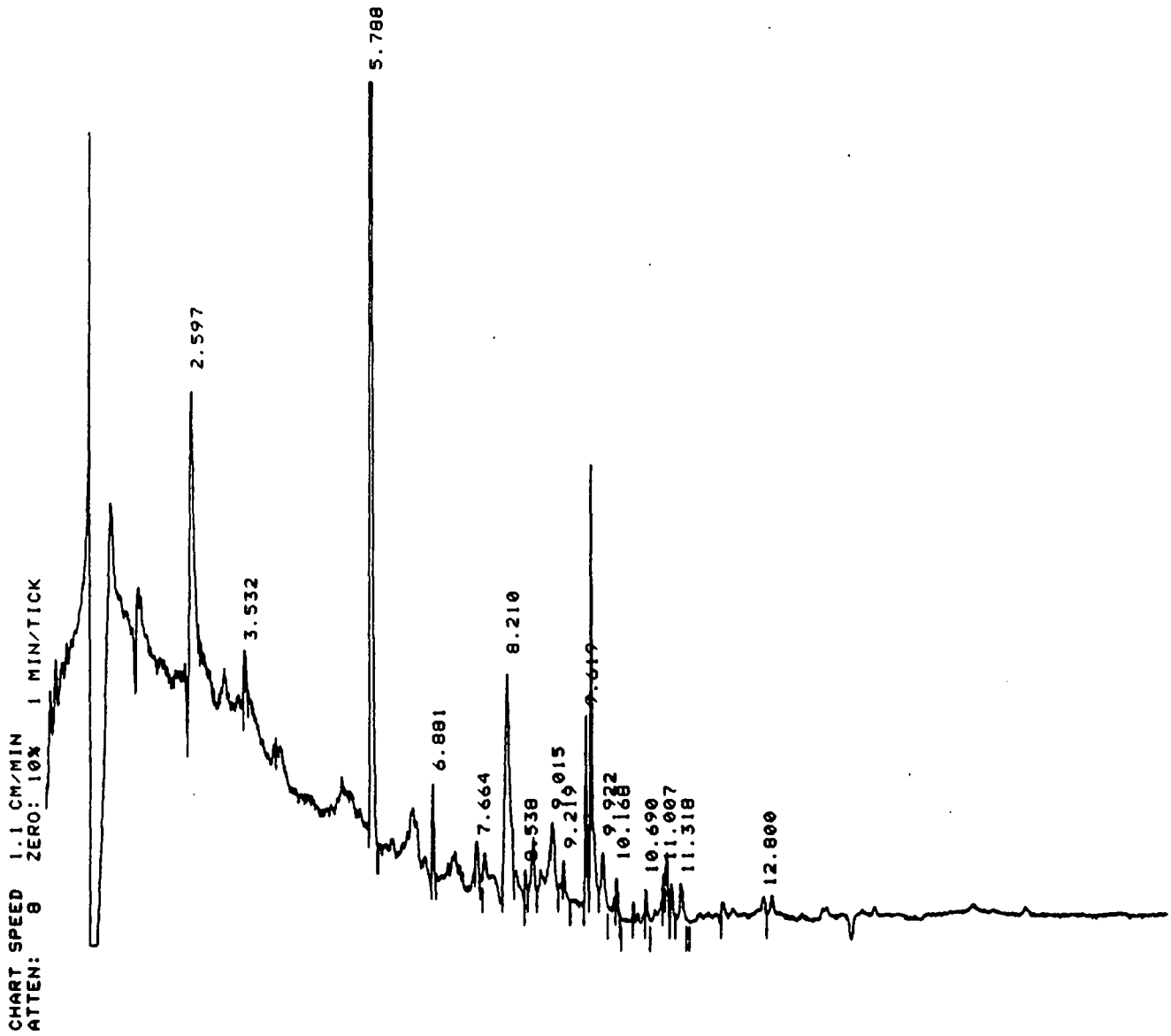


Figure 34. GC/ECD chromatogram of a hexane blank analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column; helium at 20 psi; temperature program: 120°C to 260°C (15.7 min hold) at 15°C/min, injector temperature 275°C; detector temperature 320°C; range 1; attn 8.

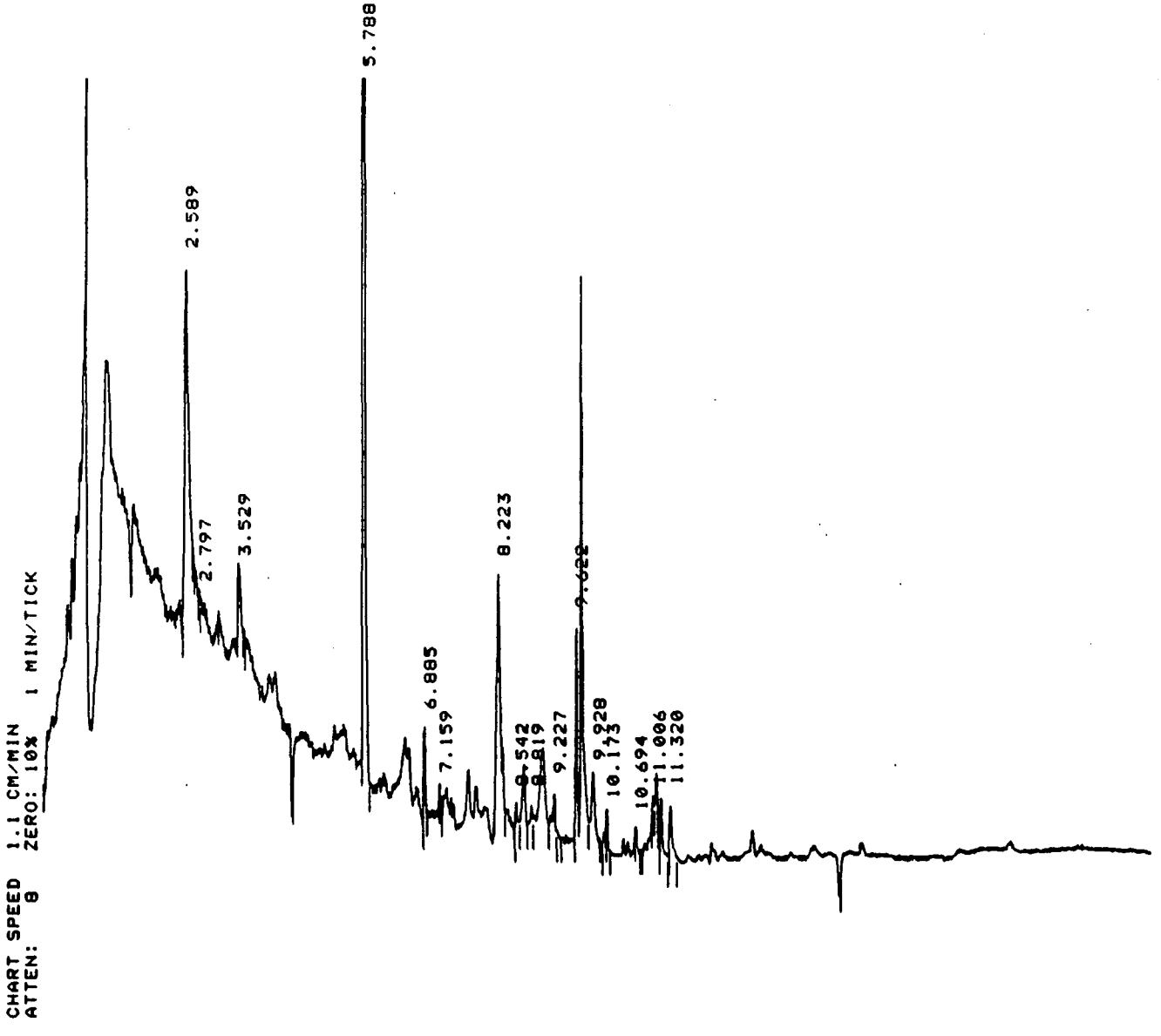


Figure 35. GC/ECD chromatogram of composite phthalate esters standard at 0.5 pg/μL analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column; helium at 20 psi; temperature program: 120°C to 260°C (15.7 min hold) at 15°C/min, injector temperature 275°C; detector temperature 320°C; range 1; attn 8.

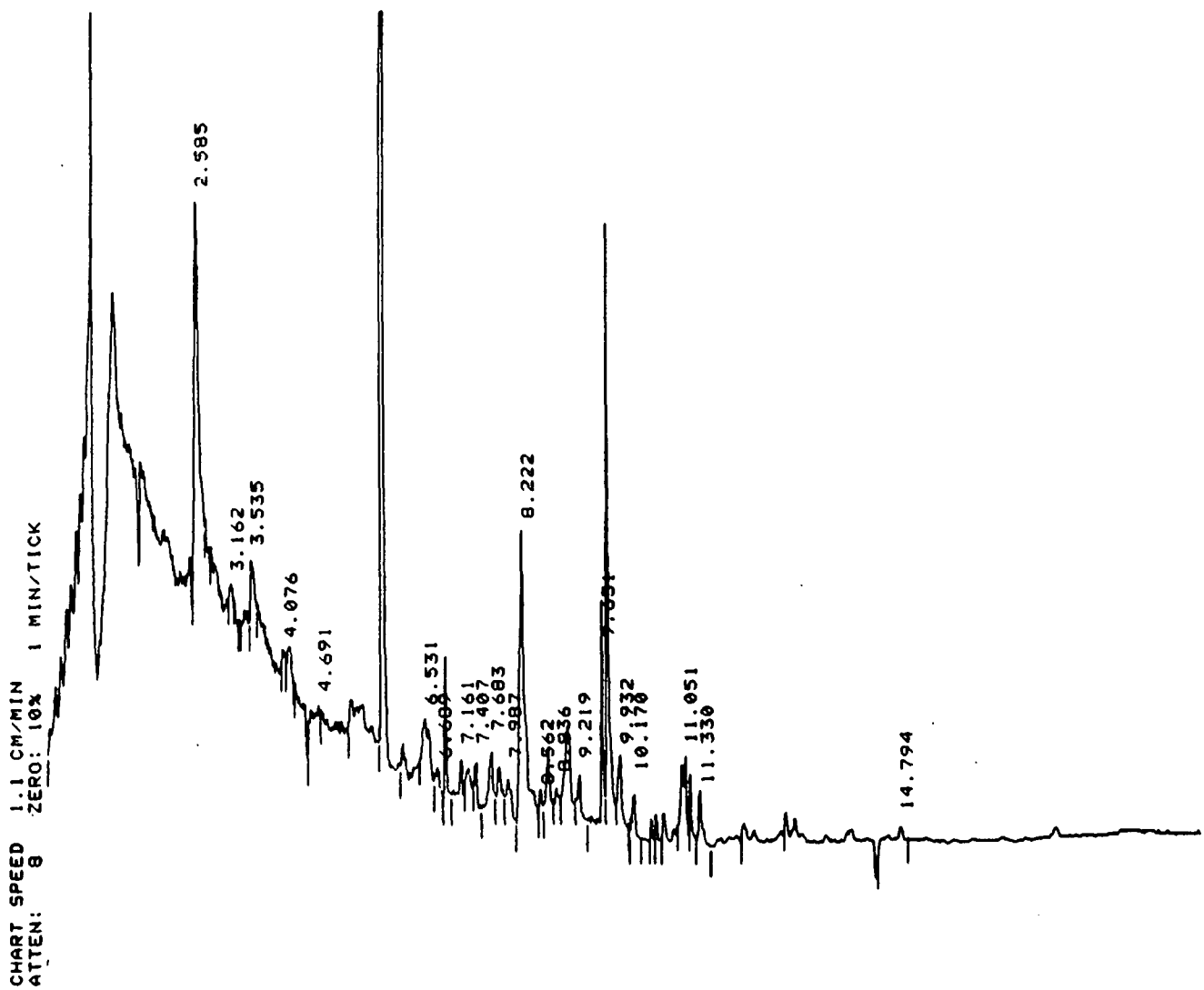


Figure 36. GC/ECD chromatogram of composite phthalate esters standard at 1 pg/μL analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column; helium at 20 psi; temperature program: 120°C to 260°C (15.7 min hold) at 15°C/min, injector temperature 275°C; detector temperature 320°C; range 1; attn 8.

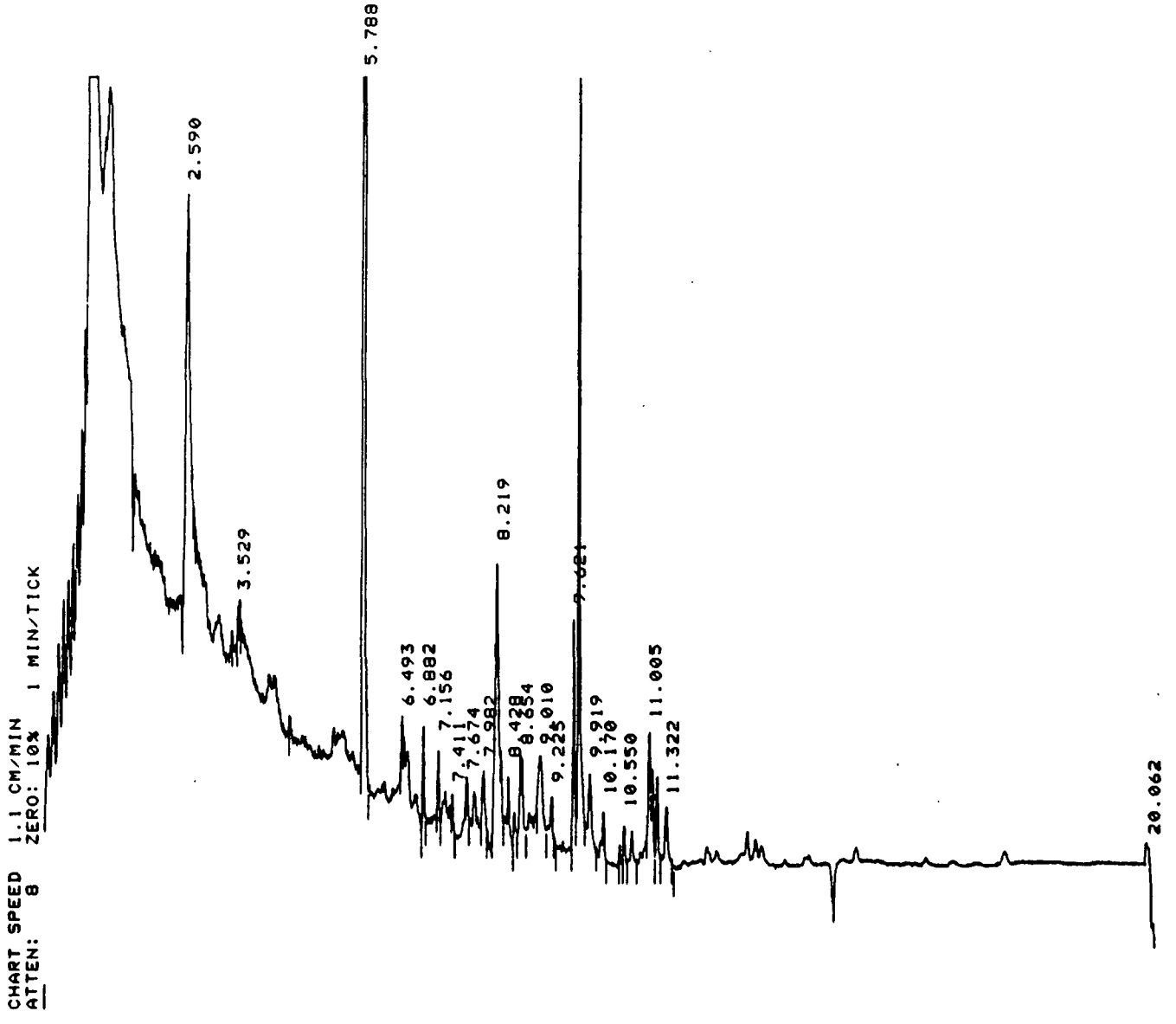


Figure 37. GC/ECD chromatogram of composite phthalate esters standard at 5 pg/μL analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column; helium at 20 psi; temperature program: 120°C to 260°C (15.7 min hold) at 15°C/min, injector temperature 275°C; detector temperature 320°C; range 1; attn 8.

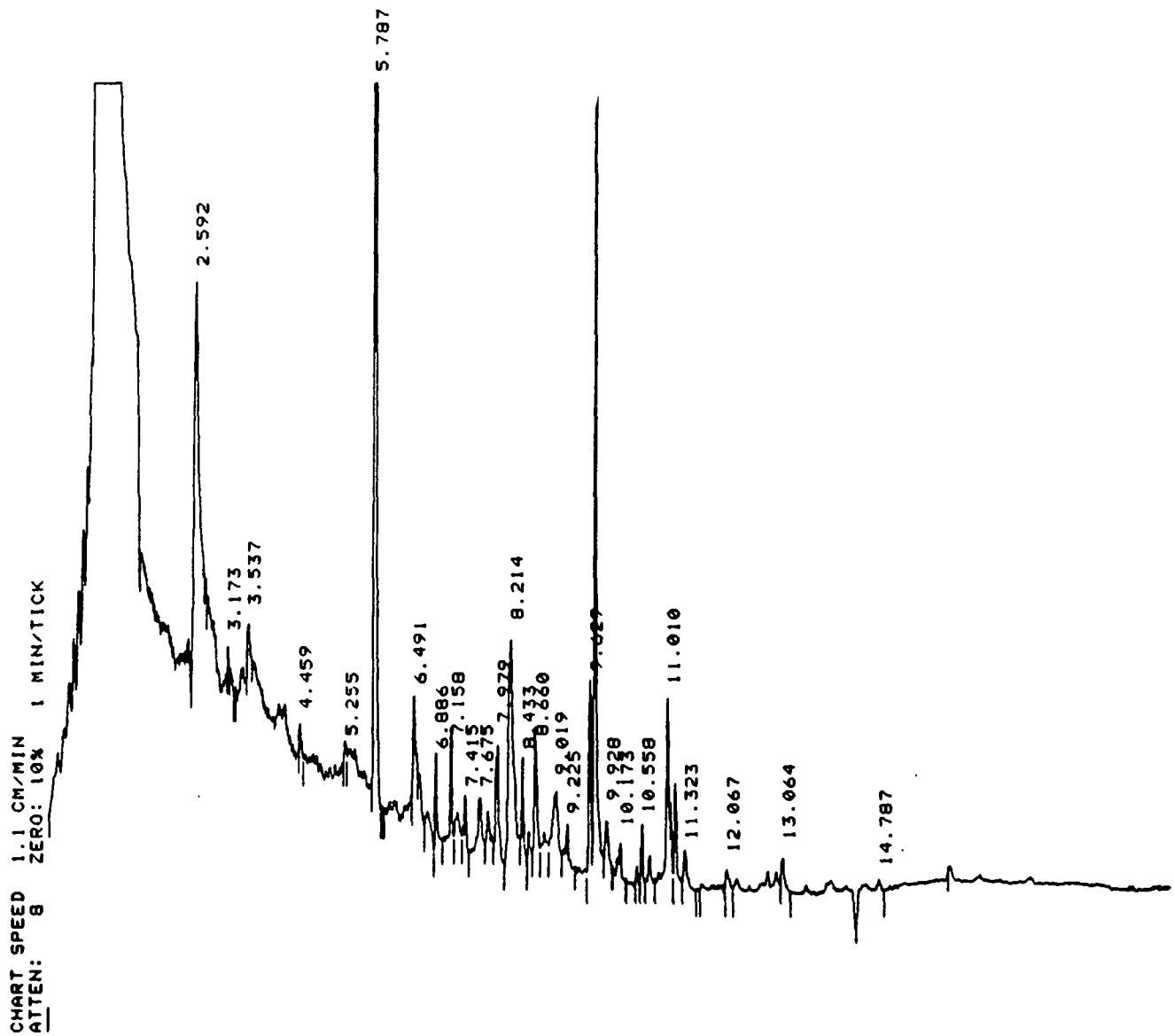


Figure 38. GC/ECD chromatogram of composite phthalate esters standard at 10 pg/μL analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column; helium at 20 psi; temperature program: 120°C to 260°C (15.7 min hold) at 15°C/min, injector temperature 275°C; detector temperature 320°C; range 1; attn 8.

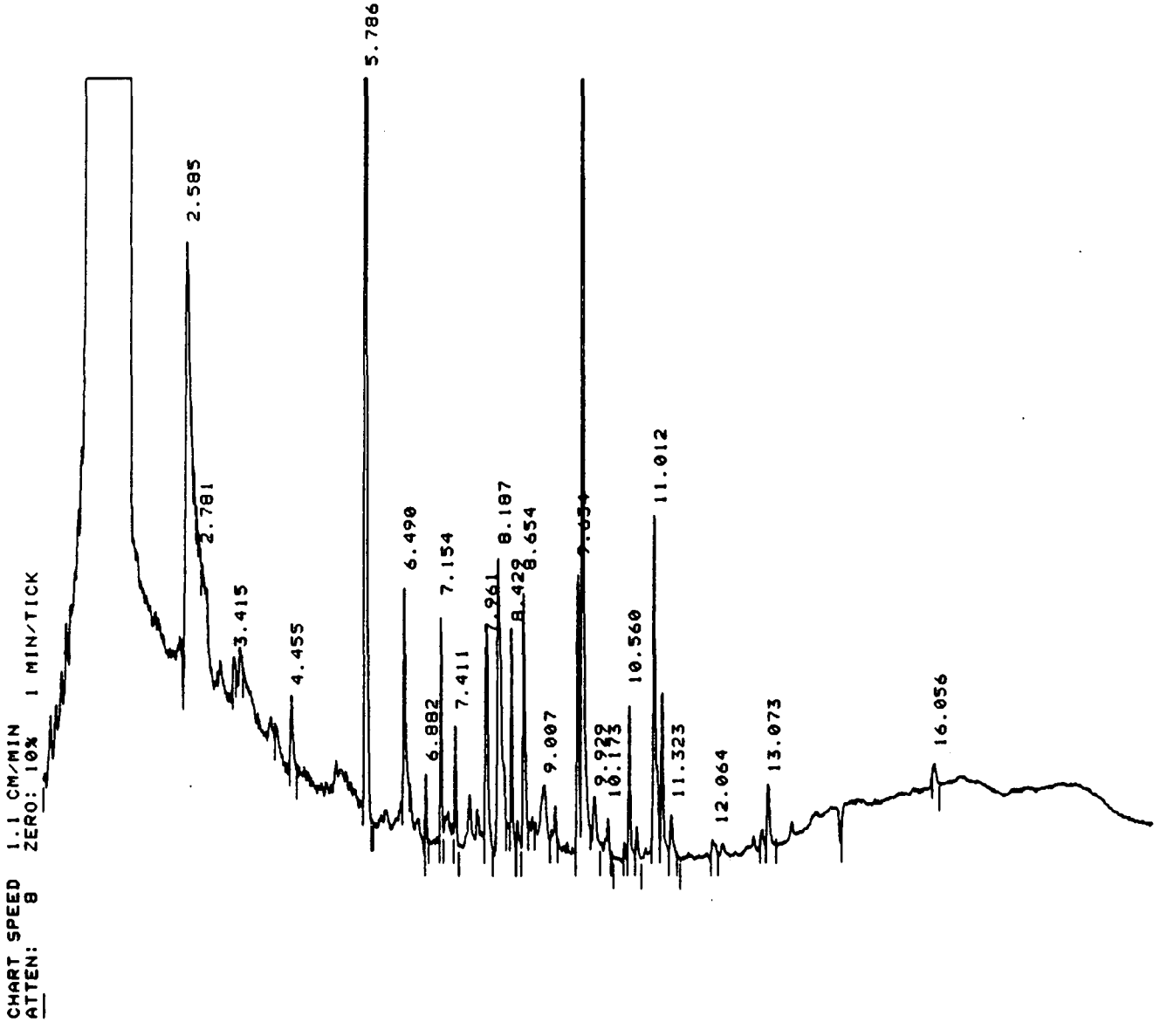


Figure 39. GC/ECD chromatogram of composite phthalate esters standard at 25 pg/μL analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column; helium at 20 psi; temperature program: 120°C to 260°C (15.7 min hold) at 15°C/min, injector temperature 275°C; detector temperature 320°C; range 1; attn 8.

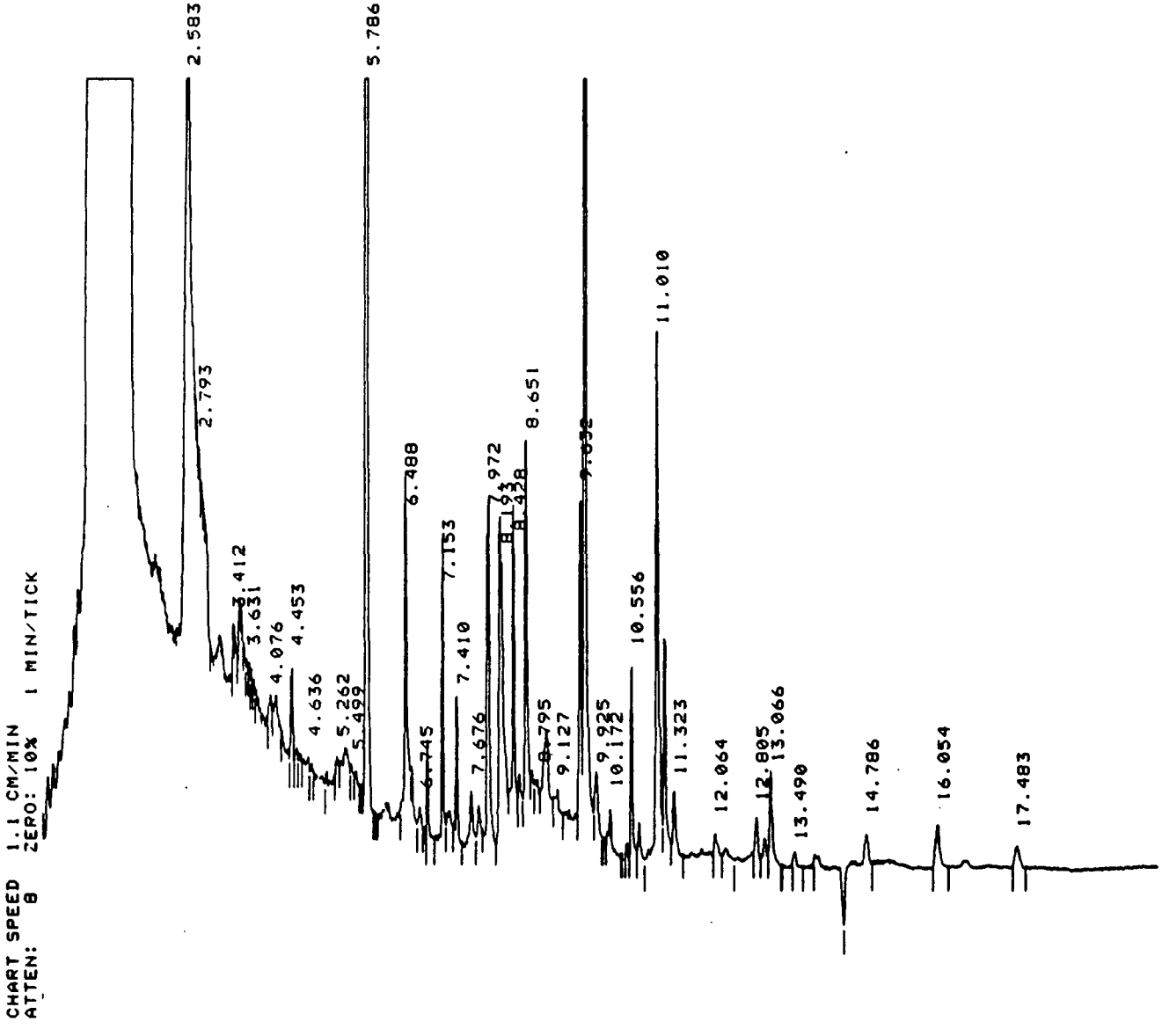


Figure 40. GC/ECD chromatogram of composite phthalate esters standard at 50 pg/μL analyzed on a 30 m x 0.25 mm ID DB-5 fused-silica capillary column; helium at 20 psi; temperature program: 120°C to 260°C (15.7 min hold) at 15°C/min, injector temperature 275°C; detector temperature 320°C; range 1; attn 8.

TABLE 96. RESULTS OF THE METHOD BLANK ANALYSES FOR THE MDL STUDY FOR WATER SAMPLES[a]

	Concentration (ng/L)						
Compound	Rep.1	Rep.2	Rep.4	Rep.5	Rep.6	Rep.7	Average ± SD
DMP							
DEP							
DIBP							
DBP	130	140	120	56		150	119 ± 37
BMPP							
BMEP							
BMPP							
DAP							
BEEP							
DAP							
HEHP							
DHP	400	160	110	220	57	170	186 ± 119
BBP	110	130	110	110	120	95	113 ± 12
BBEP							
DEHP	170	100	75	82	82	84	99 ± 36
DCP							
DOP							
DNP							
DPTP (percent recovery)	93	86	70	85	82	75	

[a] HPLC-grade water lot 880930 from Fisher Scientific. One-liter aliquots were extracted 3 times with 60 mL methylene chloride (American Burdick & Jackson, lot AR 348), and solvent-exchanged with hexane (American Burdick & Jackson, lot AQ 406). $V_{extract}$ was 10 mL. If no value is given, then the compound was not detected by GC/ECD. No Florisil cleanup was used. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 µm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

TABLE 97. METHOD DETECTION LIMIT STUDY -- FLORISIL DISPOSABLE CARTRIDGES METHOD BLANKS

	Concentration (ng/cartridge)[a]						
Compound	Rep.1	Rep.2	Rep.3	Rep.4	Rep.5	Average	SD
DMP	412	411	466	495	496	456	42
DEP	192	76.2	155	228	144	159	66
DIBP	94.7	96.6	107	119	107	105	10
DBP	129	116	142	162	132	136	17
BMPP	60.0	73.3	106	152	51.9	88.6	41
BMEP	303	134	302	291	282	262	72
DAP	28.4	40.3	140	33.6	22.0	52.9	49
BEEP	69.2	61.9	65.3	64.2	71.2	66.4	4
HEHP	43.9	16.2	40.3	12.9	4.7	23.6	17
DHP	32.9	29.3	31.6	35.8	33.2	32.6	2
BBP	16.6	16.1	16.6	24.3	18.2	18.4	3
BBEP	30.4	29.8	42.2	59.0	43.1	40.9	12
DEHP	295	267	332	320	243	291	37
DCP	<10	<10	<10	18.2	<10	<10	--
DOP	<10	<10	<10	13.8	<10	<10	--
DNP	<10	<10	<10	<10	<10	<10	--

[a] Each Florisil disposable cartridge (Supelco, Inc.) was eluted with 5 mL of 20 percent methylene chloride in hexane (Fraction 1) which was discarded, followed by 5 mL of hexane/acetone (9:1) which was concentrated to 1 mL and analyzed by GC/ECD. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.

TABLE 98. METHOD DETECTION LIMITS FOR WATER SAMPLES NOT SUBJECTED TO FLORISIL CARTRIDGE CLEANUP

Compound	Spike level (ng/L)	Concentration (ng/L)[a]									
		Rep.1	Rep.2	Rep.3	Rep.4	Rep.5	Rep.6	Rep.7	Average	SD	MDL
DMP	1,000	164	143	230	140	262	210	310	208	64	200
DEP	1,000	113	107	167	94.4	145	111	138	135	25.6	80
DIBP	200	63.0	61.0	53.4	42.2	42.8	39.8	57.0	51.3	9.6	30
DBP	200	155	163	382	89.4	90.8	216	246	192	102	320
BMPP	200	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	--	--
BMEP	200	154	127	216	50.2	113	220	228	158	66.8	210
DAP	200	7.3	33.2	41.6	10.7	13.1	25.0	47.0	25.4	15.7	49
BEEP	200	234	256	181	63.8	148	80.0	130	156	72.7	230
HEHP	200	262	220	182	230	187	200	197	183	76.9	240
DHP	200	188	173	178	145	149	150	212	171	24.7	78
BBP	20	67.4	60.8	82.8	58.0	73.8	92.4	166	85.9	37.5	120
BBEP	200	101	72.4	204	106	158	142	137	131	43.0	140
DEHP	200	90.0	97.2	a	114	134	b	164	120	30.1	95
DCP	200	37.0	37.2	61.2	34.4	33.8	44.2	95.8	49.1	22.7	71
DOP	200	[c]	[c]	78.8	[c]	[c]	[c]	67.0	72.9	8.3	26
DNP	200	14.4	16.0	[b]	[c]	[c]	[b]	64.4	31.6	28.4	89

[a] The values given were not corrected for the blank. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.
[b] Compound not quantitated because of interference.
[c] Not detected.

TABLE 99. METHOD DETECTION LIMITS FOR WATER SAMPLES SUBJECTED TO FLORISIL CARTRIDGE CLEANUP

Compound	Spike level (ng/L)	Concentration (ng/L)[a] Rep.1	Rep.2	Rep.3	Rep.4	Rep.5	Rep.6	Rep.7	Average	SD	MDL
DMP	1,000	650	496	458	292	800	776	836	615	205	640
DEP	1,000	450	416	370	334	498	384	250	387	79.6	250
DIBP	200	310	294	284	276	200	314	292	282	38.4	120
DBP	200	54	44	296	74	84	276	132	137	106	330
BMPP	200	65.6	111	226	406	154	67.0	188	174	118	370
BMEP	200	696	448	508	692	930	558	550	626	162	510
DAP	200	21.6	62.6	87.2	127	80.2	98.6	115	84.6	35	110
BEEP	200	44.2	61.0	209	32.2	51.2	213	189	114	84.5	270
HEHP	200	125	119	211	100	167	140	90.2	136	41.5	130
DHP	200	141	130	96.4	94.4	124	121	83	113	21.5	68
BBP	20	16.0	13.6	50.4	14.0	30.0	33.8	21.0	25.5	13.5	42
BBEP	200	174	172	198	152	222	154	152	175	26.6	84
DEHP	200	622	512	[b]	390	518	[b]	554	520	84.4	270
DCP	200	25.7	20.5	42.5	25.3	28.7	25.9	25.9	27.8	6.93	22
DOP	200	[c]	[c]	44.4	[c]	[c]	20.4	15.4	26.7	15.5	49
DNP	200	8.82	[c]	[b]	13.96	12.5	[b]	25.2	15.1	7.06	22

[a] The values given were not corrected for the blank. The GC/ECD operating conditions were as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column (0.25 μm film thickness); 120°C to 260°C (hold 15.7 min) at 15°C/min; carrier gas: helium at 21 psi; injector temperature 275°C; detector temperature 320°C; splitless injection.
[b] Not able to quantitate because of interference.
[c] Not detected.

TABLE 100. CONDITIONS VARIED AND ASSIGNED VALUES FOR GAS CHROMATOGRAPHIC ANALYSIS (METHOD 8060) FOR RUGGEDNESS TEST

Condition	No.	Letter	Value for capital letter	Value for lower case letter
Injector temperature (°C)	1	A,a	300	250
Detector temperature (°C)	2	B,b	350	300
Injection volume (μL)	3	C,c	3	1
Splitless time (sec)	4	D,d	60	30
Solvent	5	E,e	Hexane	Hexane/ethyl ether (80:20)
Interferences from matrix (diesel hydrocarbons)	6	F,f	With diesel hydrocarbons at 20 mg/mL	Without
Interferences from matrix (chlorinated pesticides)	7	G,g	With chlorinated pesticides at 0.5 ng/μL	Without

case (a through g). For example, the injector temperature is 300°C in the experiments 1 through 4 and 250°C in the experiments 5 through 8. Table 101 presents the design for the test of experimental conditions for the eight experiments.

Tables 102 and 103 present the analytical results. The group differences VA through VG were calculated using equations 1 through 7.

$$V_A = 1/4(s + t + u + v) - 1/4(w + x + y + z) = A-a \quad (1)$$

$$V_B = 1/4(s + t + w + x) - 1/4(u + v + y + z) = B-b \quad (2)$$

$$V_C = 1/4(s + u + w + y) - 1/4(t + v + x + z) = C-c \quad (3)$$

$$V_D = 1/4(s + t + y + z) - 1/4(u + v + w + x) = D-d \quad (4)$$

$$V_E = 1/4(s + u + x + z) - 1/4(t + v + w + y) = E-e \quad (5)$$

$$V_F = 1/4(s + v + w + z) - 1/4(t + u + x + y) = F-f \quad (6)$$

$$V_G = 1/4(s + v + x + y) - 1/4(t + u + w + z) = G-g \quad (7)$$

It appears from the data presented in Table 103 that only certain compounds are affected by changes of the various parameters in the GC procedure. DAP seems to be affected the most, followed by BMEP and the internal standard. This is not unexpected since diesel fuel components and the organochlorine pesticides overlap with these compounds, making their identification difficult, if not impossible. We have noted during the performance of the ruggedness test that the detector sensitivity decreased drastically after the diesel- or the organochlorine pesticide-containing working solutions were analyzed. It is therefore imperative that such interferents be eliminated prior to the gas chromatographic analysis, otherwise the data obtained for samples containing such interferences are unreliable.

6.6.6 Confirmation by GC/MS

Table 104 gives the retention times (as scan numbers) for 16 phthalate esters, benzyl benzoate, and 5 other compounds proposed as surrogate compounds in the revised Method 8060. A GC/MS chromatogram of a composite standard containing 16 phthalate esters is shown in Figure 41. Mass spectra in both the plot and list format are included in Appendix C of this final report. The concentration of the composite standard is 10 ng/µL per compound. The sensitivity of the GC/MS instrument is estimated to approximately 1 to 2 ng per compound.

TABLE 101. DESIGN FOR RUGGEDNESS TEST OF EXPERIMENTAL CONDITIONS

Experimental condition	Values of conditions in determination No.							
	1	2	3	4	5	6	7	8
1	A	A	A	A	a	a	a	a
2	B	B	b	b	B	B	b	b
3	C	c	C	c	C	c	C	c
4	D	D	d	d	d	d	D	D
5	E	e	E	e	e	E	e	E
6	F	f	f	F	F	f	f	F
7	G	g	g	G	g	G	G	g

TABLE 102. RUGGEDNESS TEST FOR METHOD 8060 -- CONCENTRATIONS OF TEST COMPOUNDS FOUND FOR EACH EXPERIMENT

	Concentration (μg/mL)							
Compound	Exp 1	Exp 2	Exp 3	Exp 4	Exp 5	Exp 6	Exp 7	Exp 8
DMP	1.77	6.24	2.47	1.87	4.18	7.86	3.49	0.266
DEP	2.81	5.24	2.16	1.04	4.14	9.58	5.81	2.56
BB-IS	0.93	10.5	3.74	224	1.61	258	185	6.52
DIBP	9.07	8.40	2.61	5.18	0.483	12.6	3.06	0.218
DBP	5.99	7.86	2.08	1.92	0.654	17.1	4.40	2.92
BMPP	49.8	8.66	3.40	96.2	0.068	172	67.3	20.2
BMEP	0.773	8.58	3.97	300	0.798	360	174	6.52
DAP	0.534	7.88	2.11	0.062	0.268	828	285	3.06
BEEP	0.247	7.16	3.26	4.30	2.74	7.20	3.84	2.46
HEHP	0.927	8.76	3.69	0.054	2.97	5.54	1.83	0.136
DHP	4.11	9.30	2.60	0.052	2.42	17.3	5.33	1.54
BBP	4.39	9.56	4.06	6.60	4.27	6.38	4.09	6.30
BBEP	57.3	7.86	3.04	88.2	2.72	162	68.0	3.18
DEHP	2.98	7.26	3.32	3.38	3.12	7.22	4.46	3.20
DCP	2.63	7.46	4.15	2.28	3.40	7.82	5.21	2.16
DPTP	5.79	10.3	4.61	7.90	4.68	3.56	5.06	7.14
DOP	2.22	7.52	3.33	2.62	2.57	5.50	4.72	3.78
DNP	2.81	6.58	3.26	2.42	2.75	5.88	4.81	2.86

TABLE 103. RUGGEDNESS TEST FOR METHOD 8060 -- GROUP DIFFERENCES FOR THE TEST COMPOUNDS

	Condition						
Compound	(1)	(2)	(3)	(4)	(5)	(6)	(7)
DMP	-0.86	2.99	-1.08	-1.15	-0.85	-2.99	0.46
DEP	-2.71	2.55	-0.88	-0.13	0.22	-3.06	1.29
BB-IS	-52.97	-37.03	-76.91	-71.13	-38.01	-56.07	161.42
DIBP	2.22	4.87	-2.79	-0.03	1.84	-2.93	4.55
DBP	-1.81	5.07	-4.17	-0.15	3.31	-4.99	3.97
BMPP	-25.38	10.86	-44.12	-31.43	18.29	-21.27	88.24
BMEP	-57.00	-28.58	-123.89	-118.72	-28.03	-59.61	203.73
DAP	-276.44	136.61	-137.77	-133.49	135.12	-279.77	275.07
BEEP	-0.32	0.87	-2.76	-0.95	-1.22	-2.93	-0.01
HEHP	0.74	3.12	-1.27	-0.15	-0.83	-3.93	-1.80
DHP	-2.63	5.90	-3.43	-0.52	2.11	-6.60	2.73
BBP	0.89	0.89	-3.01	0.76	-0.85	-0.63	-0.68
BBEP	-19.88	16.87	-32.55	-29.91	14.69	-22.38	89.68
DEHP	-0.27	1.56	-1.80	0.22	-0.38	-2.40	0.28
DCP	-0.52	1.88	-1.08	-0.05	-0.40	-3.54	0.19
DPTP	2.04	-0.09	-2.19	1.89	-1.71	0.49	-1.11
DOP	-0.22	0.84	-1.65	1.06	-0.65	-2.47	-0.53
DNP	-0.31	1.17	-1.03	0.69	-0.44	-2.42	0.12

TABLE 104. RETENTION TIMES (SCAN NUMBERS) AND THREE MOST INTENSE PEAKS IN THE MASS SPECTRA OF METHOD 8060 COMPOUNDS[a]

Compound No.	Compound name	Scan number	Mass spectrum m/z (relative intensity)
1	DMP	1128	163 (100), 77 (21), 164 (10)
2	DEP	1264	149 (100), 177 (23), 150 (12)
3	DIBP	1499	149 (100), 57 (28), 41 (13)
4	DBP	1573	149 (100), 41 (9.2), 150 (8.9)
5	BMPP	1662	149 (100), 85 (66), 43 (66)
6	BMEP	1602	59 (100), 58 (73), 149 (13)
7	DAP	1714	149 (100), 43 (19), 150 (8.8)
8	BEEP	1687	45 (100), 72 (94), 73 (92)
9	HEHP	1737	149 (100), 57 (19), 55 (12)
10	DHP	1844	149 (100), 43 (21), 41 (8.4)
11	BBP	1851	149 (100), 91 (69), 206 (26)
12	BBEP	1928	57 (100), 56 (82), 45 (80)
13	DEHP	1973	149 (100), 57 (39), 167 (36)
14	DCP	1962	149 (100), 167 (34), 55 (24)
15	DOP	2082	149 (100), 43 (14), 57 (12)
16	DNP	2191	149 (100), 43 (18), 150 (9.8)
	BB (IS)	1397	105 (100), 91 (43), 77 (28)
	DPP (SU)	1959	225 (100), 77 (39), 226 (15)
	DPIP (SU)	2057	225 (100), 76 (27), 104 (23)
	DPTP (SU)	2061	225 (100), 104 (44), 76 (20)
	DBZP (SU)	2087	107 (100), 91 (81), 149 (70)
	DOIP (SU)	2127	167 (100), 279 (41), 149 (21)

[a]The GC/MS operating conditions are given in Section 5.7.

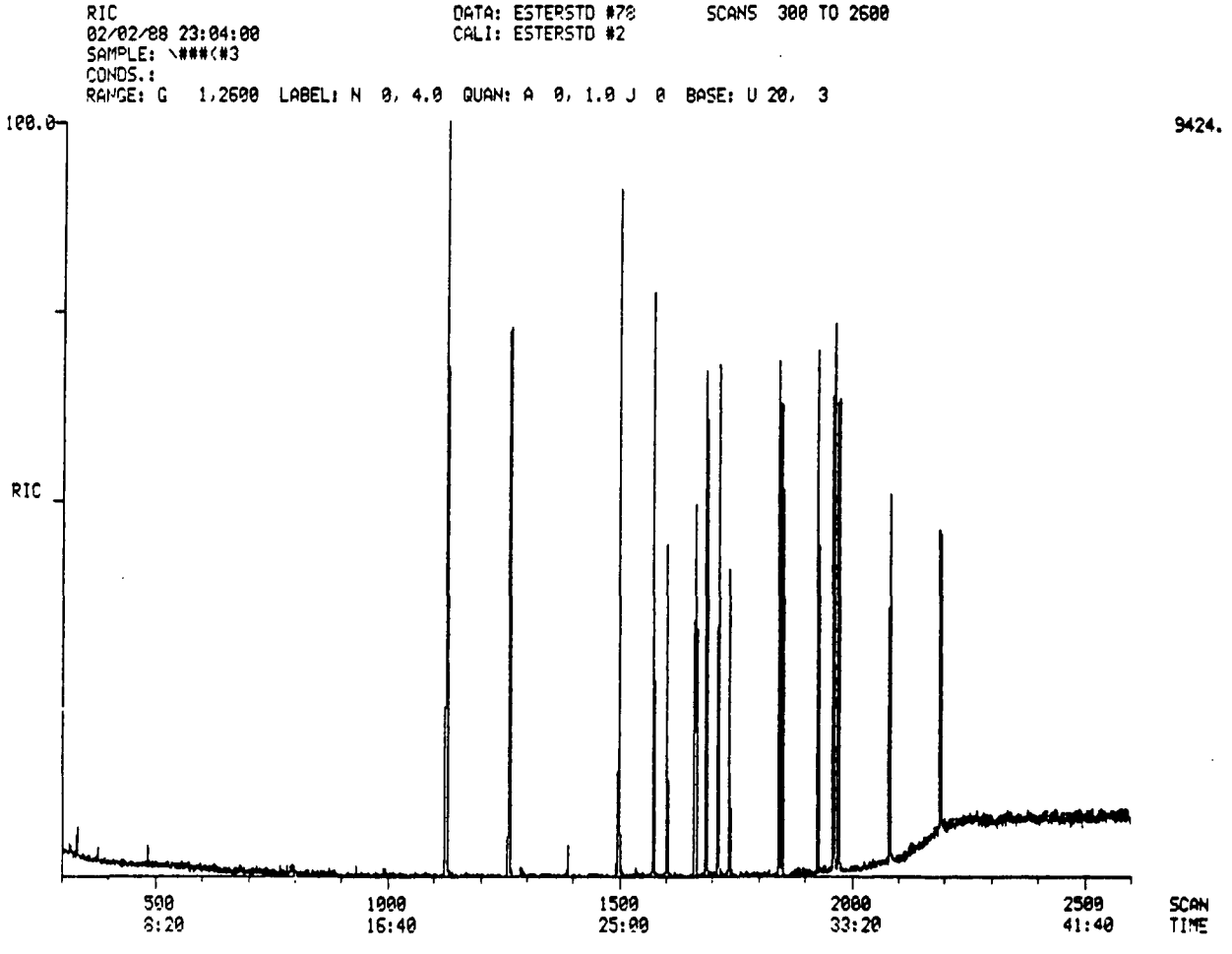


Figure 41. GC/MS chromatogram of composite standard containing the 16 phthalate esters listed in Table 104. The GC/MS operating conditions are given in Section 5.7.

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APPENDIX A

SINGLE-LABORATORY EVALUATION OF METHOD 8060, "PHTHALATE ESTERS" LITERATURE REVIEW

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SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) of 1976 and its elements require the Environmental Protection Agency (EPA) to regulate hazardous waste activities. Implementation and enforcement of RCRA requires analytical methodologies that will provide reliable data. The document "Test Methods for Evaluating Solid Waste, Office of Solid Waste Manual SW-846" (1), revised recently, provides a compilation of methods for evaluating RCRA solid wastes for environmental and human health hazards. The SW-846 Method 8060 addresses the determination of phthalate esters.

This report presents a literature review pertinent to this study. This literature review was performed using the computerized Chemical Abstracts search and several EPA reports dealing with the analysis of organic compounds in water. Furthermore, recent issues of Analytical Chemistry, the Journal of Chromatography, the Journal of Chromatographic Science, the Association of Official Analytical Chemists Journal, and Environmental Science and Technology were searched for information that had not yet been entered in the computer data bases.

The computer searches were performed using DIALOG. Chemical Abstracts files were searched back to 1977 for all references containing "phthalate esters," "gas chromatography," "extraction," and "cleanup." Eighty articles that were judged to be scientifically relevant to the objectives of this study were retrieved for the literature review.

The literature review summary that is presented in this report addresses the following:

- Sample preservation techniques
- Extraction techniques for water, soil, and sediment samples
- Sample extract cleanup techniques
- Gas chromatographic analysis (columns, retention time information, chromatographic problems)
- Compound confirmation
- Background contamination by phthalate esters.

SECTION 2

PHTHALATE ESTER STRUCTURES, PHYSICO-CHEMICAL PROPERTIES, PRODUCTION AND USES

2.1 PHTHALATE ESTER STRUCTURES AND PHYSICO-CHEMICAL PROPERTIES

Phthalate esters or phthalic acid esters are esters of phthalic acid or 1,2-benzene dicarboxylic acid.

The chemical structures, common names, Chemical Abstracts Registry Numbers (CAS), and alternate names for the 17 phthalate esters proposed for evaluation in this study are given in Table 1. Their physico-chemical properties are listed in Table 2.

In general, these compounds have low vapor pressures, low water solubilities, and high boiling points. They are colorless, odorless, viscous liquids under ambient conditions. As the lengths of the ester chains increase, the phthalate ester volatility decreases. The branching of the ester chain has the opposite effect on volatility.

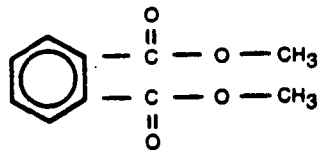
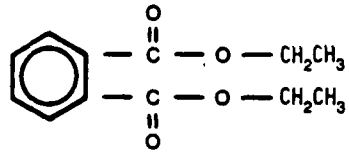
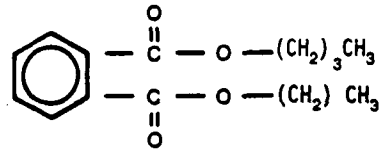
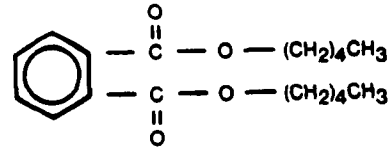
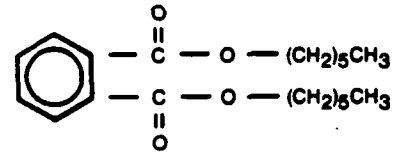
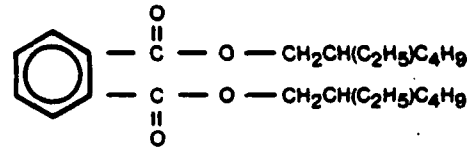
Chemical hydrolysis of the esters to the carboxylic acid and the alcohol in the presence of acid or base has been reported to occur (2). Acid hydrolysis is usually reversible, whereas alkaline hydrolysis is irreversible. Hydrolytic half-lives of 80 to 4000 days for a series of dialkyl phthalates at pH 8 and 30°C were reported (3). Photolytic degradation of the phthalate esters does not seem to be a major degradation pathway. Gledhill et al. (4) reported no significant decrease in BBP concentrations in water after 28 days for samples exposed to sunlight, as opposed to controls kept in the dark.

2.2 PRODUCTION AND USES

Phthalate esters are synthesized from phthalic anhydride which is made either from naphthalene or ortho-xylene by oxidation in the presence of vanadium pentoxide. The anhydride is further esterified with an alcohol at high temperature or in the presence of sulfuric acid.

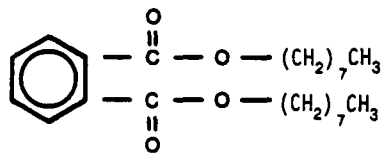
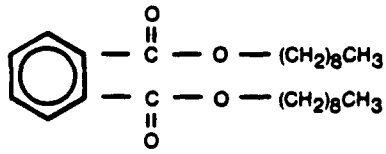
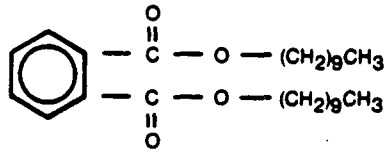
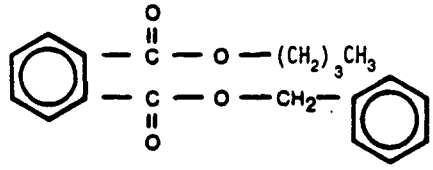
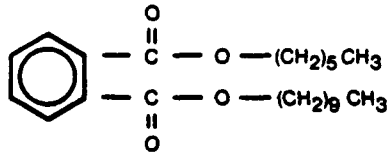
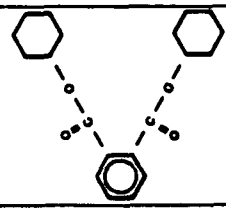
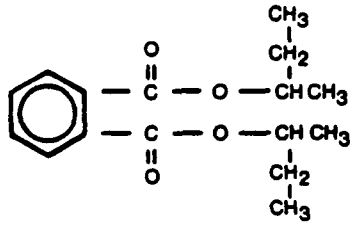
The annual production of phthalate esters in the United States amounted to more than 2×10^9 lb in 1978 (5). Although an accurate estimate of their uses is not available, most of the phthalate esters produced are used as plasticizers for polymers. Among the various plasticizers produced in the United States, the phthalate esters represent approximately 60 percent of the total amount produced (Table 3). The main uses of the plastics containing phthalates are in building and construction (e.g., wire and cable, flooring, swimming pool liners), home furnishings (e.g., furniture upholstery, wall coverings, housewares), cars, wearing apparel, food wrapping and closures,

TABLE 1. THE CHEMICAL STRUCTURES AND NOMENCLATURES OF THE PHTHALATE ESTERS

Compound name	Chemical structure	Chemical Abstracts Registry no.	Alternate names
Dimethyl phthalate		131-11-3	DMP 1,2-Benzenedicarboxylic acid, dimethyl ester Phthalic acid dimethyl ester Methyl phthalate
Diethyl phthalate		84-66-2	DEP 1,2-Benzenedicarboxylic acid, diethyl ester Ethyl phthalate
Di-n-butyl phthalate		84-74-2	DBP o-Benzenedicarboxylic acid, dibutyl ester Dibutyl phthalate Benzene-o-dicarboxylic acid, di-n-butyl ester n-Butyl phthalate
Diamyl phthalate		131-18-0	DAP o-Benzenedicarboxylic acid, di-n-pentyl ester Di-n-pentyl phthalate Amyl phthalate Pentyl phthalate
Dihexyl phthalate		84-75-3	DHP o-Benzenedicarboxylic acid, di-n-hexyl ester Di-n-hexyl phthalate Hexyl phthalate
Bis(2-ethylhexyl) phthalate		117-81-7	DEHP Di(2-ethylhexyl) phthalate Bis(2-ethylhexyl) ester, phthalic acid Di-sec-octyl phthalate Di(2-ethylhexyl)-orthophthalate 2-Ethylhexyl phthalate 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester

(continued)

TABLE 1. (continued)

Compound name	Chemical structure	Chemical Abstracts Registry no.	Alternate names
Di-n-octyl phthalate		117-84-0	DOP o-Benzenedicarboxylic acid, dioctyl ester n-Dioctyl phthalate Octyl phthalate Dioctyl-o-benzenedi-carboxylate
Dinonyl phthalate		84-76-4	DNP o-Benzenedicarboxylic acid, di-n-nonyl ester Di-n-nonyl phthalate Nonyl phthalate
Didecyl phthalate		84-77-5	DDP o-Benzenedicarboxylic acid, di-n-decyl ester Di-n-decyl phthalate Decyl phthalate
Butyl benzyl phthalate		85-68-7	BBP Benzyl butyl phthalate Butyl benzyl phthalate
Hexyldecyl phthalate		25724-58-7	HDP o-Benzenedicarboxylic acid, n-hexyl-n-decyl ester Decylhexyl phthalate
Dicyclohexyl phthalate		84-61-7	DCP o-Benzenedicarboxylic acid, di-cyclohexyl ester Cyclohexyl phthalate
Diisobutyl phthalate		84-69-5	DIBP o-Benzenedicarboxylic acid, di-(2-n-butyl) ester Di-isobutyl phthalate Isobutyl phthalate

(continued)

TABLE 1. (concluded)

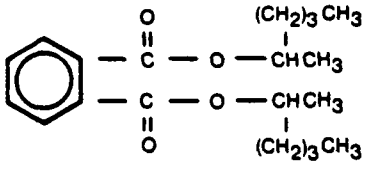
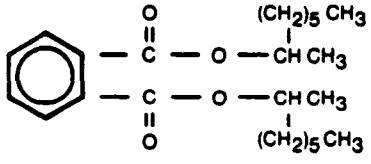
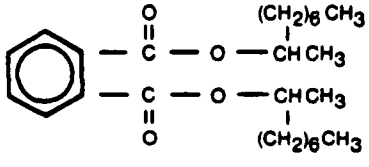
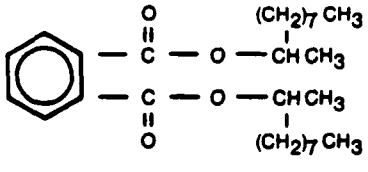
Compound name	Chemical structure	Chemical Abstracts Registry no.	Alternate names
Diisohexyl phthalate			DIHP o-Benzenedicarboxylic acid, di-(2-n-hexyl) ester Di-isohexyl phthalate Isohexyl phthalate
Diisooctyl phthalate		27554-26-3	DIOP o-Benzenedicarboxylic acid, di-(2-n-octyl) ester Di-isooctyl phthalate Isooctyl phthalate
Diisononyl phthalate		28553-12-0	DINP o-Benzenedicarboxylic acid, di(2-n-nonyl) ester Di-isononyl phthalate Isononyl phthalate
Diisodecyl phthalate		26761-40-0	DIDP o-Benzenedicarboxylic acid, di-(2-n-decyl) ester Di-isodecyl phthalate Isodecyl phthalate

TABLE 2. PHYSICAL PROPERTIES OF PHTHALATE ESTERS[a]

Phthalate	Molecular weight	Melting point °C	Boiling point °C (torr)	Vapor pressure (torr)	Water solubility (mg/L)	Log octanol/water partition coefficient
Dimethyl	194[b]	0[e]	282 (760)[e]	<0.01 (20°C)[b]	5000 (20°C)[d] 4000 (32°C)[h] 4320 (25°C)[i]	2.12[j,k]
Diethyl	222[b]	-40.5[b]	298 (760)[e]	0.05 (70°C)[b]	1000 (32°C)[h] 896 (25°C)[i]	3.22[j,k]
Di-n-butyl	278[c]	-35[e]	340 (760)[b]	0.1 (115°C)[b]	13 (25°C)[i]	5.2[j,k,l]
Diamyl	306	<-55[m]	342[m]			
Dihexyl	334			1.9 x 10-3[n]	0.24[n]	5.65 to 5.93[n]
Bis(2-ethylhexyl)	390[b]	-50[b]	386.9 (5)[b]	<0.01 (20°C)[b] 2 x 10-7 (20°C)[g]	0.4 (25°C)[i] 1.3[g]	8.7[j,k,l] 5.3[j]
Di-n-octyl	390[b]	-25[b]	220 (4)[b]	<0.2 (150°C)[b]	3 (25°C)[i]	9.2[j,k,l]
Dinonyl	418					
Didecyl	446					
Butyl benzyl	312[d]	-35[f]	377 (760)[f]		2.9[g]	5.8[j,k] 4.8[f]
Hexyldecyl	390					
Dicyclohexyl	330	58 to 65[m]	212 to 218[m]			
Diisobutyl	278		295 to 298[m]			
Diisohexyl	334					
Diisooctyl	390	<-50[m]	228 to 239[m]	7.5 x 10-4	0.09[n]	
Diisononyl	418			7.2 x 10-5[n]	0.2[n]	
Diisodecyl	446	-48[m]	255 (5)[m]		1.19[n]	

[a]Data taken from References 7,8,9.
[b] Patty 1963 cited in Reference 7.
[c] Weast 1977 cited in Reference 7.
[d] Fishbein and Albro 1972 cited in Reference 7.
[d] Verschueren 1977 cited in Reference 7.
[f] EPA-OHMIADS cited in Reference 7.
[g] Iilrzy et al. 1978 cited in Reference 7.
[h] Peakall 1975 cited in Reference 7.
[i] Determined by Wolfe et al. 1979 cited in Reference 7.
[j] Calculated as per Leo et al. 1971 cited in Reference 7.
[k] Calculated by Wolfe et al. 1979 cited in Reference 7.
[l] Value does not include a correction for the influence of molecular folding because data are not available; cited in Reference 7.
[m]Data taken from Reference 8.
[n] Data taken from Reference 9.

TABLE 3. PLASTICIZER PRODUCTION IN THE UNITED STATES[a]

Plasticizer	Production ($x\ 10^6$ lb)
Phthalic acid esters -- total	1,259
Dioctyl phthalate[b]	409
Diisodecyl phthalate	171
Diethyl phthalate	22
Dibutyl phthalate	17
n-Hexyl-n-decyl phthalate	16
Dimethyl phthalate	10
Phosphoric acid esters (cyclic) -- total	99
Trimellitic acid esters -- total	33
Trioctyl trimellitate	16
Adipic acid esters -- total	68
Di-(2-ethylhexyl)adipate	45
Epoxidizer soya esters -- total	114
All others	513
Total production -- all plasticizers	2,086

[a]Data taken from Reference 5.
[b]Mostly as bis(2-ethylhexyl) phthalate.

medical tubing, etc. Phthalate esters used otherwise are found in pesticide carriers, oils, and insect repellent formulation (6).

SECTION 3

ANALYTICAL METHODOLOGIES FOR PHTHALATE ESTER DETERMINATION

A summary of published methods for the determination of phthalate esters in water, wastewater, soils, etc. is presented in Table 4. The detection methods in this table, gas chromatography with flame ionization or electron capture detection, gas chromatography/mass spectrometry, and stable isotope dilution gas chromatography/mass spectrometry vary in sensitivity, selectivity, complexity, degree of evaluation, ease of operation, etc. A detailed discussion of each of these techniques follows. Sample preservation and the isolation of phthalate esters from water, soil, and sediment samples, are discussed first. Sample extract cleanup and analysis techniques are discussed next, followed by a discussion of the extent of background contamination by phthalate esters.

3.1 SAMPLE PRESERVATION

The importance of proper sample preservation must be emphasized. The choice of the preservation method depends on the type of sample, the types of phthalate esters that need to be determined, the duration of sample storage prior to analysis, and the analytical procedure to be used (10). The sample preservation method chosen must not impair the analytical procedure to be used. Amber glass bottles are the containers of choice because of the protection they offer from photodegradation. The bottles must not be prerinsed with sample before collection (11). Composite samples should be collected in refrigerated glass containers and, if automatic sampling equipment is to be used, it must be free of any Tygon tubing (11). Most investigators report that samples should be refrigerated (15,16) or frozen (15,16,17,18,19,20) until analysis.

The use of aluminum foil either to wrap whole samples or to line the container caps prior to freezing has been reported (16,17,19). Contamination by phthalate esters present on the aluminum foil is not a problem for whole biological samples (such as fish) where the exterior skin is not utilized for analysis (17). However, use of aluminum foil to line container caps has been shown to cause severe contamination problems due to extraction of the phthalate esters from the cork or the rubber backing of the cap by the solvent vapor in the vial. Container caps lined with Teflon were found to be superior to those lined with aluminum-foil-lined caps (21,22,23).

Sample preservation by the addition of solvents such as methylene chloride (24) or hexane (25) immediately after sample collection has been reported. The addition of small amounts of organic solvents acts as inhibitor

TABLE 4. SUMMARY OF ANALYTICAL METHODOLOGIES FOR PHTHALATE ESTERS

Method	Matrix	Compounds	Extraction procedure	Cleanup procedure	Analysis procedure	MDL (µg/L or µg/kg)	Reference
EPA Method 606	Water	DMP DEP DBP BBP DEHP DOP	Separatory funnel Methylene chloride	10 g Florisil (3% water-deactivated); 100 mL 20% ethyl ether in hexane 10 g alumina (3% water-deactivated); 140 mL 20% ethyl ether in hexane	GC/ECD 1.5% SP 2250/1.95% SP 2401 on Supelcoport (100/120 mesh) 3% OV-1 on Supelcoport (100/120 mesh)	0.29 to 3	11
EPA Method 625	Water	DMP DEP DBP BBP DEHP DOP	Separatory funnel Continuous liquid-liquid extractor Methylene chloride	None	GC/MS 3% SP 2250 on Supelcoport (100/120 mesh)	1.9 to 2.5	12
EPA Method 1625	Water	DMP DEP DBP BBP DEHP DOP	Separatory funnel Continuous liquid-liquid extractor Methylene chloride	None	Isotope dilution GC/MS 30 m x 0.25 mm ID fused-silica capillary column, 94% methyl, 4% phenyl, 1% vinyl polysiloxane bonded	10	13
EPA Method 8060	Liquids Solids	DMP DEP DBP BBP DEHP DOP	EPA Method 3510 EPA Method 3520 EPA Method 3540 EPA Method 3550	EPA Method 3610 EPA Method 3620	GC/FID or GC/ECD (GC/FID) 1.5% SP 2250/1.95% SP 2401 on Supelcoport (100/120 mesh)	14 to 31[a] (GC/FID) 0.29 to 3[a] (GC/ECD)	1
Eastman-Kodak Method	Water	DMP DEP DBP BBP DHP DEHP DIOP DINP DIDP Other	Separatory funnel Methylene chloride	None	GC/ECD 3% OV-101 on Gas Chrom Q (100/120 mesh)	[b]	14

[a]Values given are for clean waters.
[b]MDL not specified.

to bacterial degradation of the phthalate esters (16,17,18,24,25,26) and also initiates sample extraction. Addition of a single crystal of thymol as bacterial inhibitor prior to freezing was reported by Glazer et al. (18).

Aqueous solutions containing DEP decreased in DEP-concentration by 20 percent in 4 days and by 70 percent in 12 days when kept under fluorescent light, and no DEP was detected after 14 days. In the absence of light and under refrigeration, no loss in DEP was detected after 60 days (27). Shouten et al. (25) reported that DBP and DEHP concentrations decreased with time, and the losses were attributed to biodegradation. At the 50-ppb level, a 50-percent loss of DEHP occurred in 5 days. In the case of DBP, over 90 percent was lost in about 3 days. Sullivan et al. (28,29) reported significant losses of phthalate esters from seawater during storage and attributed the losses to adsorption onto glassware. A kinetic study showed that most of the adsorption of DEHP occurred within the first hour and that after 12 hrs the solid adsorbent and the aqueous phase reached equilibrium (28). The adsorbed phthalates were only partially recovered by subsequent water rinses. A solvent rinse of the containers recovered most of the compounds adsorbed onto the glassware (29).

The stability of the phthalate esters in solid matrices has not been systematically investigated. Storage of soil and sediment samples at room temperature should be avoided since bacterial degradation does occur (16,18,24,26). Freezing at -10 to -30°C appears to be the most suitable method for preservation of solid samples since it has the widest range of applications and causes the least changes in the sample matrix.

3.2 EXTRACTION

A number of methods have been reported for the isolation of the phthalate esters from water, soil, sediment, and particulate material collected on Hi-Vol glass fiber filters. The extraction techniques that have been used on water samples include stirring, separatory funnel partitioning, and liquid-liquid extraction; adsorption onto XAD-resins or other liquid chromatographic bonded stationary phases has also been reported. The methods that have been reported for soil and sediment samples include solvent partitioning, liquid-solid extraction, Soxhlet extraction, blending, and ultrasonication.

3.2.1 Extraction of Water Samples

Table 5 presents a summary of extraction methods for water samples as published in the literature. The following describes in detail some of the procedures for the extraction of phthalate esters from water samples.

3.2.1.1 Liquid-Liquid Extraction

Liquid-liquid extraction is the simplest and the most widely used technique for the extraction of organic compounds from water. This technique consists of mixing the sample with a water-immiscible solvent in the original sample container, a separatory funnel, or a continuous liquid-liquid extractor. An important parameter for the liquid-liquid extraction is the

TABLE 5. SUMMARY OF EXTRACTION TECHNIQUES FOR WATER SAMPLES

Method	Solvent	Phthalate esters	Recovery percent	Spiking level (ppb)	Reference
Solvent (separatory funnel)	Methylene chloride	DMP, DEP, DALP, DBP, DHP, BBP, DPP, DOP	--	--	16
Solvent (separatory funnel)	Petroleum ether	DMP, DBP, BBP, DEHP	25 to 130	--	17
Solvent (separatory funnel)	Methylene chloride	BBP, TPMBP C7,9benzyl-P $C_{7,9,11}$DAKP	53 to 89	0.1 to 20	24
Solvent (separatory funnel)	Methylene chloride	DMP, DEP, DBP, DHEP, DIBP, DEHP, DNP	85 to 110	0.1	30
Solvent (separatory funnel)	Methylene chloride	DMP, DEP, DBP, BBP, DHP, DEHP, $C_{6,8,10}$-DAKP, DOP, DNP, DDP, $C_{7,9,11}$-DAKP, DALP	--	--	14
Solvent (homogenizer)	Hexane	DEP	94 to 96	10 to 100	27
Solvent (separatory funnel)	Hexane	DBP, DEHP	88 to 100[a]	100	31
Solvent (separatory funnel)	Methylene chloride	DMP, DEP, DBP DOP, BBP, DEHP	--	0.7 to 106	1
Solvent (separatory funnel)	Methylene chloride	DMP, DEP, DBP, DOP, BBP, DEHP	[b]	[b]	11
Solvent (separatory funnel, continuous liquid-liquid extractor)	Methylene chloride	DMP, DEP, DBP, DOP, BBP, DEHP	[b]	[b]	12
Solvent (separatory funnel, continuous liquid-liquid extractor)	Methylene chloride	DMP, DEP, DBP, DOP, BBP, DEHP	[b]	[b]	13

(continued)

[a]Extraction efficiency was a function of the shaking times; 5 min (88 percent); 10 min (99 percent); 20 min (100 percent).
[b]Refer to methods for data.
[c]Data obtained with type A polyurethane foam plugs (density 0.030 g/mL).
[d]Data obtained with type B polyurethane foam plugs (density 0.019 to 0.022 g/mL).
[e]Value given is for preconcentration from 500 to 1,000 mL water sample.

NOTE: DALP - diallyl phthalate
DPP - diphenyl phthalate
DAKP - dialkyl phthalate
DHEP - diheptyl phthalate
TPMBM - 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate phthalate

TABLE 5. (concluded)

Method	Solvent	Phthalate esters	Recovery percent	Spiking level (ppb)	Reference
Solvent (separatory funnel, bottle stirrbar, continuous liquid-liquid extractor)	Methylene chloride	DMP, DEP, DBP, BBP, DOP, DEHP	25 to 129	--	32
C_{18}-μ-Bondapak (30 cm x 4 mm ID, 10 μm particles)	Gradient elution from 100 percent water to 100 percent methanol	DHP, DBP, DEHP, DNP	--	--	33
Polyurethane Foam	Extract with 2 mL acetone and 3 mL hexane in a glass syringe (dynamic conditions)	DMP, DEP, DBP, DIBP, DAM, DHP DEHP, DOP, DIDP, BBP	20 to 102[c] 8 to 101[d]	1.0	34
	Extract with 50 mL solvent (acetone-hexane 1:4); time varies from 1 hr to 72 hrs except for DMP from 10 min to 1 hr	DMP, DHP, DBP, DOP, DHEP	25 to 100	--	34
LiChrosorb RP-18 (2mm plug, 5 μm particles)	Elute with 85 percent methanol in water	DBP, DEHP	99[e]	--	35
Supelclean LC-18 SPE	Elute with three 1-mL aliquots of acetonitrile	DMP, DEP, DBP, BBP	85.9 to 103	2,000	36
XAD-4 (1.2-1.8 mm x 25 mm)	Elute with 50 to 100 μL acetone	DEP, DBP	85 to 99	2 to 100	37
XAD-2 XAD-4 XAD-8 (1.2 cm x 6.5 cm)	Acetone and chloroform	DMP, DBP, DEHP	19 to 116	50	38
Filtrasorb 300 (1.2 cm x 6.5 cm)	Chloroform or benzene	DMP, DBP, DEHP	0 to 45	50	38

[a]Extraction efficiency was a function of the shaking time; 5 min (88 percent); 10 min (99 percent); 20 min (100 percent).
[b]Refer to methods for data.
[c]Data obtained with type A polyurethane foam plugs (density 0.030 g/mL).
[d]Data obtained with type B polyurethane foam plugs (density 0.019 to 0.022 g/mL).
[e]Value given is for preconcentration from 500 to 1,000 mL water sample.

NOTE: DALP - diallyl phthalate
DPP - diphenyl phthalate
DAKP - dialkyl phthalate
DHEP - diheptyl phthalate
TPMBM - 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate phthalate

solvent. It must be immiscible with water, extract the organics of interest from the sample, and be compatible with the analysis procedure. In the case of the separatory funnel technique, up to 1 liter of an aqueous sample is poured into a separatory funnel and extracted by shaking with an organic solvent. The layers are allowed to separate, and the organic fraction is drawn off. Solvents with a specific gravity greater than that of water are preferred since the lower layer can be removed more easily.

Disadvantages of separatory funnel partitioning are:

- Limited sample size
- Emulsion formation with many wastewaters.

To break emulsions, it has been recommended that the extract be passed through a 25-mm-thick glass wool pad (39,40).

Several reports (14,16,17,24,27,30,31) dealing with the determination of phthalate esters in water samples involved separatory funnel partitioning; however, there appears to be little consensus as to the best organic solvent, the extracting conditions (e.g., solvent-to-liquid ratios, time, degree of agitation), or the use of salts to enhance partitioning into the organic layer. Table 5 lists the various systems used, although no data on the percent recovery for each procedure have been reported.

One of the more recent devices introduced specifically for liquid-liquid extractions is the Mixxor device. These devices come in various sizes to handle sample volumes up to 50 mL. The mixing is accomplished by moving the piston up and down in the mixing chamber 5 or 6 times (equivalent to 40 or more shakes in a separatory funnel). The system is fast, precise, and safe (41). The main disadvantage is the ease with which emulsions are generated (41).

3.2.1.2 Adsorption

Several techniques have been used to adsorb phthalate esters onto solid supports. The materials used include uncoated polyurethane foams (PUF) or PUF coated with a viscous-liquid stationary phase (34), and support-bonded polymers such as HPLC column materials (33,35). The polyurethane foams seem to work well in removing some phthalate esters from water at the part-per-million level; however, the foams do not retain the larger-molecular-weight compounds such as DEHP and DOP (34). Once adsorbed from water, the phthalate esters may be desorbed by either elution using a high-pressure liquid chromatograph (HPLC), if the preconcentration was performed on support-bonded HPLC columns (33,35), or Soxhlet extraction with organic solvents such as acetone or hexane if the preconcentration was done on PUFs (34). Table 5 lists the solid supports, compounds, and their recoveries using the eluting solvent specified in the table.

A solid-phase extraction method for the preconcentration of phthalate esters from water samples has been reported recently (36). Although there

are no solid-phase extraction methods currently approved for use by the EPA, a solid-phase extraction method for the determination of endrin, lindane, methoxychlor, and toxaphene has been recently proposed as an alternative to the current EPA method (42). Major factors influencing the reversed-phase solid-phase retention are sample pH, sample volume, sorbent mass, and analyte concentration (43). These factors are first selected a priori, based on experience, in order to optimize the elution scheme (solvent strength and solvent volume). Once the elution conditions are optimized, then the choices made initially for sample pH, sample volume, and sorbent mass are varied to maximize compound retention.

Recoveries of phthalate esters using solid-phase extraction on Supelclean LC-18 cartridges (Supelco Inc.) range from 91.6 to 102 percent (36). The experiments were conducted as follows: each tube was conditioned with 2 mL methanol followed by 4 mL purified water. The preconcentration step was done by passing 50 mL of purified water spiked with selected phthalate esters at 2000 ppb to which 3 mL of acetonitrile was added. Following sample preconcentration, each tube was washed twice with deionized water (1 mL) and then eluted with three 1-mL portions of acetonitrile (36).

The major drawback of this technique is the fact that with environmental samples a large number of contaminants will be sorbed on and eluted with the compounds of interest, which will inevitably lead to broad solvent peaks and capacity problems. To avoid this, three alternatives have been recommended (35):

- Use of gradient elution to achieve a stepwise elution of the sorbed components
- Proper selection of the stationary phase
- Use of a selective detection system (e.g., fluorescence detection or postcolumn derivatization).

Other solid adsorbents that are used as alternatives for isolation of phthalate esters from water samples include the XAD resins (37,38) and carbon (38). The recovery efficiencies of XAD-2, XAD-4, XAD-7, and XAD-8 resins and resin mixtures were reported by Tateda and Fritz (37) and Van Rosum and Webb (38). The results indicate that the resin performs well for the shorter-chain esters; the longer-chain esters such as DEHP are not retained efficiently by the resin. Activated carbon was reported to be effective in extracting phthalate esters from aqueous samples; however, the recovery of the adsorbed compounds is not quantitative when the carbon is extracted with chloroform or benzene in a Soxhlet extractor (38).

D. Blevins (45) reported recently a new procedure for preconcentrating phthalate esters and other organics from aqueous samples. The procedure involves filtration of the aqueous sample through a PTFE membrane disk impregnated with C_8-bonded silica. The membrane, known as the 3M-Empore membrane disk, consists of chemically modified 8-μm silica particles tightly bound in a densely woven "web" of micro-PTFE fibrils. The silica particles

are individually suspended, with the surface of each particle free to interact with the aqueous liquid that is filtered through or the organic solvent used in extracting the organics retained by the membrane disk. Aqueous samples containing 5 percent methanol are passed through at approximately 25 mL/min, and the compounds are extracted from the membrane disk with 10 mL acetonitrile. Typical recoveries for DMP, DEP, DBP, and DOP are in the range of 82 to 117 percent.

3.2.1.3 Microextraction

Rhoades and Nulton (44) developed a technique for the extraction of industrial wastewaters using microextraction (a one-step extraction in which the solvent-to-sample ratio is 1:40 to 1:100). Use of their method for extracting relatively nonpolar analytes is justified from both theoretical and practical viewpoints. Comparison of both the recovery and the variability of the microextraction technique with other methods is presented in Tables 6 and 7. Microextraction compares favorably with other techniques and offers several practical advantages:

- Being a single-step extraction, it offers the possibility to extract selectively the analyte of interest
- Contamination is minimized by sample preparation in a single container
- It is less labor intensive, since extract concentration is not necessary
- The need for extract cleanup is minimized.

3.2.2 Extraction of Sediment and Soil Samples

This section summarizes the extraction techniques reported in the literature for soil and sediment samples. Examples of solvent and solvent mixtures used for extraction, type of extraction, compounds investigated, and recovery data are presented in Table 8.

Techniques used for the extraction of phthalate esters from soil and sediment samples can be classified into three categories: 1) blending the sample with solvents, 2) sonication, and 3) Soxhlet extraction. Each of these techniques will be described in more detail below.

Blending consists of the extraction of 10 to 20 g soil or sediment material on a wrist-action shaker (16) or in an extraction jar (17) with various solvents. Acetone-hexane and acetonitrile have been recommended for blending (16,17). After extraction with acetonitrile, the soil was extracted twice with methylene chloride-petroleum ether (1:9), and all extracts were combined (17).

Soxhlet extraction seems to be preferred because of the ease and neatness in handling. Because of the nature of the system, freeze-dried soil

TABLE 6. SUMMARY OF SPIKE RECOVERY DATA FOR THE MICROEXTRACTION TECHNIQUE

	Microextraction			Other methods[a]		
Phthalate ester	Average percent recovery	Std. Dev.	No. of spiked samples	Average percent recovery	Std. Dev.	No. of spiked samples
Bis(2-ethylhexyl)	85	25	50	56	56	92
Di-n-butyl	61	29	13	66	66	55
Di-n-octyl	82	21	13	92	--	2

[a] Data supplied by William F. Cowen, Catalytic, Inc. Data obtained by Southwest Research Institute and several other laboratories taking part in an EPA-Effluent Guidelines verification program are also included (44).

TABLE 7. SUMMARY OF DUPLICATE ANALYSES FOR THE MICROEXTRACTION TECHNIQUE

	Microextraction			Other methods[a]		
	Variability[b]			Variability[b]		
Phthalate ester	Average	Range	No. of duplicates	Average	Range	No. of duplicates
Bis(2-ethylhexyl)	39.8	0 to 143	27	110	5 to 200	31
Di-n-butyl	31.9	0 to 67	11	86	4 to 200	14
Di-n-octyl	21.6	0 to 35	8	--	--	--

[a] Data supplied by William F. Cowen, Catalytic, Inc. Data obtained by Southwest Research Institute and several other laboratories taking part in an EPA-Effluent Guidelines verification program are also included (44).
[b] All values in absolute difference between duplicates expressed as the percent of mean value: $100|x_1 - x_2|/x$.

TABLE 8. SUMMARY OF THE EXTRACTION TECHNIQUES FOR SOILS AND SEDIMENTS

Solvent	Type of extraction	Phthalate ester	Recovery (percent)	Spiking level (ng/g)	Reference
Acetone/hexane	Blending	DMP, DEP, DAP, DBP, DHP, BBP, DEHP, DPP, DOP	--	35-1,000	16
Acetonitrile, methylene chloride/ petroleum ether (1:9)	Blending	DMP, DBP, BBP, DEHP	61-81	300-700	17
Water/cyclohexane (1:1)	Sonication	BBP, TPMBP, DAKP	91-160	50-20,000	24
Methylene chloride or Acetone/hexane (1:1)	Sonication	DMP, DEP, DBP, DEHP, DOP, BBP	53-99	20,000	32
Benzene	Sonication	DMP, DEP, DBP, DOP	--	--	47
Hexane/acetone/ methanol (8:1:1)	Soxhlet	DBP, DEHP	90-110	--	46
Acetonitrile	Soxhlet	DEP	90-94	200-2,000	27
Methylene chloride	Soxhlet	DMP, DEP, DBP, DHP, DEHP, DNP	85-110	--	30
Methylene chloride, toluene/methanol (10:1) or Acetone/ hexane (1:1)	Soxhlet	DMP, DEP, DBP, DEHP, DOP, BBP	--	--	1
Chloroform/methanol (1:1)	Soxhlet	DBP, DEHP	--	1-5	48

NOTE: TPMBP - 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate phthalate
DAKP - dialkyl phthalate

is preferred (46). The extraction time varies from solvent to solvent. Soxhlet extraction with acetonitrile gave DEP recoveries of 90 to 94 percent after 4 hours (27), while 90 to 100 percent recoveries for DBP and DEHP were achieved after 17 hours extraction with 8:1:1 hexane-acetone-methanol (46).

A comparison of the extraction efficiencies obtained by blending, sonication, and Soxhlet has not been reported. Furthermore, the choice of solvent appears to be a matter of personal preference at the present time.

3.3 SAMPLE EXTRACT CLEANUP

Several types of cleanup techniques are available for the removal of coextractants from a sample matrix. They are:

- Liquid-liquid partitioning
- Gel permeation chromatograpy
- Sulfur removal
- Liquid-solid chromatography (Florisil, silica gel, alumina).

3.3.1 Liquid-Liquid Partitioning

This technique is widely used for removing fats, waxes, and polar materials. It consists of partitioning the sample extract with an immiscible solvent of different polarity. For example, an extract in hexane, petroleum ether, or benzene can be partitioned with a polar solvent such as acetonitrile. The waxes and fatty materials will remain in the nonpolar phase (hexane, petroleum ether, or benzene) while the phthalate esters will partition into the acetonitrile. The polar phase containing the phthalate esters is then diluted with water, and a sodium sulfate or sodium chloride solution is added to "salt out" the phthalate esters from the polar phase back into another nonpolar solvent. Giam et al. (15) reported that partitioning of extracts containing lipids and DEHP with acetonitrile and dimethyl formamide did not selectively remove the lipids and DEHP coextracted with the lipids when the hexane extract was partitioned with acetonitrile.

Solvent systems used for liquid-liquid partitioning of the phthalate esters are listed in Table 9.

Poole and Wibberley (49) have devised a very simple 3-step liquid-liquid partitioning procedure. After sample homogenization with acetonitrile and filtration, hexane-water is used to partition the phthalate esters from polar coextractants. Dimethyl formamide-water (94:6) and hexane is then used to further partition the moderately polar species. Finally, hexane-acetonitrile is used to partition the nonpolar species into the hexane phase, leaving the phthalate esters in the acetonitrile.

TABLE 9. LIQUID-LIQUID SOLVENT PARTITIONING SYSTEMS

Initial solvent system	Partitioning system	Secondary partitioning	Reference
Acetonitrile	Methylene chloride/ petroleum ether (1:5); water (5 percent NaCl)	Methylene chloride/ petroleum ether phase partitioned with water	15
Hexane/acetone	Water	Water/acetone phase partitioned with hexane	16
Acetonitrile and methylene chloride/ petroleum ether	Water (5 percent NaCl)	Acetonitrile/water phase partitioned with methylene chloride/petroleum ether	17
Ethylene glycol	Hexane		50
Acetonitrile	Hexane	Hexane phase partitioned with water	51
Acetonitrile	Hexane/water		27
Acetonitrile	Hexane/water	Dimethyl formamide/ water (94:6); hexane; hexane/ acetonitrile	49

3.3.2 Gel Permeation Chromatography (GPC)

In gel permeation chromatography the separation mechanism is based on differences in molecular size. Large molecules are excluded from the pores of the gel and elute first, while smaller molecules which can diffuse into the pores are eluted last.

The GPC techniques reported for the phthalate esters are summarized in Table 10. The elution volume of DEHP from Biobeads SX-3 and 1:1 methylene chloride/cyclohexane is reported in Table 11. The elution volumes of other phthalates, isophthalates, and terephthalates also have been reported (52).

GPC with Biobeads SX-2 as a preparative technique prior to GC analysis of phthalates has been investigated by Baker (53). It was demonstrated that small amounts of phthalate esters can be separated from an excess of lipids, providing sufficiently clean sample extracts. Burns et al. (20) separated lipids and phthalate esters using Biobeads SX-3 and methylene chloride/cyclohexane (1:1).

Problems with GPC stem mainly from samples with high lipid content, where broad elution of the lipid fraction overlaps the elution of the phthalate esters. The presence of triglycerides affects the performance of

TABLE 10. SUMMARY OF GPC TECHNIQUES

Column/solvent system	Phthalate esters	Detector/level	Reference
HP-GPC Shodex A801 Styrene-divinylbenzene resin (exclusion limit 1,000 as polystyrene)/ chloroform	DMP,DEP,DBP, DHEP, DEHP, DDP	Ultraviolet at 243 nm/20 ppb	31
LP-GA Biobeads SX-3/1:1 methylene chloride-cyclohexane	DBP,DEP, DEHP,DHEP	Ultraviolet at 254 nm; preparatory column	20
HP-GPC Shodex A801 Styrene-divinylbenzene resin (exclusion limit 1,000 as polystyrene)/ chloroform	C1 to C18 DAKP	Ultraviolet at 254 nm	52
Biobeads SX-2/benzene	DEHP,DNP,DMP	Ultraviolet at 281 nm/20 μg	53

NOTE: DHEP - diheptyl phthalate
DDP - didecyl phthalate
DAKP - dialkyl phthalate

TABLE 11. GPC ELUTION VOLUMES OF THE PHTHALATE ESTERS[a]

Eluate (mL)	Lipid (percent removal)	Phthalate ester (percent recovery)
0 to 50	--	--
50 to 60	0.6	--
60 to 70	41.1	--
70 to 80	44.7	--
80 to 90	5.3	36.4
90 to 100	1.3	62.5
100 to 110	0.6	--
110 to 120	--	--
120 to 130	--	--
130 to 140	--	--
Total	93.6	98.9

[a]Data taken from Reference 52.

electron-capture detectors, generating negative peaks in that portion of the chromatogram where the phthalate esters elute. Additionally, gradual deterioration of both the column and the detector may occur due to lipid materials (20).

3.3.3 Sulfur Removal

Sulfur and other organosulfur compounds, if present, may give large solvent peaks which could mask the region from the solvent peak to the earliest eluting phthalate ester peaks.

Sulfur may be removed as a discrete fraction by GPC (54). Alternatively, several chemical methods are available for the removal of sulfur: reaction with metallic mercury (55), activated copper (56), Raney Nickel (57), tetrabutyl ammonium sulfite $(TBA+)_2\ SO_3^{2-}$ (58), or potassium cyanide (59). Suzuki et al. (51) used a silver-nitrate-coated Florisil column for the cleanup of interfering coextractants (carotenes) and organic sulfides derived from some vegetables.

3.3.4 Liquid-Solid Chromatography

The following discussion will demonstrate the application of Florisil, silica gel, and alumina to the cleanup of sample extracts prior to the determination of phthalate esters.

3.3.4.1 Florisil

Florisil is a synthetic magnesium silicate manufactured by the Floridin Company from magnesium sulfate and sodium silicate. Following precipitation from solution, the magnesium silicate is filtered, dried, and calcinated at 650°C. Examples of cleanup methods for phthalate esters using Florisil are listed in Table 12.

Giam et al. (15) in their study of the determination of trace phthalate esters in open-ocean biota samples noted that DDTs and PCBs were present in virtually all biological samples in the ppb range, and that this required a separation scheme for the phthalate esters, since some peaks overlap (Aroclor 1260/DEHP, Aroclor 1254/DBP). They found that 3-percent water-deactivated Florisil gave the best recoveries for the phthalate esters, and that elution followed the pattern determined previously: 6 percent diethyl ether in petroleum ether for elution of the PCBs, then 15 percent diethyl ether in petroleum ether for DEHP, and 20 percent diethyl ether in petroleum ether for DBP. Spiked sample recoveries ranged from 70 to 100 percent depending on the type and amount of tissue used. Giam et al. (15) encountered an interference from lipid and other tissue components which eluted with DEHP in the 15-percent ether fraction. Solvent partitioning of the lipid prior to column cleanup was attempted; however, that resulted in loss of phthalates. It was further noted that, if the sample size was adjusted to maintain lipid levels to 3 g per sample, then the interference was reduced to minimum.

TABLE 12. SUMMARY OF CLEANUP PROCEDURES WITH FLORISIL

Material	Eluting solvents	Percent recovery	Reference
3 percent water-deactivated Florisil, 35 g	• 6 percent diethyl ether in petroleum ether (DDT, PCBs); 200 mL • 15 percent diethyl ether in petroleum ether (DEHP); 200 mL • 20 percent diethyl ether in petroleum ether (DBP); 200 mL	70 to 100	15
3 percent water-deactivated Florisil, 3 g	• Petroleum ether (PCBs, DDT); 10 mL • 20 percent diethyl ether in petroleum ether (phthalates) 25 mL	--	17
Florisil, 25 cm x 1 cm ID (2 cm anhydrous sodium sulfate on top)	• Hexane (80 mL) • 25 percent diethyl ether in hexane (80 mL) • Diethyl ether (phthalates); 200 mL	100	50
$AgNO_3$-coated Florisil, 3 g (top with 3 cm anhydrous sodium sulfate)	• Hexane • 2 percent ethyl acetate in hexane (chlorinated pesticides and phthalates) • 3 percent benzene in hexane (organochlorine pesticides); 40 mL • 2 percent ethyl acetate in hexane (phthalates); 60 mL	--	51
Florisil, 7 g	• 100 mL hexane/diethyl ether (50:3); discard • 100 mL hexane/diethyl ether (17:3) (DEHP, DPB)	--	46
2 percent water-deactivated Florisil	• 30 percent methylene chloride in hexane (PCBs, pesticides); 250 mL • 10 percent ethyl acetate in hexane (phthalates); 100 mL	--	19, 60
3 percent water-deactivated Florisil 30 g (top with 2.5 cm layer of anhydrous sodium sulfate)	• 6 percent diethyl ether in petroleum ether • 15 percent diethyl ether in petroleum ether (DEHP DBP) • 20 percent diethyl ether in petroleum ether (DBP, DEP, DMP)	--	61
Florisil, 10 g (top with 1 cm anhydrous sodium sulfate)	• Hexane, 40 mL, discard • 20 percent diethyl ether in hexane, 100 mL	--	1, 11

Similar elution schemes involving diethyl ether and petroleum ether have been reported by others (17,46,50,61). Other eluting solvents, such as 2 percent ethyl acetate in hexane (51) and 10 percent ethyl acetate in hexane, have also been used (19,60). In both cases, however, the organochlorine pesticides interfere and must be removed from the phthalate esters either with 3 percent benzene in hexane (51) or 30 percent methylene chloride in hexane (19,60).

Suzuki et al. (51) separated the phthalate esters from the organochlorine pesticides using $AgNO_3$-coated Florisil; the pesticides were eluted with 40 mL of 3 percent benzene in hexane, while the phthalate esters were eluted with 60 mL of 2 percent ethyl acetate in hexane (51).

A method for the standardization of the Florisil activity by measurement of its adsorptive capacity has been developed by Mills (62). Lauric acid (present in excess) is adsorbed from hexane solution onto the Florisil column; the amount not adsorbed is determined by alkali titration of the eluant. Calculation of the Florisil activity (equivalents per gram) allows comparison of different batches of activated Florisil.

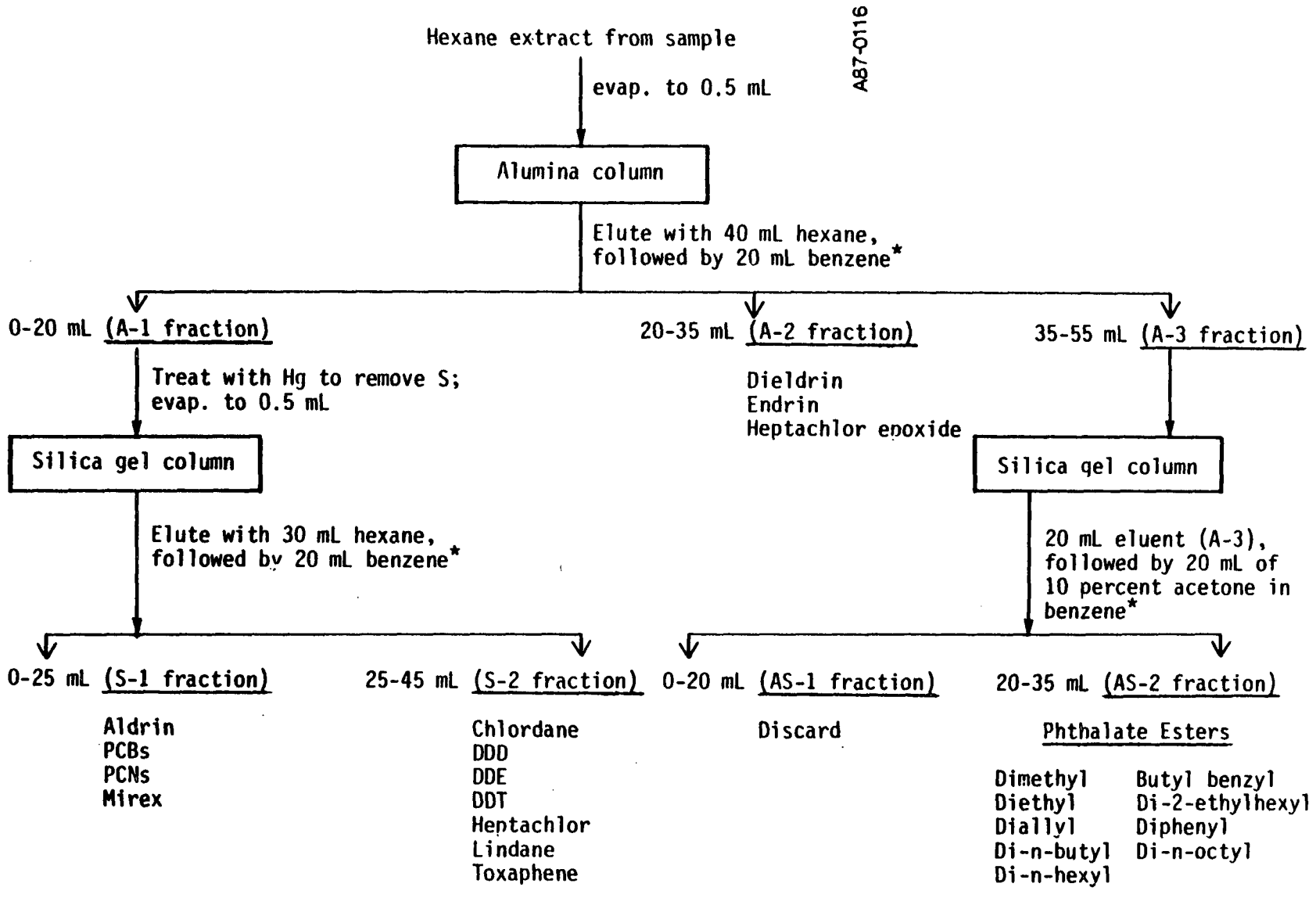
3.3.4.2 Silica Gel

Andersen and Lam (23) reported the use of a Celite column for the separation of phthalate esters from edible oils. The Celite column was first coated with an edible oil (triolein), and DEHP was eluted with propylene carbonate. Experiments were carried out using different amounts of stationary phase. To determine the elution of DEHP, the propylene carbonate eluant was collected in 1-mL fractions and analyzed by gas chromatography.

3.3.4.3 Alumina

Persson et al. (63) and Webster and Nickless (64) reported sample cleanup using alumina and deactivated alumina, respectively. The sediment or water extract was applied to a 20-g column of deactivated alumina and eluted with 40 mL hexane (Fraction 1), 100 mL of 6 percent diethyl ether in hexane (Fraction 2), 100 mL of 15 percent diethyl ether in hexane (Fraction 3), 100 mL of 25 percent diethyl ether in hexane (Fraction 4), and 100 mL of 50 percent diethyl ether in hexane (Fraction 5). Most phthalate esters elute in Fraction 3, the more oxygenated esters elute in Fraction 4, and bis(methoxy ethyl) phthalate was recovered in Fraction 5 (64). A simple separation of neutral lipids and phthalate esters from polar lipids was carried out by Waldock (30) using 5-percent water-deactivated alumina. Recoveries ranged from 98 to 101 percent when phthalate ester standards dissolved in fish oil were eluted from the alumina column with methylene chloride.

Phthalate esters were separated from organochlorine pesticides and PCBs using combined alumina-silica gel chromatography (16) as shown in Figure 1. The separation of the organochlorine pesticides, PCBs, and phthalate esters is first achieved on an alumina column (16). The organochlorine pesticides and PCBs are then eluted with hexane while the phthalate esters are eluted with benzene. Further fractionation of the benzene fraction is achieved on



*Approximately 5 mL of eluting liquid is retained by column.

Figure 1. Combined alumina-silica gel chromatographic cleanup technique. Figure taken from Reference 16.

a silica gel column; the phthalate esters are eluted with 10 percent acetone in benzene. Benzene was chosen since it is compatible with GC/ECD. Such a fractionation scheme was needed because of some interfering polar substances that could not be retained on the alumina column.

Burns et al. (20) and Hazelton Laboratories (65) utilized sulfuric-acid-impregnated alumina to increase the separation of lipid materials from the phthalate esters. Ordinary alumina removed only about one-half of the lipid which remained after GPC, and it was, therefore, inefficient if used alone. Elution with 2 percent diethyl ether in hexane removed early coextractants, while elution with 10 percent diethyl ether in hexane removed the phthalate esters. Degradation of the phthalate esters was minimal on the acid-impregnated alumina. However, it was recommended that fresh acid-impregnated alumina be prepared every 2 weeks.

Several difficulties with the above method were noted (65):

- The capacity of the alumina column was low
- Because of the ubiquitous nature of DEHP, the blank levels for DEHP were in the range of 50 to 100 ppb, with occasional values as high as 1,000 ppb
- GC/MS analysis indicated a distinct change in retention times, and broad peak shapes for DEHP were attributable to a buildup of extraneous high-boiling sample materials.

3.3.5 Selection of a Cleanup Technique

The choice of the adsorbent depends upon many factors, but the type of matrix and the interfering coextractants present seem to be the most important considerations. Alumina has been found to be more efficient than silica gel and Florisil in the removal of fats (16,20). Silica gel can remove edible oils efficiently when a suitable solvent such as propylene carbonate is used (23). Florisil cleanup has had the most attention. Though not quantitatively compared with other methods for specific sample types, Florisil appears to enable the separation of phthalate esters from a greater number of extracts of different matrices than any other method presently used. Lopez-Avila et al. (66) reported elution patterns and recovery data for 16 phthalate esters in the presence of interferents such as corn oil, diesel hydrocarbons, organochlorine pesticides, and chlorinated phenols using 1-g Florisil disposable cartridges. Hexane, hexane/diethyl ether (1:1), hexane/acetone (9:1), and various combinations of hexane/methylene chloride were used as eluants. The authors reported that organochlorine pesticides can be removed efficiently with hexane/methylene chloride (4:1); under these conditions, the phthalate esters are retained on the Florisil cartridge and can be recovered by elution with hexane/acetone (9:1).

When dealing with multicomponent analyses, and especially in those cases where the GC analysis does not allow complete separation of all the sample components, a combination of cleanup techniques may be required.

Combined techniques may offer the advantage of fractionating several sample constituents (phthalates, PCBs, pesticides, etc.) for analysis in the same sample with a minimum amount of preparation time and materials.

3.4 GC ANALYSIS

This section will address only the GC analysis techniques, including gas chromatography/mass spectrometry (GC/MS). Basically, the phthalate esters are separated on the chromatographic column, either packed or capillary, at elevated temperatures, and the compounds are detected with an electron capture detector (ECD), a flame ionization detector (FID), or a mass spectrometer (MS). Section 3.5 addresses the high performance liquid chromatographic (HPLC) techniques. A comparison of GC and HPLC detection limits is presented in Table 13.

3.4.1 Gas Chromatographic Columns

Several factors must be considered when selecting columns for the GC analysis of phthalate esters.

- Operating parameters should yield maximum resolution and detector response at a minimal retention time
- The stationary phases should be stable and not bleed during the GC analysis

TABLE 13. INSTRUMENTAL DETECTION LIMITS FOR PHTHALATE ESTERS[a]

		Detection limit	
Method	Detector	Amount injected (ng)	Concentration/ volume injected (ng/mL)
HPLC	U.V. (254 nm)	10	100 (100 μL)
	U.V. (224 nm)	2	20 (100 μL)
GC	FID	1	1,000 (1 μL)
	ECD	0.02	20 (1 μL)
	MS(SIM)	0.01	10 (1 μL)
	MS	1	1,000 (1 μL)

[a]Data taken from Reference 5.
SIM -- selected ion monitoring.

- The columns should be durable enough to allow analysis of very complex matrices.

Single and mixed stationary phases, both nonpolar and polar, in packed and capillary columns have been used for the analysis of phthalate esters. Some of the more commonly used columns and GC conditions are listed in Table 14. Representative chromatograms of phthalates on various columns are shown in Figures 2 through 4.

The majority of the reports in the literature discusses packed columns for the separation of phthalate esters. Capillary columns are beginning to emerge as suitable alternatives to packed columns. Though the resolution of capillary columns is superior to that of packed columns, the small loading factors of a capillary column have limited its sensitivity unless coupled with a very sensitive detector such as ECD. By using large-bore capillary columns with a relatively thick layer of stationary phase, sample loadings, and therefore sensitivity, can be greatly increased without significant losses in resolution.

Gas chromatographic retention data for 13 phthalate esters and mixtures have been compiled by Banerjee et al. (82). Table 15 contains operating conditions and retention data from the GC portion of the study. It should be noted from Table 15 that in GC analysis of phthalate esters (especially commercial preparations) problems may be encountered arising from the distribution of alkyl isomers, which overlap to a great extent. The GC profile of a particular phthalate ester is influenced by the branching of alkyl groups and also by the inclusion of asymmetric phthalate esters. High-resolution capillary columns may be required to completely characterize specialty phthalate ester plasticizers in commercial use.

Compound identification is usually done by retention time match on two dissimilar columns, or by mass spectrometry. Quantitation is accomplished by use of an internal standard such as di-n-nonyl phthalate (48), bis(2-ethylhexyl) sebacate (23), or a stable-isotope internal standard if GC/MS is used in the analysis (12,13,14,65,72).

3.4.2 Problems With Gas Chromatography

Three separate problems with the analysis of phthalate esters by GC have been identified:

- Column and detector performance degradation caused by insufficient sample cleanup (15,18,30,67)
- Loss of sensitivity at high ECD temperatures (16,17,73)
- Interferences by overlapping peaks (e.g., PCBs, organochlorine pesticides, sulfur, or triglycerides).

Mass spectrometry appears to be the solution to interference problems (30,73). Losses in sensitivity of the ECD can be minimized by operation of

TABLE 14. GC COLUMNS AND CONDITIONS REPORTED FOR THE ANALYSIS OF PHTHALATE ESTERS

Column	GC conditions	Detector	Detection limit	Reference
3% SE-30 on Gas Chrom Q (100/200 mesh)	220°C iso	ECD	1 ppb	15
1.5% SP-2250 and 1.95% SP-2401 on Supelcon AW-DMCS (100/200 mesh)	195°C iso	ECD		15
1.5% SP-2250 and 1.95% SP-2401 on Supelcoport (100/120 mesh)	180°C (4 min hold) at 4°C/min to 240°C (10 min hold)	ECD	1-100 ppb	16
15 m x 0.25 mm ID Capillary SE-52 (on-column injection)	70°C to 150°C at 40°C/min, 150°C 260°C at 6°C/min	ECD	0.05-0.1 ppb	17
8% Diethylene glycol succinate polyester (DEGS)	180°C iso	FID		67
3% SE-30	230°C iso			
2% OV-17	230°C iso			
1.5% SE-52	180°C iso			
3% QF-1	230°C iso			
10% Polyethylene glycol -- 20 M	230°C iso			
10% Apiezon M	250°C iso			
3% SE-30 (Ultraphase) on Chromosorb W (AW-DMCS, 60/80 mesh)	210°C iso	ECD		50
10% OV-25 Gas Chrom Q (100/120 mesh)	180°C iso	FID	0.5 nmoL/mL	68
10% OV-225 HP Chromosorb W (100/120 mesh)	175°C iso			
50 m x 0.3 mm ID Capillary (0.35)m film thickness) OV-101	230°C iso	FID		69
42 m x 0.3 mm ID Capillary (0.39)m film thickness) SE-30	250°C iso			
Aue packing	80°C to 250°C at 4°C/min	FID	0.5 ng/mL	21
Aue packing (100/120 mesh)	100°C (4 min hold) to 240°C (20 min hold) at 4°C/min	FID		22
1.5% SE-52 Chromosorb W (60/80 mesh)	230°C iso	FID	10 ppb	48
1.5% OV-17 Shimalite W (80/100 mesh)	240°C iso			
3% Silar-10C Gas Chrom Q (100/120 mesh)	150°C to 250°C (7 min hold) at 16°C/min	MS	0.1-8 ppb	24

(continued)

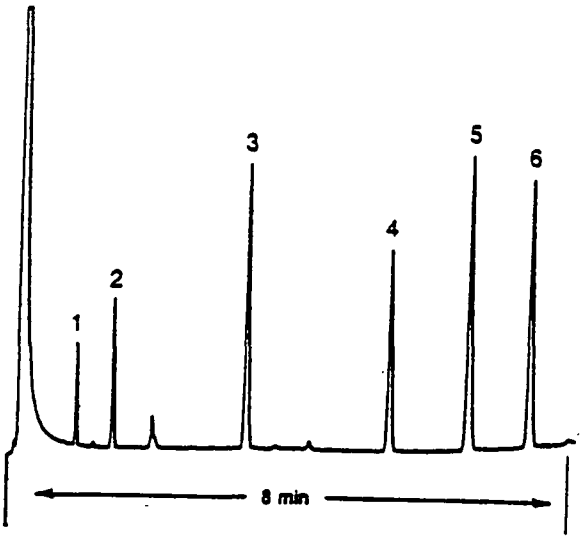
TABLE 14. (continued)

Column	GC conditions	Detector	Detection limit	Reference
2% DEGS -0.5% phosphoric acid	--	--	--	51
3% SE-30 Gas Chrom Q (100/120 mesh) 3% SE-30 Chromosorb WHP (100/120 mesh)	200°C iso 200°C iso	ECD ECD	1 ng	76
3% SE-30 Gas Chrom Q (80/100 mesh)	200°C iso	ECD	0.5 ng	27
5% OV-101 AW-Chromosorb W (80/100 mesh)	230°C iso	FID		23
3% OV-17 on Chromosorb G (80/100 mesh)	280°C iso	FID		71
4% OV-101 Chromosorb WHP (80/100 mesh)	220°C iso	ECD FID	10 ng	46
6% Dexsil 300 on Chromosorb W	255°C iso	MS		72
3% OV-1 Chromosorb Q (100/120 mesh)	150°C (2 min hold) to 240°C, (5 min hold) at 5°C/min	MS		73
24 m x 0.3 mm ID Capillary SE-54	25°C initial; 100°C to 250°C at 10°C/min	MS	30 pg	30
30 m x 0.32 mm ID Capillary SE-52	50°C to 320°C at 6°C/min	MS		74
3% XE-60 Gas Chrom Q (80/100 mesh)	199°C iso	ECD	1.4 ppb	26
3% OV-101 Supelcoport (80/100 mesh)	210°C iso	ECD		20
Outlet end 3% SP-2100/3% OV-210 Inlet end 1% SP-2100/2% SP-2401 Supelcoport (100/120 mesh)	200°C iso	ECD	1 ng/g	
3% OV-17 Chromsorb W DMCS (60/80 mesh)	--	ECD	--	34
Aue packing	90°C to 250°C (15 min hold) at 4°C/min	FID		47
3% SE-30 Gas Chrom Q (100/200 mesh)	180°C iso	ECD	30 ng	75
6% OV-210 + 4% SE-30 Chromosorb W (AW) (60/80 mesh)	202°C iso	ECD		60

(continued)

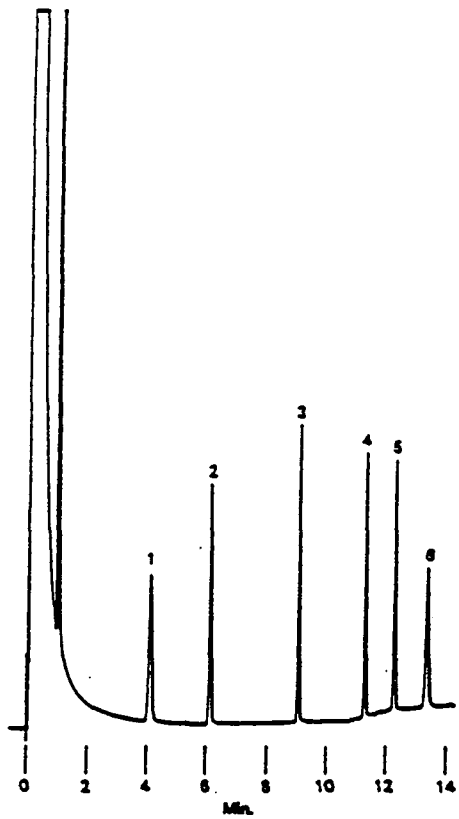
TABLE 14. (concluded)

Column	GC conditions	Detector	Detection limit	Reference
2% OV-225 Gas Chrom Q (80/100 mesh)	180°C iso	ECD	0.1 pg	26
6% OV-210 + 4% SE-30 Chromosorb W (AW)	203°C iso	ECD		19
Aue packing (AP) (ultrathin, thermally treated layer of Carbowax 20M deposited as a 0.2% layer on acid-washed 100/120 mesh Chromosorb W)	100°C (4 min hold) to 240°C (50 min hold) a 4°C/min	FID MS		77
3% OV-17 Gas Chrom Q (100/120 mesh)	230°C iso	ECD	0.01 ng/m^3	78
SE-30 OV-1				79
2.5% silicone gum E-301 Chromosorb (BDH)	223°C iso	FID		53
3% SE-30 Gas Chrom Q (80/100 mesh)	--	FID		63
1% DC-560 Gas Chrom Q (100/120 mesh)				
3% OV-101 Gas Chrom Q (100/120 mesh)	125°C (2 min hold) to 275°C, (7 min hold) at 15°C/min	FID		14
30 m x 0.32 mm ID Capillary SPB-5	70°C (1 min hold) to 250°C (hold) at 20°C/min	MS	20-50 ppb	65



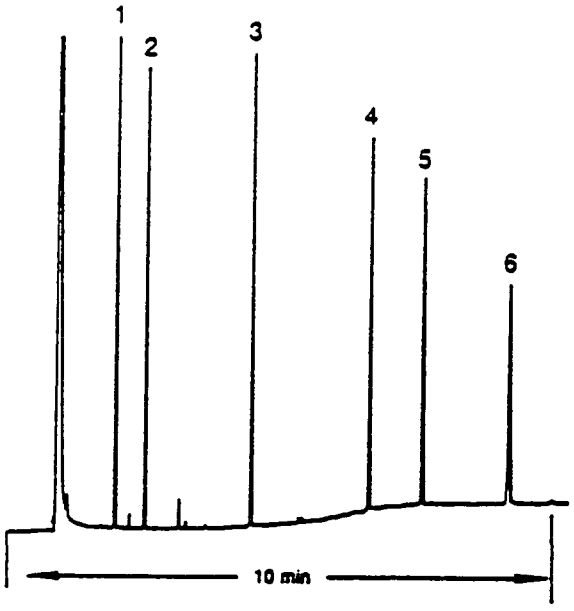
1. Dimethyl phthalate
2. Diethyl phthalate
3. Di-n-butyl phthalate
4. Butyl benzyl phthalate
5. Bis(2-ethylhexyl) phthalate
6. Di-n-octyl phthalate

Figure 2. GC/FID chromatogram of phthalate esters analyzed on a 15 m x 0.53 mm ID DB-1 fused-silica capillary column (1.5 μm film thickness); temperature program 150°C to 275°C at 15°C/min; helium at 21 mL/min. Figure taken from Reference 80.



1. Dimethyl phthalate
2. Diethyl phthalate
3. Di-n-butyl phthalate
4. Butyl benzyl phthalate
5. Bis(2-ethylhexyl) phthalate
6. Di-n-octyl phthalate

Figure 3. GC/FID chromatogram of phthalate esters analyzed on a 15 m x 0.53 mm ID SPB-5 fused-silica capillary column (1.5 μm film thickness); temperature program 115°C (4 min hold) to 250°C (15 min hold) at 16°C/min; helium at 30 mL/min. Figure taken from Reference 81.



1. Dimethyl phthalate
2. Diethyl phthalate
3. Di-n-butyl phthalate
4. Butyl benzyl phthalate
5. Bis(2-ethylhexyl) phthalate
6. Di-n-octyl phthalate

Figure 4. GC/FID chromatogram of phthalate esters analyzed on a 30 m x 0.25 mm ID DB-1301 fused-silica capillary column (0.25 μm film thickness); temperature program 180°C (1 min hold) to 270°C at 15°C/min; hydrogen at 50 cm/sec. Figure taken from Reference 80.

TABLE 15. GC CONDITIONS AND RETENTION DATA FOR THE PHTHALATE ESTERS[a,b]

Ester	GC conditions	Retention time (min)	Percent area	Alkyl chain length
Dimethyl	160°C iso Injector temperature: 225°C Detector temperature: 260°C Flowrate: 42 mL/min	1.11	--	6
Diethyl	160°C iso Injector temperature: 225°C Detector temperature: 260°C Flowrate: 42 mL/min	1.88	--	8
Di-n-butyl	160°C iso Injector temperature: 225°C Detector temperature: 260°C Flowrate: 42 mL/min	8.32	--	12
Butylbenzyl	200°C iso Injector temperature: 225°C Detector temperature: 260°C Flowrate: 40 mL/min	6.74	--	--
Dihexyl	190°C iso Injector temperature: 225°C Detector temperature: 260°C Flowrate: 40 mL/min	7.11 7.66 8.58 9.31 10.51	<5 17 30 31 22	12 12 12 12 12
Butyl-2-ethylhexyl	160°C (1 min hold) to 220°C at 30°C/min Injector temperature: 225°C Detector temperature: 260°C Flowrate: 42 mL/min	3.63 5.54 9.20	<8 34 66	8 12 16
	200°C (1 min hold) to 250°C at 30°C/min Injector temperature: 250°C Detector temperature: 300°C Flowrate: 41 mL/min	3.68 4.75 6.26 8.61	1 14 33 38	12 14 16 18
Bis(2-ethylhexyl)	160°C (1 min hold) to 220°C at 30°C/min Injector temperature: 250°C Detector temperature: 300°C Flowrate: 41 mL/min	9.64	--	16

(continued)

[a]Data taken from Reference 82.
[b]GC column 6' x 1/8" glass column packed with 3% OV-1 on Supelcoport 100/120.

TABLE 15. (concluded)

Ester	GC conditions	Retention time (min)	Percent area	Alkyl chain length
Diisooctyl	220°C iso	6.13	7	15, 16
	Injector temperature: 225°C	7.18	39	16
	Detector temperature: 260°C	8.42	54	16
	Flowrate: 30 mL/min			
Diisononyl	180°C (2 min hold) to 250°C at 30°C/min	7.74[c]	26	18
	Injector temperature: 250°C	8.05[c]	8	18
	Detector temperature: 300°C	8.23[c]	28	18
	Flowrate: 28 mL/min	8.74[c]	38	19
Di(heptyl,nonyl, undecyl)	180°C (2 min hold) to 250°C at 30°C/min	5.97	7.2	14
	Injector temperature: 250°C	6.37	11.2	14
	Detector temperature: 300°C	7.26	11.6	16
	Flowrate: 39 mL/min	7.88	19.2	16
		9.19	13.1	18
		10.26	21.1	18
		12.32	6.01	20
		14.09	10.7	20
		17.42	<3.0	22
		20.56	<3.0	22
Diisodecyl	200°C (1 min hold) to 250°C at 30°C/min	8.26	--	19, 20
	Injector temperature: 250°C	Unresolved		
	Detector temperature: 300°C	envelope		
	Flowrate: 41 mL/min			
Diundecyl	180°C (2 min hold) to 250°C at 30°C/min	13.13	3	22
	Injector temperature: 250°C	15.06	14	22
	Detector temperature: 300°C	16.36	8	22
	Flowrate: 39 mL/min	17.48	28	22
		20.50	43	22
Ditridecyl	250°C iso	16.7	--	24, 25,
	Injector temperature: 250°C	Unresolved		26, 27
	Detector temperature: 300°C	envelope		
	Flowrate: 41 mL/min			

[a]Data taken from Reference 82.
[b]GC column 6 ft x 1/8 in ID glass column packed with 3% OV-1 on Supelcoport 100/120.
[c]Poor peak resolution.

the detector below 300°C. The only requirement is maintaining the detector above the highest column temperature, which is usually 240 to 260°C. The decrease in sensitivity with temperature has been attributed to a nondissociative electron capture mechanism (16). Figure 5 shows ECD response as a function of molecular weight, and Tables 16 and 17 list the ECD responses at 320 and 255°C for various phthalate esters, respectively.

The "reaction ECD," reported recently by Hall (83) enhances the performance of the ECD by altering the molecular structure of the compound being analyzed as it passes through a high-temperature, flowthrough reactor mounted at the inlet of the ECD. The ECD response in the case of the phthalate esters increases at moderately high temperatures because the phthalate esters are converted to the phthalic anhydride, which gives a greater response than the ester (83).

3.5 HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

3.5.1 HPLC Methods

High-performance liquid chromatography can be performed in normal phase, reversed phase, and gel permeation. Normal-phase operation utilizes a polar stationary phase such as silica or a bonded phase such as cyanopropyl silane, and elution from this stationary phase by a progressively more polar solvent gradient. Reversed-phase operation makes use of a nonpolar bonded phase such as octadecyl silane, and elution from this stationary phase by a progressively less polar solvent. Gel permeation uses a porous polymer phase similar to that used in preparative work, but with a smaller particle size. High-molecular-weight compounds elute first because of their exclusion from the gel pores, and low-molecular-weight compounds elute later depending on their diffusion into and out of the pores of the gel. All three techniques have been investigated for the separation of phthalate esters (27,31,33,35,46,53,84).

Banerjee et al. (82) studied the retention of 13 phthalate esters and mixtures using reversed-phase HPLC and reported retention at several mobile phase compositions (Table 18).

Mori (31) utilized a Shodex HP-255 porous polymer bead column for adsorption (normal- and reversed-phase) chromatography with n-hexane for normal-phase operation (Figure 6) or methanol for reversed-phase operation (Figure 7). Also, a Shodex A801 styrene-divinylbenzene resin column was used for gel permeation chromatography, with an exclusion limit of 1,000 as polystyrene, with chloroform as eluant (Figure 8). UV detection at 224 nm for hexane and methanol, and 243 nm for chloroform were reported (31). Other chromatographic methods operating in the normal-phase mode are listed in Table 19.

Otsuki (33) investigated the use of hyperbolic gradients for the separation of phthalate esters by reversed-phase HPLC on a C-18 column using a methanol-water gradient. Figure 9 shows the separation obtained, while Figure 10 shows the relationship between retention time and linear alkyl chain

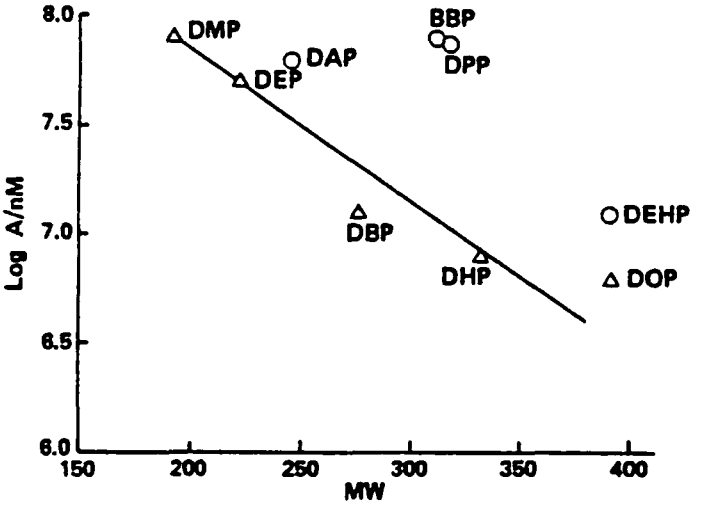


Figure 5. ECD response as a function of phthalate ester molecular weight. Figure taken from Reference 16.

TABLE 16. ECD RESPONSES AT 320°C

Compound	Retention time (min)	Detector response area/ng (x 10-3)
Dimethyl phthalate	6.0	43
Dibutyl phthalate	12.1	29
Butyl benzyl phthalate	17.1	334
Bis(2-ethylhexyl) phthalate	20.6	52

[a]Data taken from Reference 17.

TABLE 17. ECD RESPONSES AT 255°C

Compound	GC retention time (min)	Detector response[a] area/nmol (x10-6)
Dimethyl phthalate	2.5	74
Diethyl phthalate	3.7	51
Diallyl phthalate	6.4	67
Dibutyl phthalate	10.5	13
Dihexyl phthalate	18.0	8
Butylbenzyl phthalate	18.8	90
Bis(2-ethylhexyl) phthalate	21.0	16
Diphenyl phthalate	25.5	78
Dioctyl phthalate	26.5	5

[a]Data taken from Reference 16.
GC: 1.5% SP-2250 and 1.95% SP-2401 on 100/120 mesh Supelcoport.

TABLE 18. HPLC CONDITIONS AND RETENTION DATA FOR THE PHTHALATE ESTERS[a,b]

Phthalate	HPLC conditions mobile phase		No. of peaks	Retention volume (mL)
	Acetonitrile (percent)	Water (percent)		
Dimethyl	70	30	1	5.2
	50	50	1	7.6
Diethyl	80	20	1	4.4
Di-n-butyl	70	30	1	7.2
	60	40	1	10.4
	50	50	1	22.0
Butylbenzyl	80	20	1	5.5
	70	30	1	5.9
	60	40	1	8.7
Dihexyl	70	30	1	10.1
	60	40	2	16.8, 19.3
Butyl-2-ethylhexyl	70	30	3	6.4, 8.7, 13.3
Di(n-hexyl,n-octyl, n-decyl)	90	10	1	4.6
	80	20	4	5.5, 6.4, 7.8, 9.7
	70	30	5	8.3, 10.6, 13.3, 17.9, 23.9
	60	40	5	17.9, 25.8, 38.2, 58.9, 89.2
Bis(2-ethylhexyl)	80	20	1	8.3
	70	30	1	15.2
	65	35	1	19.3
Diisooctyl	70	30	1	14.3
	60	40	1	29.4
Diisononyl	80	20	2	6.4, 7.4
	70	30	3	9.7, 11.0, 12.0
	65	35	3	26.2, 31.7, 38.6
Di(heptyl, nonyl undecyl)	80	20	5	6.9, 9.2, 11.0, 11.7, 13.3
	70	30	6	11.0, 12.4, 15.6, 19.8, 23.9, 34.5
	65	35	6	12.0, 15.6, 21.2, 28.5, 38.2, 53.3
Diisodecyl	85	15	1	8.3
	80	20	3	9.2, 10.1, 11.5
	70	30	3	18.4, 22.1, 26.7
	65	35	3	27.1, 33.1, 40.5
Diundecyl	85	15	1	10.1
	70	30	1	32.7
Ditridecyl	95	5	2	9.7, 10.1
	90	10	2	9.7, 10.6
	80	20	4	20.2, 24.8, 27.6, 32.7

[a]Data taken from Reference 82.
[b]HPLC column 10 μm RP-2, UV 200 nm.

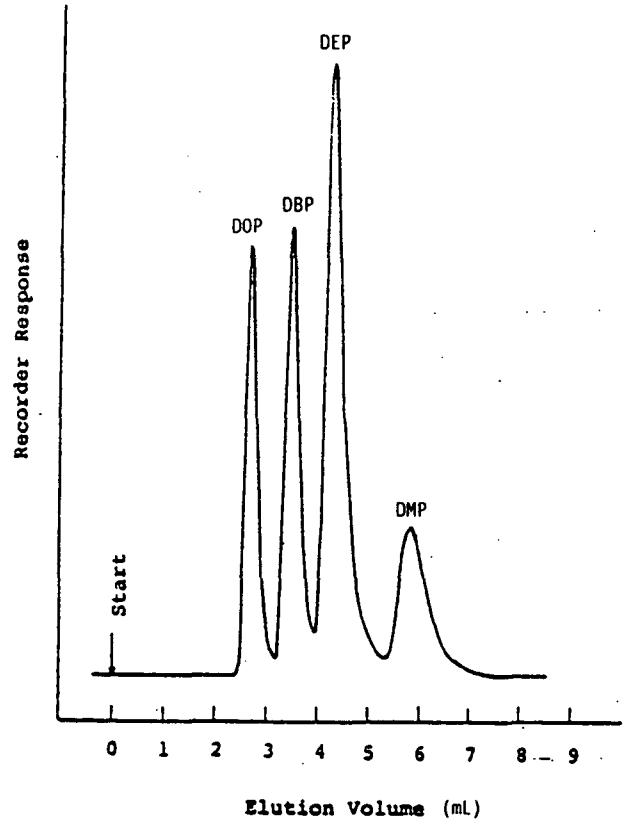


Figure 6. Normal-phase HPLC separation of phthalate esters (Shodex Polymer Beads HP-255, n-hexane). Figure taken from Reference 32.

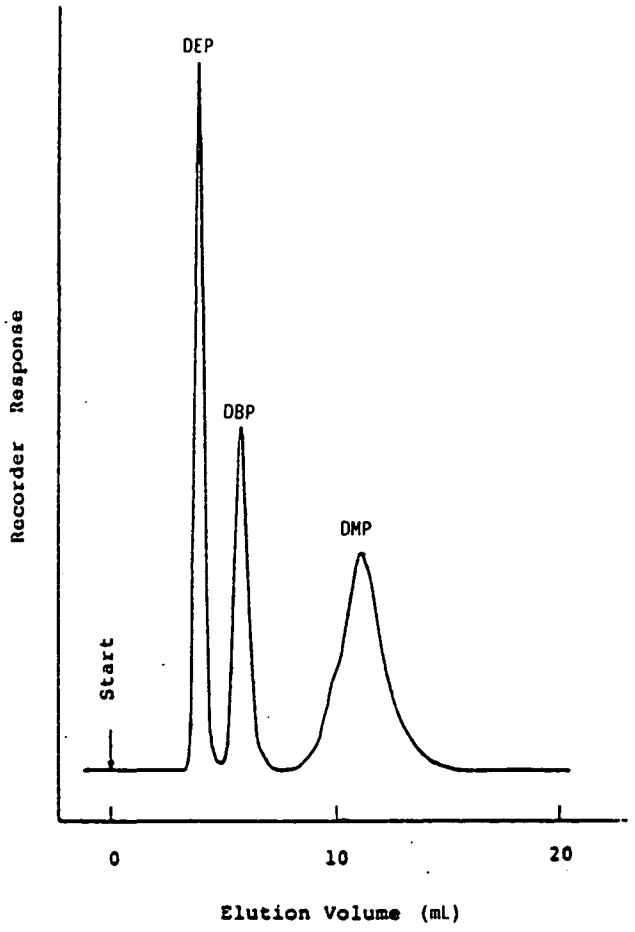


Figure 7. Reversed-phase HPLC separation of phthalate esters (Shodex Polymer Beads HP-255, methanol). Figure taken from Reference 31.

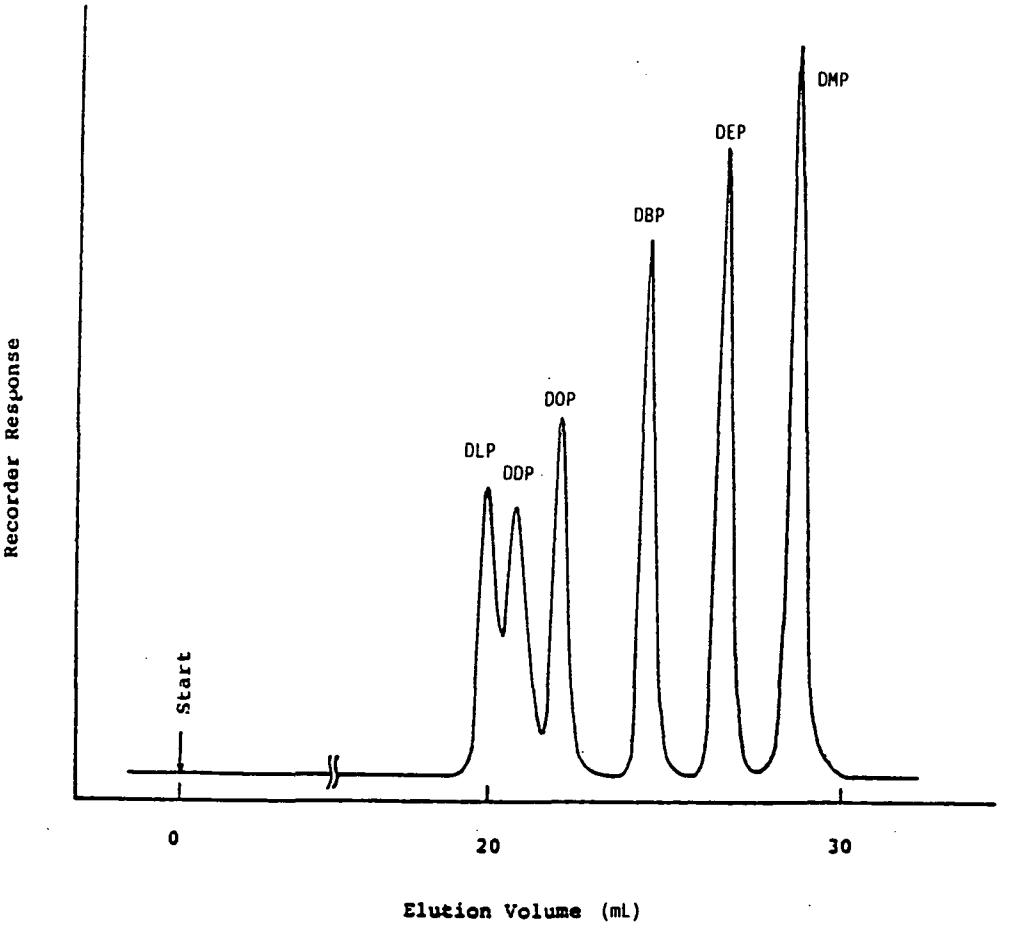


Figure 8. High-performance GPC separation of phthalate esters (Shodex A801, chloroform). Figure taken from Reference 31.

TABLE 19. SUMMARY OF CONDITIONS FOR NORMAL-PHASE HPLC SEPARATIONS OF PHTHALATE ESTERS

Column	Eluant	Detector	Detection limit	Reference
Porasil 10 μm	1:1 Methylene chloride/ isooctane	UV-254 nm	0.05 μg	84
Shodex Porous Polymer Beads HP-255	n-hexane	UV-254 nm UV-224 nm	2 ng[a]	31
Pellicular Perisorb A	2% diisopropyl ether in n-hexane	UV-281 nm	--	53
Silica gel LiChrosorb SI 60 (5 μm)	1:2 n-hexane/methylene chloride with 0.2% ethanol	UV-233 nm UV-224 nm	10 ng	46
Zorbax-CN	2% isopropanol/hexane	UV-224 nm	20 ng	27

[a]Value given is for DOP at 224 nm.

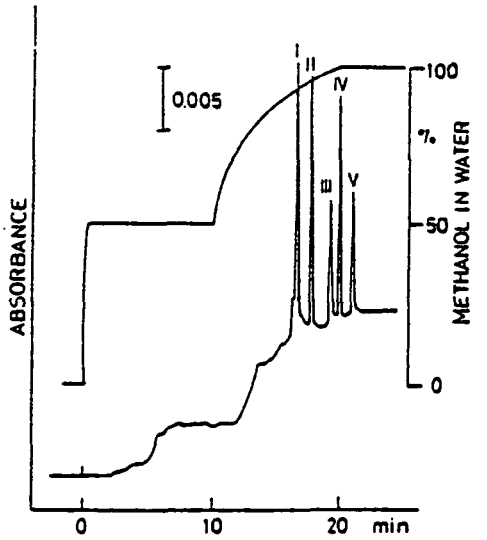


Figure 9. C_{18} Reversed-phase HPLC separation of phthalate esters using methanol-water. Figure taken from Reference 33.

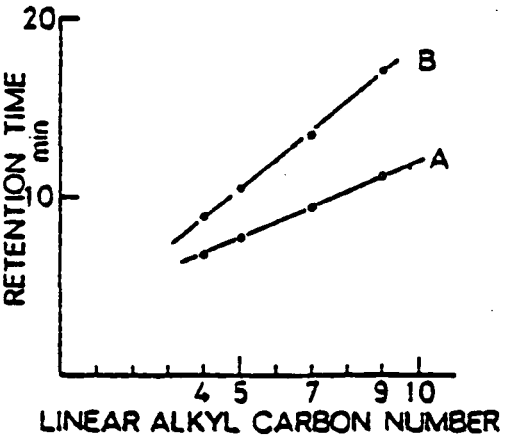


Figure 10. Retention time of phthalate esters as a function of alkyl chain length (A - gradient elution with a 10-min holding time; B - gradient elution without the holding process). Figure taken from Reference 33.

number. The phthalate esters were found to be completely adsorbed onto the bonded phase with 100-percent water eluant. The hyperbolic gradient with the introduction of a holding time during the gradient allowed elution of other organic compounds prior to that of the phthalate esters.

Van Vliet et al. (35) combined sample collection, preconcentration, and sample preparation into a single step to decrease the amount of contamination introduced by handling during each step in the process. Water samples were passed through a C_{18} precolumn where phthalates were completely adsorbed onto the stationary phase. Later, elution, using a methanol gradient, separated the phthalate esters. Experiments indicated that the passage of too large a sample volume resulted in breakthrough of those sample components that had very small capacity ratios. Three solutions to the problem were offered (35):

- Carefully designed gradient profile to achieve separation of the compounds of interest from the contaminants
- Selection of more selective stationary phases for the trace enrichment step
- More selective detection (e.g., fluorescence, MS, post-column derivatization).

Post-column derivatization is particularly attractive since, after the separation step, the phthalate esters could be detected as a fluorescent derivative of phthalic acid. This derivative could be independent of the particular ester, and the added selectivity of the derivatization step combined with a highly sensitive detection method could greatly increase the utility and scope of method.

3.6 CONFIRMATION OF COMPOUND IDENTITY

Three basic techniques have been used for the confirmation of the identities of phthalate esters:

- Comparison of the retention times on two or more stationary phases
- Formation of a derivative and either analysis of the derivative or observation of the loss of the suspected phthalate peak in the chromatogram
- Identification by gas chromatography/mass spectrometry.

Confirmation of phthalate esters by hydrolysis and peak disappearance has been reported (20). The samples are analyzed both before and after treatment with alkaline methanol, which saponifies the esters to the corresponding alkanols and phthalic acid salts.

Conversion of phthalate esters to the corresponding phthalic acid followed by reaction to produce a very ECD-sensitive ester derivative has been reported by several investigators (18,26,75,76,85).

Giam et al. (75) confirmed phthalate esters in environmental samples by derivatization involving: (a) hydrolysis to the acid; (b) fusion with 2-chloroethylamine hydrochloride to yield N-(2-chloroethyl)phthalimide, (c) back extraction of the reaction mixture into isooctane, and (d) analysis by GC/ECD. The method is simple, fast, inexpensive, and sensitive. It produces the derivative in high yield (90 percent), free from most other contaminants, and requires minimal amounts of glassware and reagents.

Takashita et al. (76) utilized a more complicated procedure in which the phthalate esters were also hydrolyzed, esterified with BF_3-2,2,2-trifluoro-ethanol solution, and extracted into hexane before GC/ECD analysis. Derivatization yields of 100 percent were achieved, and the overall recoveries ranged from 70 to 110 percent (76). The detection limit of the derivative was 0.1 pg; this represents approximately a 100-fold increase in sensitivity over that generally obtained when the phthalate esters are directly analyzed by GC/ECD. No impurities from byproducts were noted.

Glazer et al. (18) developed a procedure using BF_3-methanol for the esterification reaction and 4-chlorophthalate as internal standard. The method determines phthalates, isophthalates, and terephthalates simultaneously.

Arbin and Ostelius (26) performed derivatization by a solid-liquid phase-transfer catalysis, utilizing hexyl iodide to form a di-ester for GC/ECD analysis. This approach allowed the determination of both phthalate diesters and metabolite monoesters to be analyzed simultaneously. Cleanup of the reaction mixture by extraction with 1M H_2SO_4, followed by addition of silver sulfate to the organic phase, was necessary to prevent tailing caused by degradation products from quaternary ammonium halides (byproducts of the alkylation reaction). The efficiency of the reaction was >99 percent.

Mass spectrometry has been used for compound confirmation by Michael et al. (24) and Safe and Hutzinger (86). Mes et al. (60) confirmed the presence and identity of phthalate esters by MS after separation by alumina thin-layer chromatography.

Because of the high phthalate ester concentrations relative to other trace organics, Cautreels and van Cauwenberghe (87) suggest using secondary ions since the fragment ions at mass 149 may overload the collector.

Dziwinski et al. (71) reported that the identification of long-chain dialkyl phthalates by electron impact MS is made difficult because the molecular ions M+ are not detectable in the MS. Better results are obtained with field ionization or chemical ionization. Addison (73) noted a decrease in $[M+H]^+$ at higher reaction temperatures. Comparison of electron impact and chemical ionization for the identification of phthalate demonstrated that isobutane is the preferred gas, since isobutane produces simpler spectra,

gives greater abundance of the quasimolecular >$[M+H]^+$ ions, and forms no adduct ions.

Hunt et al. (88) have reported the use of an MS/MS technique to avoid the preparation and separation steps usually involved in environmental analysis. They identify several disadvantages of the current analytical methods involving GC and GC/MS:

- Inability to detect highly polar, nonvolatile, or thermally labile compounds
- High labor costs associated with sample preparation
- Large amount of time required per analysis.

MS/MS with collision-activated dissociation (CAD) utilizing a triple quadrupole offers several advantages:

- Direct analysis
- Rapid qualitative and semi-qualitative analysis
- Applicable to both liquid and solid matrices
- Analysis at the 10 to 100 ppb level
- Elimination of most sample preparation and chromatographic steps
- Detection of both knowns and unknowns by molecular weight and functional group
- Total analysis time of under 30 minutes per sample.

Figure 11 shows the phthalate ester fragmentation scheme upon electron-impact. The mass 149 fragment, corresponding to the protonated phthalic anhydride, is produced in high abundance for all but the dimethyl phthalate. Electron impact mass spectra of 5 phthalate esters are shown in Figure 12.

3.7 BACKGROUND CONTAMINATION

Interferences in the determination of phthalate esters are common, though few detailed studies have been undertaken. Background contamination from the ubiquitous nature of phthalate esters (DEHP and DBP) has become a greater concern since much lower levels of phthalate esters are being traced in the environment. Giam et al. (15) stated that the major problem in the phthalate ester analysis is the reduction of background contamination to levels less than the levels generally present in samples. Phthalate esters are present on almost all laboratory equipment. Giam et al. (15) also indicated that nonplastic materials (cork, glass wool, Teflon sheets, and aluminum foil) contain DEHP. When reported, the procedure blank levels tended

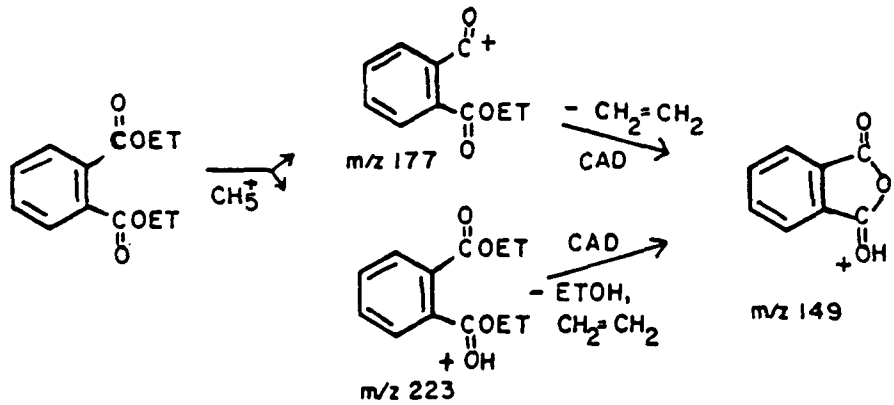


Figure 11. Phthalate ester fragmentation scheme. Figure taken from Reference 88.

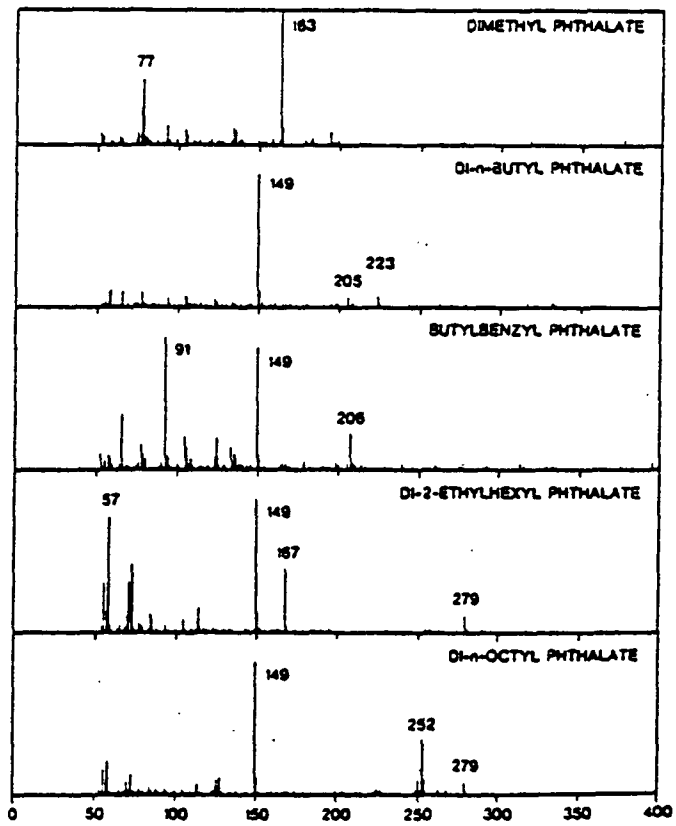


Figure 12. Electron impact mass spectra of common phthalate esters. Figure taken from Reference 5.

to be very high (1,500 ng for DEHP, 100 ng for DBP), regardless of careful preparation. The problem stems from four areas related to most analytical techniques used to determine phthalate esters:

- Contamination by traces of phthalate esters in high-purity solvents which becomes appreciable when solvent is concentrated to a few milliliters
- Contamination from laboratory items containing parts comprised of phthalates, or processed with equipment containing phthalate esters
- Contamination from adsorption of phthalate esters from the laboratory onto equipment and glassware
- Losses incurred in the concentration step when the sample extract is evaporated to dryness.

Each of these background sources will be discussed in detail below.

Bowers et al. (21) have undertaken a detailed study of high-purity solvents used in trace organic analysis. Distilled-in-glass and pesticide-grade solvents commonly used in the analyses of environmental samples for organic compounds at trace levels were concentrated 200-fold and analyzed by GC and GC/MS to determine contaminants and contaminant levels. Table 20 lists the total amount of impurities found in the different solvents. Lower levels were determined by selected ion monitoring (SIM) and are presented in Table 21.

Distilled-in-glass cyclohexane, methylene chloride, and methanol solvents contained an estimated total of 1 to 150 ng of organic impurities per mL of uncondensed solvent. At a 200-fold concentration, this corresponds to 0.2 to 3 μg/mL of impurities. Included were phthalate esters, n-hydrocarbons, and chlorinated hydrocarbons (21). Up to 21 compounds were identified in pesticide-grade solvents, with a maximum single component concentration of 30 to 50 ng/mL of uncondensed solvent. It was found that distilled-in-glass grade solvents contained fewer and lesser amounts of similar impurities, and therefore are most suitable for trace organic analysis (21).

Ishida et al. (48) detected phthalate esters in plastic laboratory apparatus and in benzene, chloroform, n-hexane, and light petroleum ether. They studied this contamination problem in greater detail, examining solvents, water, solids, and laboratory apparatus. Table 22 lists the concentrations of DBP and DEHP in solvents and water. Table 23 shows the levels of phthalate esters present in solids commonly used in the laboratory, and Table 24 lists the concentrations found in various materials. Removal techniques for these phthalate esters contaminants were also investigated. It was found that the phthalate esters could be removed from organic solvents by distillation. Solids could be cleaned by either heating to 300°C for 12 hours (where applicable) or by extraction with chloroform-methanol.

TABLE 20. IDENTITIES AND CONCENTRATIONS OF ORGANIC COMPOUNDS IN SOLVENTS BY GC/MS[a]

	Caledon Labs			Burdick & Jackson			Fisher Scientific		
Solvent	RI[b]	Compound	Concentration (ng/mL)	RI	Compound	Concentration (ng/mL)	RI	Compound	Concentration (ng/mL)
Cyclohexane	1150	$C_6H_{12}O$	49	2180	Diethyl phthalate	3.5	1085	n-Butyl-n-butyrate	29
				2878	Dioctyl phthalate	1.8	1705	Tributyl phosphate isomer	2.9
							1828	Tributyl phosphate isomer	0.89
Methylene chloride				2200	Diethyl phthalate	0.52	1027	1,1,1-Trichloropropane	16
				2350	Dibutyl phthalate	7.7		1,2,3-Trichloropropane	
							1038	1,1,1,2-Tetrachloropropane	21
							1155	Tetrachloroethane	1.9
							1655	Phthalic anhydride	0.42
							2760	Dioctyl phthalate	14
Methanol							1265	C_8H_{12}; 1,4-Bis(methylene)-cyclohexane	1.6
							1475	$C_8H_{10}O$; 2,6-Dimethylphenol	2.6

[a]Data taken from Reference 21.
[b]RI -- retention index.

TABLE 21. IDENTITIES AND CONCENTRATIONS OF ORGANIC COMPOUNDS IN SOLVENTS BY SIM[a]

	Caledon Labs		Burdick & Jackson		Fisher Scientific	
Solvent	Compound	Concentration (ng/mL)	Compound	Concentration (ng/mL)	Compound	Concentration (ng/mL)
Cyclohexane	Dibutyl phthalate	0.1	Dibutyl phthalate	0.5	Dimethyl phthalate	<0.1
	Dioctyl phthalate	<0.1	Dioctyl phthalate	0.2	Diethyl phthalate	0.4
			Tetracosane	0.1	Dibutyl phthalate	7
			Pentacosane	0.2	Dioctyl phthalate	1
			Hexacosane	0.2		
			Heptacosane	0.2		
			Octacosane	0.2		
			Nonacosane	0.1		
			Triacontane	0.1		
Methylene chloride	Dibutyl phthalate	0.2	Dibutyl phthalate	0.9	Dimethyl phthalate	<0.1
	Dioctyl phthalate	0.2	Dioctyl phthalate	0.2	Diethyl phthalate	0.1
					Dibutyl phthalate	0.7
					Dioctyl phthalate	11
Methanol	Dibutyl phthalate	0.4	Dibutyl phthalate	0.1	Dimethyl phthalate	<0.1
	Dioctyl phthalate	0.2	Dioctyl phthalate	0.1	Diethyl phthalate	0.1
					Dibutyl phthalate	1
					Dioctyl phthalate	0.6

[a]Data taken from Reference 21.

TABLE 22. CONCENTRATIONS OF DBP AND DEHP IN ORGANIC SOLVENTS AND WATERS[a]

Sample	Concentration	
	DBP	DEHP
City water[b]	2.04 ppb	--
Well water[c]	2.49 ppb	4.82 ppb
Tap water (well water)	1.93 ppb	3.85 ppb
Ion-exchanged water	0.83 ppb	1.31 ppb
Benzene	0.17 ppm	1.96 ppm
Acetone	Trace	--
n-Hexane	--	--
Chloroform	--	--
Diethyl ether	--	43.6 ppb
Methanol	--	78.7 ppb
Ethanol	69.3 ppb	61.7 ppb
Light petroleum	--	--
Dichloromethane	--	--
Ethyl acetate	--	--
Acetonitrile	--	0.18 ppm

[a]Data taken from Reference 48.
[b]From Tohoku University.
[c]Less than 10 ppb (10^9).

TABLE 23. CONCENTRATIONS OF DBP AND DEHP IN SOLID REAGENTS[a]

Reagent	Concentration		Company
	DBP	DEHP	
Silicic acid[b]	0.59 ppm	2.36 ppm	E. Merck
Silicic acid[c]	0.23 ppm	0.97 ppm	Mallinkcrodt
Wakogel S-1	1.61 ppm	0.84 ppm	Wako
Floridil (PR)[d]	23.8 ppb	63.5 ppb	Floridin
Floridil (EP)[e]	91.9 ppb	87.5 ppb	Wako
Alumina powder	41.8 ppb	44.8 ppb	Wako
Celite (GR)[f]	0.12 ppm	Trace[g]	Wako
Activated charcoal powder	95.8 ppb	47.9 ppb	Wako
Na_2SO_4 (EP)	0.09 ppm	0.04 ppm	Wako
Na_2SO_4 (GR)	24.3 ppb	16.9 ppb	Wako
Na_2SO_4 (PR)	24.3 ppb	14.5 ppb	Wako
Drierite	16.7 ppb	Trace	W. A. Hammond
$CaCO_3$ (GR)	18.7 ppb	21.6 ppb	Wako
NaCl (EP)	Trace	0.11 ppm	Wako
NaCl (GR)	Trace	11.8 ppb	Wako
DEAE-cellulose	0.25 ppm	0.41 ppm	Pharmacia
CM-cellulose	9.89 ppm	4.12 ppm	Pharmacia
Sephadex G-100	4.32 ppm	Trace	Pharmacia
Amberlite IR-45	2.27 ppm	0.25 ppm	Rohm and Haas
Dowex L-X8	9.76 ppm	0.19 ppm	Dow Chemical

[a]Data taken from Reference 48.
[b]For thin layer chromatography.
[c]For column chromatography.
[d]Chemical for analysis of pesticide residues.
[e]Extra-pure reagent.
[f]Guaranteed reagent.
[g]Less than 10 ppb.

TABLE 24. CONCENTRATIONS OF DBP AND DEHP IN VARIOUS MATERIALS[a]

Material	Concentration		Company
	DBP	DEHP	
Heavy-walled tubing (elicon tubing)	--	67.2%	Seimi
Polyvinyl tubing	23.3%	11.6%	Plastec
Black rubber tubing	--	0.2%	Seimi
PTFE tubing	--	--	Niplon Products
Black rubber stopper	Trace[b]	0.3%	Seimi
Red rubber stopper	--	--	Seimi
Injection packing[c]	Trace	0.25 ppm	Hitachi
Vial cap	22.5 ppm	0.65 ppm	Seimi
Wash bottle	--	--	Seimi
Cork stopper	--	--	Seimi
Thimble filter-paper	0.05%	1.34 ppm	Toyo Roshi
Filter-paper No. 2	5.28 ppm	0.62 ppm	Toyo Roshi
Chromatography paper	0.01%	2.28 ppm	Whatmann
Glass-wool	0.83 ppm	4.15 ppm	Wako
Kimwipe	41.9 ppm	--	Kimberly-Clark
Parafilm	--	--	American Can
Saranwrap	8.28 ppm	8.35 ppm	Asahidow
Aluminum foil A	0.13 ppm	4.85 ppm	Toyo Alumi
Aluminum foil B	1.62 ppm	1.01 ppm	Showa Alumi
Aluminum foil C	0.97 ppm	0.60 ppm	Mitsubishi Alumi

[a]Data taken from Reference 48.
[b]Less than 10 ppb.
[c]Injection packing for gas chromatograph.

Giam et al. (15) found that normally all reagents were pure enough except for diethyl ether, which had to be freshly distilled because of contamination problems during storage. Materials for their work were either extracted with petroleum ether, or heated to 320°C for 10 hours, and covered with purified aluminum foil. A check was made of all solvents and reagents prior to use by 200-fold concentration and GC/ECD analysis. Giam et al. (15) found filter paper to be a major problem; the use of glass fiber filters, which can be heated, was suggested. Previously cleaned Teflon sheets were used in place of rubber stoppers to hold Buchner funnels to minimize extraction of phthalate esters from the rubber. Also reported was a possible problem posed by airborne contaminants; levels of DEHP at air conditioning vents were found to be about 35 ng/m^3.

Table 25 lists the various cleanup and testing methods reported in the literature to determine and control the extent of phthalate ester background contamination.

Glass sample vials with foil-lined screw caps are generally considered to be sufficiently inert to produce no sample contamination. Bowers et al. (21) and Denney et al. (22) noted that storage of samples in a methanol solvent for several weeks caused substantial changes in composition. These samples had been stored in glass sample vials with Sn-Pb alloy foil-lined screw caps at room temperature. They concluded that the contaminants originated from the cork backing of the metal foil. This, they postulated, occurred through permeation by the methanol solvent vapor. To determine the cause, extent, and prevention of the contamination, Denney et al. (22) tested sample vials with foil or PTFE liners. The vials were filled with methanol and sealed for 8, 24, 48, and 72 hours, and the solvent was then analyzed by GC/MS. The analysis after only 8 hours indicated the presence of three compounds in the vial with the foil-lined screw cap, while the PTFE-lined samples showed no contamination. After 72 hours, the vials with the foil-liner showed nine contaminants while the PTFE-lined vials still showed no contamination. Solvents with vapor pressures different from that of methanol may produce different degrees of contamination. It was recommended (22) that PTFE-rubber laminated discs, or their equivalent, be used in conjunction with screw cap vials to insure sample integrity. The effect of sample storage temperature was not investigated.

Burke et al. (89) reported losses of phthalate esters whenever extracts were concentrated to below 500 μL, independent of the concentration technique. Chiba reported that the use of petroleum ether as the extraction solvent resulted in greater losses upon condensation of the solvent as compared to benzene (90). Detectable sample loss was observed even when a viscous solvent, such as ethylene glycol, was used. Bowers et al. (47) examined the problems which could occur when samples or sample extracts are taken to dryness and then reconstituted as part of the analytical preparative scheme. Surface-active agents were used to prevent losses occurring by irreversible adsorption onto glass surfaces, since silylation only masks silanol groups leaving active metal sites accessible. The surface coating technique appeared to make little difference in the case of phthalate esters (47). Greater losses were noted for samples with low concentrations (10 ng/μL versus

TABLE 25. CLEANUP PROCEDURES USED ON REAGENTS, GLASSWARE, AND OTHER LABORATORY ITEMS

Item	Procedure	Comments	Reference
Water	• Liquid-liquid extraction with petroleum ether	Phthalates not removed by distillation	15,27,70
	• Doubly-distillation in all glass still		16
	• Adsorption on a series of Sep Pak columns		17
	• Adsorption onto charcoal filters		68
	• Extraction with n-hexane		48,76
	• Extraction with methylene chloride		30
	• Redistillation from potassium permanganate/potassium hydroxide		33
	• Redistillation		34
	• Distillation/hexane extraction		35
Diethyl ether	• Distillation	Check by concentration and GC/ECD analysis	15,70
	• Extraction with methanol/sodium hydroxide after reflux, washing with water, then drying		68
			23
			15,19,27,30,48, 50,70,76
Sodium chloride	• Heating at 320°C		15,27,70
	• Heating at 400°C for 10 hours		17
Sodium sulfate	• Heating at 320°C		15,27,70
	• Heating at 210°C for several hours		16
	• Heating at 400°C for 10 hours		17
	• Heating at 650°C for 3 hours		51
	• Heating at 500°C for 3 hours		23
	• Extraction with methylene chloride		30
	• Washing with methylene chloride, acetone, then hexane, drying at 120°C		20
	• Washing with acetone, then hexane		34
Florisil	• Heating at 320°C		15,27,70
	• Soxhlet extraction for 12 hours with hexane, storage in n-hexane		46
Alumina	• Heating at 210°C for several hours		16
	• Extraction with methylene chloride		30
	• 800°C for 4 hours		20
Silica gel	• Heating at 210°C for several hours		16
	• Extraction with methylene chloride		30
Celite	• Heating at 500°C for 3 hours		26

(continued)

TABLE 25. (continued)

Item	Procedure	Comments	Reference
Polyurethane foam (PUF)	• Soxhlet extraction for 14 hours with acetone • Soxhlet extraction sequentially with: methanol, toluene, methylene chloride, acetone, and petroleum ether		34
Paper filters	• Soxhlet extraction for 12 hours with hexane		46
Soxhlet thimbles	• Soxhlet extraction for 12 hours with hexane		46
Glass fiber filters	• Heating at 320°C		15,27,70,78
Glassware	• Acid washing, rinsing with acetone, then hexane • Washing with Alconox, sonication, rinsing with tap water, then deionized water. Heating at 300°C for 1 hour. • Washing in 5% "Decon 90," soaking in 10% nitric acid, rinsing with tap water, soaking in methylene chloride-methanol (1:1) 24 hours, rinsing with methylene chloride before use • Rinsing with acetone, then hexane, drying at 150°C • Detergent washing, rinsing with hot tap water, acetone, then hexane • Keeping in chromic acid for >3 hours before use • Washing in acetone and n-hexane before use • Washing in water, heating at 250°C for 10 hours, or rinsing with acetone (4x) and hexane (2x) • Rinsing with acetone • Cleaning with Extran solution, washing with deionized water, heating at 400°C for 10 hours, and storing in aluminum foil • Detergent washing rinsing in: tap water, reagent grade acetone, heating at 210°C overnight, hexane rinsing before use • Washing with cleaning solution (Micro), rinsing with deionized water, distilled acetone, nanopure acetone (distilled over 5-ft column and potassium permanganate). Heating at 320°C for 10 hours; covering with aluminum foil (treated); rinsing with nanograde petroleum ether before use.	Use only glass or stainless-steel labware	19,34,60 47 30 34 46 23 51 48,51 68 17 16 15,27,70

(continued)

TABLE 25. (concluded)

Item	Procedure	Comments	Reference
Aluminum foil	• Heating at 350°C to 400°C for 14 hours		48
	• Washing with cleaning solution (Micro), rinsing with deionized water, distilled acetone, nanopure acetone (distilled over 5-ft column and potassium permanganate). Heating at 320°C for 10 hours; covering with aluminum foil (treated), rinsing with nanograde petroleum ether before use.		15,27,70
	• Cleaning with Extran solution, washing with deionized water, heating at 400°F for 10 hrs.		17
Stopcocks	• Washing and rinsing as above for glassware		15,27,70
	• Washing with petroleum ether		17
Spoons, Porcelain ware, Blender, Spatulas, Forceps, Dissecting knives	• Washing with cleaning solution (Micro), rinsing with deionized water, distilled acetone, nanopure acetone (distilled over 5 ft column and potassium permanganate). Heating at 320°C for 10 hours; covering with aluminum foil (treated); rinsing with nanograde petroleum ether before use.	Check prior to use by screening: rinse with methylene chloride or hexane and analyze by GC/MS	
	• Cleaning with Extran solution, washing with deionized water, heating at 400°C for 10 hours, and storing in aluminum foil		
	• Rinsing with methylene chloride and drying at 180°C		24
Glass wool	• Heating at 500°C for 3 hours		23
	• Extraction with methylene chloride		30
GLC septa	• Baking at 250°C for several weeks before using, then backing with Teflon discs		30
Volumetric flasks	• Washing in acetone, hexane, drying in vacuum		34

100 ng/μL, or 1 percent versus 10 percent). Slight concentration increases, as well as losses, were noted for the phthalate esters (Table 26).

Van Vliet et al. (35) developed a preconcentration method using an HPLC precolumn for HPLC analysis of phthalate esters which eliminates much of the contamination stemming from laboratory apparatus and solvents. Preconcentration methods based on the precolumn collection technique cannot be recommended for complex matrices and heavily contaminated samples, because resolution of the phthalate esters from matrix components may be insufficient.

3.8 STABILITY OF PHTHALATE ESTERS

Little information was obtained from the literature on the stability of the phthalate esters in various matrices. However, storage of samples at room temperature should be avoided since bacterial degradation and base-catalyzed hydrolysis do occur (16,18,24,26).

Payne and Benner (27) studied the losses of phthalate esters as a function of time at room temperature and at 4°C. The data are presented in Table 27. Losses incurred in samples kept under fluorescent light were higher than in samples kept in the dark. The best storage method was found to be refrigeration (no loss in 60 days). However, environmental samples must be analyzed for phthalates immediately, since sample losses of 64 percent in 1 day and 89 percent in 2 days were noted for DEHP (27).

Freezing at -10 to -30°C appears to be the most suitable method for storage of solid matrices since it has the widest range of application, causes the least changes in the samples, and makes the addition of preservatives unnecessary.

TABLE 26. COMPONENT LOSSES AFTER EVAPORATION-RECONSTITUTION OF 100-ng/μL AND 10-ng/μl STANDARD SOLUTIONS[a]

Phthalate ester	Retention time (min)	Original solution (ng/μL)	Loss (ng/μL)			
			Deactivated No. 1	Deactivated No. 2	Untreated No. 1	Untreated No. 2
Dimethyl	8.4	134	36	40	42	31
Diethyl	10.6	101	17	21	24	15
Dibutyl	18.0	102	8	14	19	12
Dioctyl	28.9	101	6	13	17	10
Dimethyl	8.4	13.4	13.4	13.4	13.4	13.4
Diethyl	10.6	10.1	5.0	6.9	5.1	4.8
Dibutyl	18.0	10.2	+1.2	0.8	0.4	1.1
Dioctyl	28.9	10.1	+1.0	0.5	0.5	1.0

[a]Data taken from Reference 47.

TABLE 27. BIS(2-ETHYLHEXYL) PHTHALATE LOSS AS A FUNCTION OF STORAGE CONDITIONS AND STORAGE TIME[a]

Conditions	Time interval	Losses (%)
Evaporation to dryness in an air stream (solvent methylene chloride)	0.5 hours	10 to 25
(Solvent: water) Ambient temperature (fluorescent lighting)	4 Days	20
	12 Days	70
	14 Days	>99
(Solvent: water) Refrigeration at 4°C	60 Days	<1
Environmental water sample	24 Hours	64
	48 Hours	89

[a]Data taken from Reference 27.

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APPENDIX B

METHOD 8061[a]
PHTHALATE ESTERS

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[a]Method 8061 is the revised version of Method 8060.

METHOD 8061

PHTHALATE ESTERS

1.0 SCOPE AND APPLICATION

1.1 Method 8061 is used to determine the identities and concentrations of various phthalate esters in liquid and solid matrices. Table 1 lists compounds that may be determined by this method, their CAS Registry Numbers, and their method detection limits (MDL) in a water matrix. The MDLs for the components of a specific sample may differ from those listed in Table 1 because MDLs depend on the nature of interferences in the sample matrix. Table 2 lists the practical quantitation limits (PQL) for other matrices.

1.2 When this method is used to analyze for any or all of the compounds listed in Table 1, compound identification should be supported by at least one additional qualitative technique. This method describes conditions for parallel column, dual electron capture detector analysis which fulfills the above requirement. Retention time information obtained on two megabore fused-silica open tubular columns is given in Table 1. Alternatively, gas chromatography/mass spectrometry could be used for compound confirmation.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 liter for liquids, 10 to 30 g for solids) is extracted by using the appropriate sample extraction technique specified in Methods 3510, 3540, and 3550. Method 3520 is not recommended for the extraction of aqueous samples because the longer chain esters dihexyl phthalate, bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and dinonyl phthalate tend to adsorb to the glassware and consequently, their extraction recoveries are <40 percent. Aqueous samples are extracted at a pH of 5 to 7 with methylene chloride in a separatory funnel (Method 3510). Alternatively, aqueous samples could be filtered through 3M-Empore membrane disks that contain C_{18}-bonded silica. The phthalate esters are retained by the silica and later eluted with acetonitrile. Solid samples are extracted with hexane/acetone (1:1) or methylene chloride/acetone (1:1) in a Soxhlet extractor (Method 3540) or with a sonicator (Method 3550). After cleanup, the extract is analyzed by gas chromatography with electron capture detection (GC/ECD).

2.2 The sensitivity of Method 8061 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, cleanup of the sample extracts is necessary. Either Method 3610 or 3620 alone or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis. Method 3640, gel-permeation cleanup, is applicable for samples that contain high amounts of lipids and waxes.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities for the target analytes.

3.3 Glassware must be scrupulously clean. All glassware require treatment in a muffle furnace at 400°C for 2 to 4 hrs or thorough rinsing with pesticide-grade solvent prior to use. Refer to Chapter 4, Step 4.1.4 for further details regarding the cleaning of glassware. Volumetric glassware should not be heated in a muffle furnace.

Soxhlet extractors cannot be baked in the muffle furnace, and thorough rinsing with hot tap water, followed by deionized water and acetone is not adequate. Even after a Soxhlet extractor was refluxed with acetone for three days, with daily solvent changes, the levels of bis(2-ethylhexyl) phthalate were as high as 500 ng per washing. Storage of glassware in the laboratory introduces contamination even if the glassware is wrapped in aluminum foil. Therefore, any glassware used in Method 8061 should be cleaned immediately prior to use.

3.4 Florisil and alumina may be contaminated with phthalate esters and, therefore, use of these materials in sample cleanup should be employed cautiously. Washing of these materials prior to use with the solvent(s) that is/are used for elution during extract cleanup was found helpful, however, heating at 320°C for Florisil and 210°C for alumina is recommended. Phthalate esters were detected in Florisil cartridge method blanks at levels ranging from 10 to 460 ng, with 5 phthalate esters in the 105 to 460 ng range. Complete removal of the phthalate esters from Florisil cartridges does not seem possible, and it is therefore desirable to keep the steps involved in sample preparation to a minimum.

3.5 Paper thimbles and filter paper must be exhaustively washed with the solvent that will be used in the sample extraction. Soxhlet extraction of paper thimbles and filter paper for 12 hrs with fresh solvent should be repeated for a minimum of three times. Method blanks should be obtained before any of the precleaned thimbles or filter papers are used. Storage of precleaned thimbles and filter paper in precleaned glass jars covered with aluminum foil is recommended.

3.6 Glasswool used in any step of sample preparation should be a specially treated pyrex wool, pesticide grade, and must be baked at 400°C for 4 hrs immediately prior to use.

3.7 Sodium sulfate must be purified by heating at 400°C for 4 hrs in a shallow tray. To avoid recontamination, the precleaned material must be stored in glass bottles, covered with precleaned aluminum foil. The storage period should not exceed two weeks. To minimize contamination, extracts

should be dried directly in the glassware in which they are collected by adding small amounts of precleaned sodium sulfate until excess of free flowing material is noted.

3.8 The presence of elemental sulfur will result in large peaks which often mask the region of the compounds eluting before dicyclohexyl phthalate (Compound No. 14) in the gas chromatograms shown in Figure 1. Method 3660 is suggested for removal of sulfur.

3.9 Waxes and lipids can be removed by gel-permeation chromatography (Method 3640). Extracts containing high amounts of lipids are viscous and may even solidify at room temperature.

4.0 APPARATUS AND MATERIALS

4.1 Glassware, see Methods 3510, 3540, 3550, 3610, 3620, 3640, and 3660 for specifications.

4.2 Kuderna-Danish (K-D) apparatus, standard taper 19/22 ground-glass joints (Kontes K-570025-0500):

4.2.1 Concentrator tube, 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of solvents or analytes after removal from the concentration apparatus.

4.2.2 Evaporation flask, 500 mL (Kontes K-570001-50 or equivalent). Attach to concentrator tube with springs.

4.2.3 Snyder column, three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Springs, 1/2 in (Kontes K-662750).

4.2.5 Boiling chips, approximately 10/40 mesh. Heat to 400°C for 30 min or Soxhlet-extract with methylene chloride prior to use.

4.3 Gas chromatograph:

4.3.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column and split/splitless injection, 8-in injection tee (Supelco, Inc., Catalog No. 2-3665) or J&W Scientific "press-fit" glass Y splitter for megabore columns (Catalog No. 705-0733) and all required accessories, including syringes, analytical columns, gases, electron capture detectors, and data system.

4.3.2 Columns:

4.3.2.1 Column 1, 30 m x 0.53 mm i.d. DB-5 fused-silica open tubular column or equivalent, 1.5 µm film thickness.

4.3.2.2 Column 2, 30 m x 0.53 mm i.d. DB-1701 fused-silica open tubular column or equivalent, 1.0 µm film thickness.

4.4 Vacuum system for eluting disposable solid-phase extraction cartridges.

4.4.1 Vacuum manifold consisting of individually adjustable, easily accessible flow-control valves for up to 24 cartridges, sample rack, chemically resistant cover and seals, heavy-duty glass basin, removable stainless steel solvent guides, built-in vacuum gauge and valve.

4.4.2 Vacuum trap made of 500-mL side arm flask fitted with a one-hole stopper and glass tubing.

4.4.3 6-mL, 1-g solid-phase extraction cartridges, LC-Florisil or equivalent, prepackaged, ready to use.

4.5 Water bath, heated, with concentric ring cover, capable of temperature control (±2°C).

4.6 Apparatus for filtration of aqueous samples through 3M-Empore extraction disks (optional).

4.6.1 Vacuum apparatus:

4.6.1.1 1-L suction flask.

4.6.1.2 Disk base.

4.6.1.3 Graduated funnel.

4.6.1.4 Clamp.

4.6.1.5 Vacuum gauge.

4.6.1.6 Pinch clamp.

4.6.1.7 25 x 200 mm test tube.

4.6.2 47-mm 3M-Empore C_{18}-extraction disks (Analytichem International, Catalog No. 1214-5004, or equivalent).

5.0 REAGENTS

5.1 Reagent-grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently

high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent-grade water. All references to water in this method refer to HPLC-grade water unless otherwise specified.

5.3 Sodium sulfate (ACS certified), granular, anhydrous. Purify by heating at 400°C for 4 hrs in a shallow tray.

5.4 Florisil -- J. T. Baker, Lot No. 442707, 60/80 mesh, activated at 400°C for 16 hrs, then deactivated with water (3 percent by weight).

5.5 Florisil disposable cartridges -- Supelclean™ SPE tubes or equivalent consisting of serological-grade 6-mL polypropylene tubes, packed each with 1 g LC-Florisil (40-µm particles, 60-A pores) held between polyethylene frits.

5.6 Alumina -- Alumina Woelm N Super I, activated/deactivated as described for Florisil.

5.7 Hexane, methylene chloride, acetone, acetonitrile, and methanol. Pesticide quality or equivalent for hexane, methylene chloride, and acetone and HPLC grade for methanol and acetonitrile.

5.8 Stock standard solutions:

5.8.1 Prepare stock standard solutions at a concentration of 1 µg/µL by dissolving 0.0100 g of assayed reference material in hexane and diluting to volume in a 10-mL volumetric flask. When compound purity is assayed to be 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.8.2 Transfer the stock standard solutions into Teflon-lined screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked periodically by gas chromatography for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.8.3 Stock standard solutions must be replaced after 6 months, or sooner, if comparison with check standards indicates a problem.

5.9 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest are prepared through dilution of the stock standard solutions with hexane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after 1 to

2 months, or sooner, if comparison with calibration verification standards indicates a problem.

5.10 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Benzyl benzoate has been tested and found appropriate for Method 8061.

5.10.1 Prepare a spiking solution of benzyl benzoate in hexane at 5 µg/µL. Addition of 10 µL of this solution to 1 mL of sample extract is recommended. The spiking level of the internal standard should be kept constant for all samples and calibration standards. Store the internal standard spiking solution at 4°C in a Teflon-sealed container. Standard solution should be replaced when ongoing QC (Section 8) indicates a problem.

5.11 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), analytical system, and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and blank with surrogates. Three surrogates are suggested for Method 8061: diphenyl phthalate, diphenyl isophthalate, and dibenzyl phthalate.

5.11.1 Prepare a surrogate standard spiking solution in acetone which contains 50 ng/µL of each compound. Addition of 500 µL of this solution to 1 L of water or 30 g solid sample is equivalent to 25 µg/L of water or 830 ng/g of solid sample. The spiking level of the surrogate standards may be adjusted accordingly if the final volume of extract is reduced below 2 mL for water samples or 10 mL for solid samples. Store the surrogate spiking solution at 4°C in a Teflon-sealed container. The solution must be replaced after 6 months or sooner if ongoing QC (Section 8) indicates problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See introductory material to this chapter, Organic Analytes, Section 4.1.

6.2 The stability of the phthalate esters in soil or sediment samples has not been systematically investigated. Storage of soil samples at room temperature should be avoided since degradation of some phthalate esters has been reported to occur. Deep-freezing at -10°C or -20°C appears to be the most suitable method for storage of solid matrices since it has the widest range of application, causes the least changes in the samples, and makes the addition of preservatives unnecessary.

6.3 All aqueous samples must be extracted within 7 days of sample collection; all soil and sediment samples must be extracted within 30 days

of sample collection. Extracts must be stored at <4°C and must be analyzed within 30 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a pH of 5 to 7 with methylene chloride in a separatory funnel (Method 3510). Method 3520 is not recommended for the extraction of aqueous samples because the longer chain esters dihexyl phthalate bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and dinonyl phthalate tend to adsorb to the glassware and consequently, their extraction recoveries are <40 percent. Solid samples are extracted with hexane/acetone (1:1) or methylene chloride/acetone (1:1) in a Soxhlet extractor (Method 3540) or with a sonicator (Method 3550). Immediately prior to extraction, spike 500 µL of the surrogate standard spiking solution (concentration 50 ng/µL) to 1 L aqueous sample or 30 g solid sample.

7.1.2 Spiked samples are used to verify the applicability of the chosen extraction technique for each new sample type. Each matrix must be spiked with the compounds of interest to determine the percent recovery and the limit of detection for that matrix. Spiking of water samples should be performed by adding appropriate amounts of phthalate esters, dissolved in methanol or acetone, to the water sample immediately prior to extraction. After addition of the spike, mix the samples manually for 1 to 2 minutes. Typical spiking levels for water samples are 5 to 10 µg/L for samples in which phthalate esters were not detected and 2 to 5 times the background level in those cases where phthalate esters are present. Spiking of solid samples should be performed by adding appropriate amounts of phthalate esters which are dissolved in methanol or acetone to the solid samples. The solid sample should be wet prior to the addition of the spike (at least 40 percent moisture) and should be mixed thoroughly with a blender for 10 minutes to homogenize the material. Transfer the whole portion that was spiked with the test compounds to the extraction thimble for Soxhlet extraction (Method 3540) or proceed with the sonication extraction (Method 3550).

7.1.3 Extraction of aqueous samples using the 3M-Empore C_{18}-extraction disks (optional):

7.1.3.1 Disk preconditioning: Place the 3M-Empore C_{18}-extraction disk into the filtration apparatus and prewash the disk with 10 to 20 mL acetonitrile. Apply vacuum to pull the solvent through the disk. Maintain vacuum to pull air through for 5 min. Follow with 10 mL of methanol. Apply vacuum and pull most of the methanol through the disk. Release vacuum before the disk gets dry. Follow with 10 mL HPLC-grade water. Apply vacuum and pull most of

the water through the disk. Release the vacuum before the disk gets dry.

7.1.3.2 Sample preconcentration: Add 2.5 mL methanol to the 500 mL aqueous sample in order to get reproducible results. Pour the sample into the filtration apparatus. Adjust vacuum so that it takes approximately 20 min to process 502.5 mL of sample. After all sample has passed through the membrane disk, pull air through the disk for 5 to 10 min to remove any residual water.

7.1.3.3 Sample elution: Break the vacuum and place the tip of the filter base into the test tube that is contained inside the suction flask. Add 10 mL acetonitrile to the graduated funnel making sure to rinse the walls of the graduated funnel with the solvent. Apply vacuum to pass the acetonitrile through the membrane disk.

7.1.3.4 Extract concentration: Concentrate the extract to 2 mL or less using a gentle stream of pure nitrogen.

7.2 Prior to Florisil cleanup or gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed as follows:

7.2.1 Following K-D concentration of the methylene chloride or methylene chloride/acetone extracts obtained according to Section 7.1.2 to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.2.2 Momentarily remove the Snyder column, add 50 mL hexane, a new glass bead, and attach the macro-Snyder column. Concentrate the extract using 1 mL hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 2 mL for water samples or 10 mL for solid samples. Stopper the concentrator tube and store at 4°C if further processing will be performed immediately. If the extract will be stored for two days or longer, it should be transferred to a Teflon-lined screw-cap vial. Proceed with the gas chromatographic analysis.

7.3 Cleanup/Fractionation:

7.3.1 Cleanup may not be necessary for extracts from a relatively clean sample matrix. If polychlorinated biphenyls (PCBs) and organochlorine pesticides are known to be present in the sample, proceed with the procedure outlined in Methods 3610 or 3620. Collect Fraction 1 by eluting with 140 mL (Method 3610) or 100 mL (Method 3620) of 20-percent diethyl ether in hexane. Note that, under these conditions, bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, and bis(2-n-butoxyethyl) phthalate are not recovered from the Florisil column. The elution patterns and compound recoveries are given in Table 3.

7.3.2 As an alternative to Method 3620, the following Florisil cartridge procedure can be used for extract cleanup. With this method, bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, and bis(2-n-butoxyethyl) phthalate are recovered quantitatively.

7.3.2.1 Every lot of Florisil cartridges must be checked prior to use as follows. Install 1-g cartridges in the vacuum manifold. Wash each cartridge with 4 mL of pesticide-grade hexane and discard the eluate. Add to each cartridge 2 mL of a composite standard containing the test compounds at 5 to 10 µg/mL and elute each cartridge with 5 mL of 10-percent acetone in hexane. Concentrate the eluate to a final volume of 2 mL and analyze by GC/ECD. The lot of Florisil cartridges is acceptable if all 16 target compound recoveries, except bis(2-methoxyethyl) phthalate, are between 80 and 120 percent and if no other interferences are detected.

7.3.2.2 Prior to cleanup of sample extracts, the cartridges must be washed with hexane. This is accomplished by placing 10, 12, or 24 cartridges in the vacuum manifold (the number depends on the type of vacuum manifold; for example, Vac Elut SPS24 from Analytichem International can accommodate 24 cartridges) and passing at least 4 mL of pesticide-grade hexane through each cartridge. While washing the cartridges, adjust the vacuum applied to each cartridge so that the flows through the cartridges are approximately equal. Do not allow the cartridges to go dry after they have been washed.

7.3.2.3 After the cartridges have been washed, release the vacuum and replace the collecting vials with 5-mL volumetric flasks or culture tubes. Care must be taken to ensure that the solvent line from each cartridge is placed inside the correct volumetric flask or culture tube.

7.3.2.4 After the volumetric flasks or the culture tubes have been set in the vacuum manifold, the vacuum is restored and the sample extracts (the whole extract for the aqueous sample and 2 mL of the 10-mL extract for the solid samples) are added to the

appropriate cartridges. Use a syringe or a volumetric pipet for transferring the extracts.

7.3.2.5 Elute each cartridge with 5 mL of 10-percent acetone in hexane and collect the eluate in a 5-mL volumetric flask or culture tube held inside the vacuum manifold. Adjust to the 5-mL mark if not all solvent is recovered. Transfer the eluates to clean sample vials for further concentration using nitrogen blow-down evaporation with a gentle stream of pure nitrogen. The elution patterns and compound recoveries are given in Table 3.

7.3.3 If PCBs and organochlorine pesticides are known to be present in the sample, and if the Florisil cartridge procedure is considered, then two fractions are collected: Fraction 1 is eluted with 5 ml of 20-percent methylene chloride in hexane and Fraction 2 is eluted with 5 mL of 10-percent acetone in hexane. The elution patterns and compound recoveries are given in Table 4. Fraction 1 contains the organochlorine pesticides and PCBS and can be discarded. Fraction 2 contains the phthalate esters and is analyzed by GC/ECD.

7.4 Gas chromatography conditions (recommended):

7.4.1 Column 1 (DB-5) and Column 2 (DB-1701): Temperature program 150°C (0.5 min hold) to 220°C at 5°C/min, then to 275°C (13 min hold) at 3°C/min; carrier gas helium at 6 mL/min; makeup gas nitrogen at 20 mL/min; injector temperature 250°C; detector temperature 320°C.

7.4.2 Table 1 gives the retention times and MDLs that can be achieved by this method for the 16 phthalate esters. An example of the separations achieved with the DB-5 and DB-1701 fused-silica open tubular columns is shown in Figure 1.

7.5 Calibration:

7.5.1 Refer to Method 8000 for proper calibration techniques. Use Tables 1 and 2 for guidance on selecting the lowest point on the calibration curve.

7.5.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for the description of each of these procedures.

7.6 Gas chromatographic analysis:

7.6.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard solution at 5 µg/µL to the sample prior to injection.

7.6.2 Follow step 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria.

7.6.3 Record the sample volume injected and the resulting peak areas.

7.6.4 Using either the internal or the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.6.5 If the response of a peak exceeds the working range of the system, dilute the extract and reanalyze.

7.6.6 Identify compounds in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The retention time window used to make identifications is based upon measurements of actual retention time variations over the course of 10 consecutive injections. Three times the standard deviation of the retention time can be used to calculate a suggested window size.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC specified in Method 3600 and in the specific cleanup method.

8.2 Mandatory quality control to evaluate the GC system operation is found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain the test compounds at 5 to 10 ng/µL.

8.3 Calculate the recoveries of the surrogate compounds for all samples, method blanks, and method spikes. Determine if the recoveries are within limits established by performing QC procedures outlined in Method 8000 Step 8.10.

8.3.1 If the recoveries are not within limits, the following are required:

- Make sure there are no errors in calculations, surrogate solutions and internal standards. Also check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem, or flag the data as "estimated concentration."

8.4 An internal standard peak area check must be performed on all samples. The internal standard must be evaluated for acceptance by

determining whether the measured area for the internal standard deviates by more than 50 percent from the average area for the internal standard in the calibration standards. When the internal standard peak area is outside that limit, all samples that fall outside the QC criteria must be reanalyzed.

8.5 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory-generated detection limits.

8.5.1 The GC/MS would normally require a minimum concentration of 10 ng/μL in the final extract for each single-component compound.

8.5.2 The sample extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.5.3 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the phthalate esters identified by GC/ECD.

8.6 Include a mid-level calibration standard after each group of 20 samples in the analysis sequence. The response factors for the mid-level calibration must be within ±30 percent of the average values for the multilevel calibration.

8.7 Demonstrate through the analyses of standards that the Florisil fractionation scheme is reproducible. When using the fractionation schemes given in Methods 3610 or 3620, batch-to-batch variations in the composition of the alumina or Florisil material may cause variations in the recoveries of the phthalate esters.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined as the minimum concentration of the test compound that can be measured and reported with 99 percent confidence as being greater than zero. The MDL concentrations listed in Table 1 were obtained by using reagent water. Details on how to determine MDLs are given in Reference 1. The MDL actually achieved in a given analysis will vary as it is dependent on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory by using different types of aqueous samples and solid samples which were fortified with the test compounds at two concentrations. Single-operator precision, overall precision, and method accuracy were found to be related to the concentration of the compounds and the type of matrix. For exemplification, results of the single-laboratory method evaluation are given in Tables 5, 6, and 7.

9.3 The accuracy and precision obtained will be determined by the sample matrix, sample preparation technique, cleanup techniques, and calibration procedures used.

10.0 REFERENCES

(1) Glazer, J.A.; Foerst, G.D.; McKee, G.D.; Quave, S.A., and Budde, W.L. "Trace Analyses for Wastewaters," Environ. Sci. and Technol. 15: 1426, 1981.

TABLE 1. GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE PHTHALATE ESTERS[a]

Compound No.	Compound name	Chemical Abstract Registry No.	Retention time (min)		MDL[b]
			Column 1	Column 2	Liquid (ng/L)
1	Dimethyl phthalate (DMP)	131-11-3	7.06	6.37	640
2	Diethyl phthalate (DEP)	84-66-2	9.30	8.45	250
3	Diisobutyl phthalate (DIBP)	84-69-5	14.44	12.91	120
4	Di-n-butyl phthalate (DBP)	84-74-2	16.26	14.66	330
5	Bis(4-methyl-2-pentyl) phthalate (BMPP)	146-50-9	18.77	16.27	370
6	Bis(2-methoxyethyl) phthalate (BMEP)	117-82-8	17.02	16.41	510
7	Diamyl phthalate (DAP)	131-18-0	20.25	18.08	110
8	Bis(2-ethoxyethyl) phthalate (BEEP)	605-54-9	19.43	18.21	270
9	Hexyl 2-ethylhexyl phthalate (HEHP)	75673-16-4	21.07	18.97	130
10	Dihexyl phthalate (DHP)	84-75-3	24.57	21.85	68
11	Benzyl butyl phthalate (BBP)	85-68-7	24.86	23.08	42
12	Bis(2-n-butoxyethyl) phthalate (BBEP)	117-83-9	27.56	25.24	84
13	Bis(2-ethylhexyl) phthalate (DEHP)	117-81-7	29.23	25.67	270
14	Dicyclohexyl phthalate (DCP)	84-61-7	28.88	26.35	22
15	Di-n-octyl phthalate (DOP)	117-84-0	33.33	29.83	49
16	Dinonyl phthalate	84-76-4	38.80	33.84	22
IS	Benzyl benzoate	120-51-4	12.71	11.07	[c]
SU-1	Diphenyl phthalate (DPP)	84-62-8	29.46	28.32	[c]
SU-2	Diphenyl isophthalate (DPIP)	744-45-6	32.99	31.37	[c]
SU-3	Dibenzyl phthalate (DBZP)	523-31-9	34.40	32.65	[c]

[a] Column 1 is a 30 m x 0.53 mm ID DB-5 fused-silica open tubular column (1.5-μm film thickness). Column 2 is a 30 m 0.53 mm ID DB-1701 fused-silica open tubular column (1.0-μm film thickness). Temperature program is 150°C (0.5 min hold) to 220°C at 5°C/min, then to 275°C (13 min hold) at 3°C/min. An 8-in Supelco injection tee or a J&W Scientific press fit glass inlet splitter is used to connect the two columns to the injection port of a gas chromatograph. Carrier gas helium at 6 mL/min; makeup gas nitrogen at 20 mL/min; injector temperature 250°C; detector temperature 320°C.

[b] MDL is the method detection limit. The MDL was determined from the analysis of seven replicate aliquots of reagent water processed through the entire analytical method (extraction, Florisil cartridge cleanup, and GC/ECD analysis using the single column approach: DB-5 fused-silica capillary column). MDL = t(n-1, 0.99) x SD where t(n-1, 0.99) is the student's t value appropriate for a 99-percent confidence interval and a standard deviation with n-1 degrees of freedom, and SD is the standard deviation of the seven replicate measurements. Values measured were not corrected for method blanks.

[c] Not applicable.

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Groundwater	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Nonwater miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For nonaqueous samples, the factor is on a wet-weight basis.

TABLE 3. AVERAGE RECOVERIES OF METHOD 8061 COMPOUNDS USING METHODS 3610, 3620, AND THE ALUMINA AND FLORISIL DISPOSABLE CARTRIDGE PROCEDURE

Compound	Method 3610 alumina[a]	Method 3620 Florisil[a]	Alumina cartridge[b]	Florisil cartridge[d]
Dimethyl phthalate	64.5	40.0	101	89.4
Diethyl phthalate	62.5	57.0	103	97.3
Diisobutyl phthalate	77.0	80.0	104	91.8
Di-n-butyl phthalate	76.5	85.0	108	102
Bis(4-methyl-2-pentyl) phthalate	89.5	84.5	103	105
Bis(2-methoxyethyl) phthalate	70.5	0	64.1[c]	78.3[e]
Diamyl phthalate	75.0	81.5	103	94.5
Bis(2-ethoxyethyl) phthalate	67.0	0	111	93.6
Hexyl 2-ethylhexyl phthalate	90.5	105	101	96.0
Dihexyl phthalate	73.0	74.5	108	96.8
Benzyl butyl phthalate	87.0	90.0	103	98.6
Bis(2-n-butoxyethyl) phthalate	62.5	0	108	91.5
Bis(2-ethylhexyl) phthalate	91.0	82.0	97.6	97.5
Dicyclohexyl phthalate	84.5	83.5	97.5	90.5
Di-n-octyl phthalate	108	115	112	97.1
Dinonyl phthalate	71.0	72.5	97.3	105

[a] The number of determinations was 2; alumina and Florisil chromatography were done according to Methods 3610, and 3620, respectively.
[b] 1-g alumina cartridges were used; Fraction 1 was eluted with 5 mL of 20-percent acetone in hexane. The number of determinations was 2. The amount spiked was 40 µg per component per cartridge.
[c] The amount recovered by elution with an additional 5 mL of 20-percent acetone in hexane was 36.8 percent.
[d] 1-g Florisil cartridges were used; Fraction 1 was eluted with 5 mL of 10-percent acetone in hexane. The number of determinations was 2. The amount spiked was 40 µg per component per cartridge.
[e] The amount recovered by elution with an additional 5 mL of 10-percent acetone in hexane was 14.4 percent.

TABLE 4. ELUTION PATTERNS AND AVERAGE RECOVERIES OF METHOD 8061 COMPOUNDS USING THE FLORISIL DISPOSABLE CARTRIDGES

Compound	Percent recovery[a]	
	Fraction 1	Fraction 2
Dimethyl phthalate	0	130 (52)
Diethyl phthalate	0	88 (2.8)
Diisobutyl phthalate	0	118 (16)
Di-n-butyl phthalate	12	121 (13)
Bis(4-methyl-2-pentyl) phthalate	0	123 (5.7)
Bis(2-methoxyethyl) phthalate	0	32 (31)
Diamyl phthalate	3.3	94 (8.3)
Bis(2-ethoxyethyl) phthalate	0	82 (19)
Hexyl 2-ethylhexyl phthalate	0	126 (6.4)
Dihexyl phthalate	0	62 (15)
Benzyl butyl phthalate	0	98 (6.5)
Bis(2-n-butoxyethyl) phthalate	0	135 (34)
Bis(2-ethylhexyl) phthalate	0	110 (2.7)
Dicyclohexyl phthalate	0	106 (3.3)
Di-n-octyl phthalate	0	123 (7.0)
Dinonyl phthalate	0	102 (8.7)

[a] The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries.

TABLE 5. ACCURACY AND PRECISION DATA FOR EXTRACTION USING THE 3M EMPORE DISKS AND METHOD 8061

Compound	HPLC-grade water		Groundwater	
	Average recovery (%)	Precision (% RSD)	Average recovery (%)	Precision (% RSD)
Dimethyl phthalate	88.6	17.7	86.6	14.3
Diethyl phthalate	92.3	10.3	92.6	7.2
Diisobutyl phthalate	87.6	16.2	89.3	1.6
Di-n-butyl phthalate	90.3	13.2	95.0	1.5
Bis(4-methyl-2-pentyl) phthalate	87.2	9.5	86.7	4.9
Bis(2-methoxyethyl) phthalate	107	13.6	113	2.8
Diamyl phthalate	93.6	21.0	78.9	5.8
Bis(2-ethoxyethyl) phthalate	108	8.9	102	4.0
Hexyl 2-ethylhexyl phthalate	93.9	22.4	83.4	8.8
Dihexyl phthalate	98.4	5.0	97.7	14.8
Benzyl butyl phthalate	97.3	2.6	66.0	39.3
Bis(2-n-butoxyethyl) phthalate	94.8	6.3	98.7	6.0
Bis(2-ethylhexyl) phthalate	91.3	7.4	96.3	7.9
Dicyclohexyl phthalate	106	19.9	108	13.3
Di-n-octyl phthalate	84.9	3.8	90.1	6.1
Dinonyl phthalate	96.9	11.1	95.2	12.7

[a]The number of determinations was 4. The spiking level was 100 µg/L per component.

TABLE 6. ACCURACY AND PRECISION DATA FOR METHOD 3510 AND METHOD 8061[a]

Compound	Spike level (20 µg/L)			Spike level (60 µg/L)		
	Estuarine water	Leachate	Groundwater	Estuarine water	Leachate	Groundwater
Dimethyl phthalate	84.0 (4.1)	98.9 (19.6)	87.1 (8.1)	87.1 (7.5)	112 (17.5)	90.9 (4.5)
Diethyl phthalate	71.2 (3.8)	82.8 (19.3)	88.5 (15.3)	71.0 (7.7)	88.5 (17.9)	75.3 (3.5)
Diisobutyl phthalate	76.0 (6.5)	95.3 (16.9)	92.7 (17.1)	99.1 (19.0)	100 (9.6)	83.2 (3.3)
Di-n-butyl phthalate	83.2 (6.5)	97.5 (22.3)	91.0 (10.7)	87.0 (8.0)	106 (17.4)	87.7 (2.7)
Bis(4-methyl-2-pentyl) phthalate	78.6 (2.6)	87.3 (18.2)	92.6 (13.7)	97.4 (15.0)	107 (13.3)	87.6 (2.9)
Bis(2-methoxyethyl) phthalate	73.8 (1.0)	87.2 (21.7)	82.4 (4.4)	82.5 (5.5)	99.0 (13.7)	76.9 (6.6)
Diamyl phthalate	78.2 (7.3)	92.1 (21.5)	88.8 (7.5)	89.2 (2.8)	112 (14.2)	92.5 (1.8)
Bis(2-ethoxyethyl) phthalate	75.6 (3.3)	90.8 (22.4)	86.4 (5.8)	88.7 (4.9)	109 (14.6)	84.8 (5.9)
Hexyl 2-ethylhexyl phthalate	84.7 (5.3)	91.1 (27.5)	81.4 (17.6)	107 (16.8)	117 (11.4)	80.1 (4.1)
Dihexyl phthalate	79.8 (7.2)	102 (21.5)	90.9 (7.6)	90.1 (2.4)	109 (20.7)	88.9 (2.4)
Benzyl butyl phthalate	84.1 (6.4)	105 (20.5)	89.6 (6.1)	92.7 (5.6)	117 (24.7)	93.0 (2.0)
Bis(2-n-butoxyethyl) phthalate	78.5 (3.5)	92.3 (16.1)	89.3 (3.6)	86.1 (6.2)	107 (15.3)	92.4 (0.6)
Bis(2-ethylhexyl) phthalate	81.4 (4.1)	93.0 (15.0)	90.5 (4.9)	86.5 (6.9)	108 (15.1)	91.1 (3.0)
Dicyclohexyl phthalate	77.4 (6.5)	88.2 (13.2)	91.7 (15.2)	87.7 (9.6)	102 (14.3)	71.9 (2.4)
Di-n-octyl phthalate	74.9 (4.9)	87.5 (18.7)	87.2 (3.7)	85.1 (8.3)	105 (17.7)	90.4 (2.0)
Dinonyl phthalate	59.5 (6.1)	77.3 (4.2)	67.2 (8.0)	97.2 (7.0)	108 (17.9)	90.1 (1.1)
Surrogates:						
Diphenyl phthalate	98.5 (2.6)	113 (14.9)	110 (3.3)	110 (12.4)	95.1 (7.2)	107 (2.4)
Diphenyl isophthalate	95.8 (1.9)	112 (11.7)	109 (3.3)	104 (5.9)	97.1 (7.1)	106 (2.8)
Dibenzyl phthalate	93.9 (4.4)	112 (14.0)	106 (3.8)	111 (5.9)	93.3 (9.5)	105 (2.4)

[a] The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries.

TABLE 7. ACCURACY AND PRECISION DATA FOR METHOD 3550 AND METHOD 8061[a]

Compound	Spike level (1 µg/g)			Spike level (3 µg/g)		
	Estuarine sediment	Municipal sludge	Sandy loam soil	Estuarine sediment	Municipal sludge	Sandy loam soil
Dimethyl phthalate	77.9 (42.8)	52.1 (35.5)	[c]	136 (9.6)	64.8 (11.5)	70.2 (2.0)
Diethyl phthalate	68.4 (1.7)	68.6 (9.1)	54.7 (6.2)	60.2 (12.5)	72.8 (10.0)	67.0 (15.1)
Diisobutyl phthalate	103 (3.1)	106 (5.3)	70.3 (3.7)	74.8 (6.0)	84.0 (4.6)	79.2 (0.1)
Di-n-butyl phthalate	121 (25.8)	86.3 (17.7)	72.6 (3.7)	74.6 (3.9)	113 (5.8)	70.9 (5.5)
Bis(4-methyl-2-pentyl) phthalate	108 (57.4)	97.3 (7.4)	[c]	104 (1.5)	150 (6.1)	83.9 (11.8)
Bis(2-methoxyethyl) phthalate	26.6 (26.8)	72.7 (8.3)	0	19.5 (14.8)	59.9 (5.4)	0
Diamyl phthalate	95.0 (10.2)	81.9 (7.1)	81.9 (15.9)	77.3 (4.0)	116 (3.7)	82.1 (15.5)
Bis(2-ethoxyethyl) phthalate	[c]	66.6 (4.9)	[c]	21.7 (22.8)	57.5 (9.2)	84.7 (8.5)
Hexyl 2-ethylhexyl phthalate	[c]	114 (10.5)	57.7 (2.8)	72.7 (11.3)	26.6 (47.6)	28.4 (4.3)
Dihexyl phthalate	103 (3.6)	96.4 (10.7)	77.9 (2.4)	75.5 (6.8)	80.3 (4.7)	79.5 (2.7)
Benzyl butyl phthalate	113 (12.8)	82.8 (7.8)	56.5 (5.1)	72.9 (3.4)	76.8 (10.3)	67.3 (3.8)
Bis(2-n-butoxyethyl) phthalate	114 (21.1)	74.0 (15.6)	[c]	38.3 (25.1)	98.0 (6.4)	62.0 (3.4)
Bis(2-ethylhexyl) phthalate	[c]	76.6 (10.6)	99.2 (25.3)	59.5 (18.3)	85.8 (6.4)	65.4 (2.8)
Dicyclohexyl phthalate	36.6 (48.8)	65.8 (15.7)	92.8 (35.9)	33.9 (66.1)	68.5 (9.6)	62.2 (19.1)
Di-n-octyl phthalate	[c]	93.3 (14.6)	84.7 (9.3)	36.8 (16.4)	88.4 (7.4)	115 (29.2)
Dinonyl phthalate	[c]	80.0 (41.1)	64.2 (17.2)	[c]	156 (8.6)	115 (13.2)

[a]The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries. All samples were subjected to Florisil cartridge cleanup.
[b]The estuarine sediment extract (Florisil, Fraction 1) was subjected to sulfur cleanup (Method 3660 with tetrabutylammonium sulfite reagent).
[c]Not able to determine because of matrix interferent.

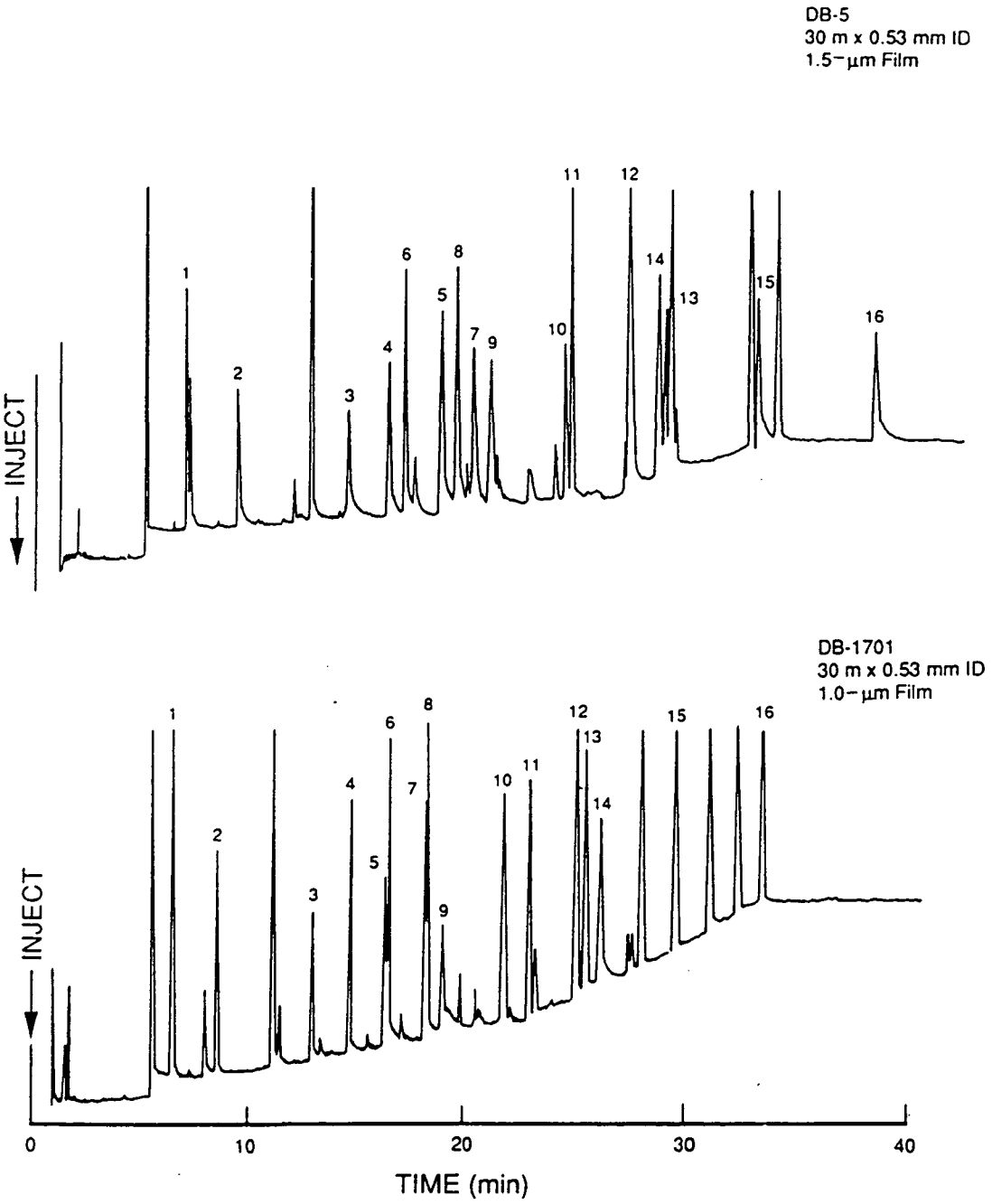
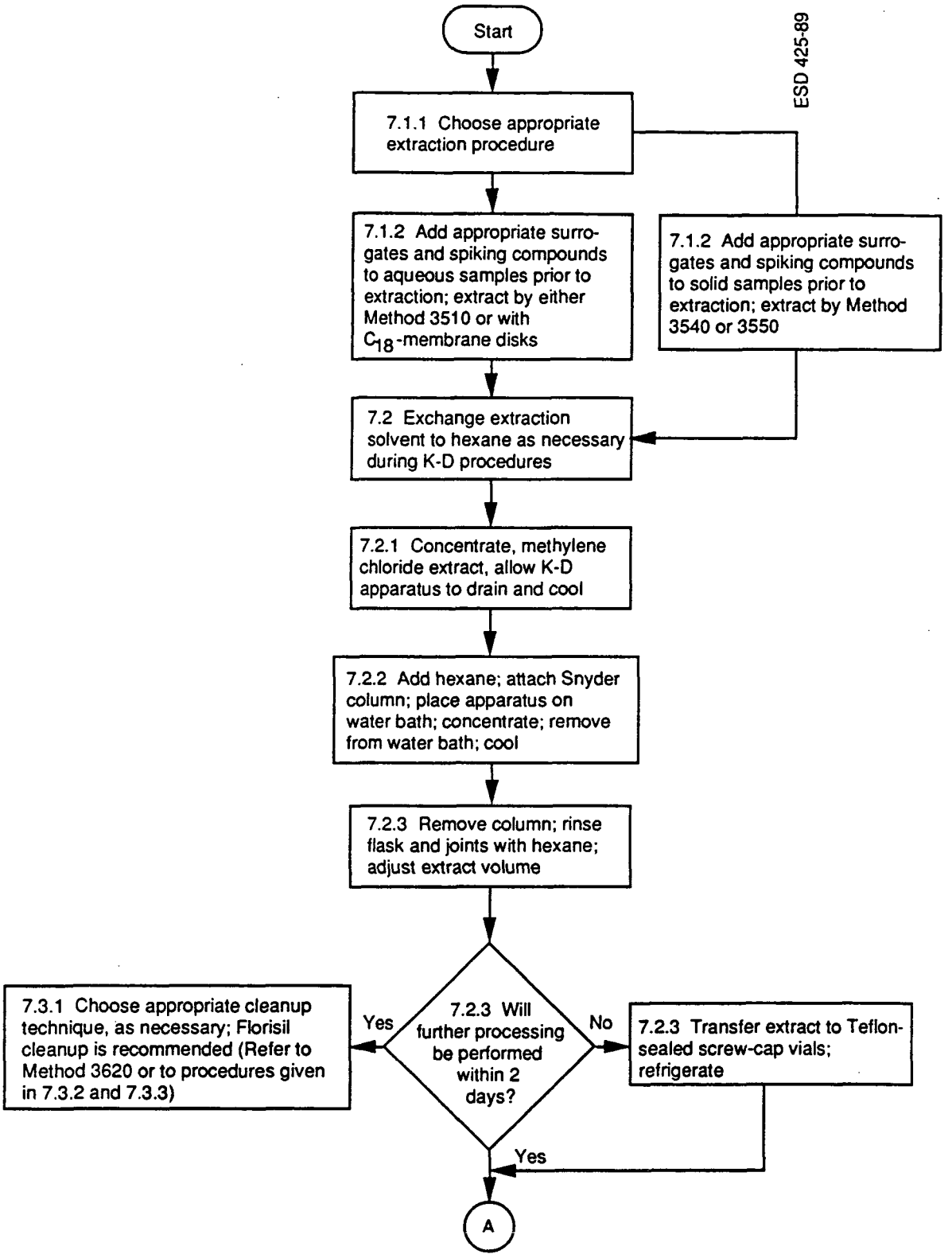
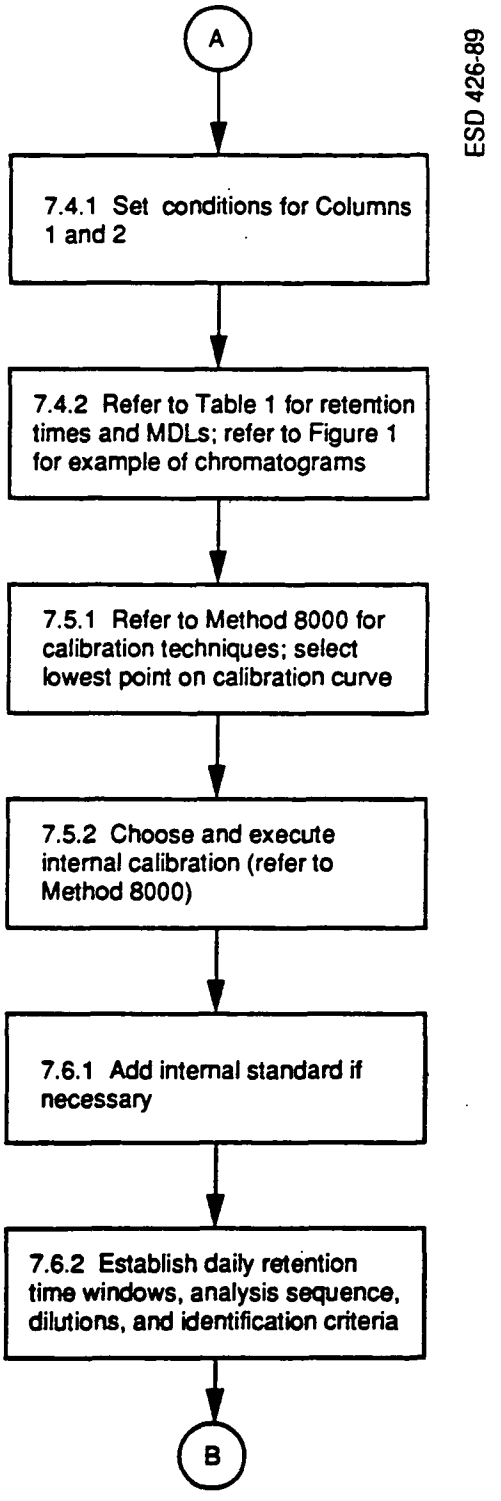
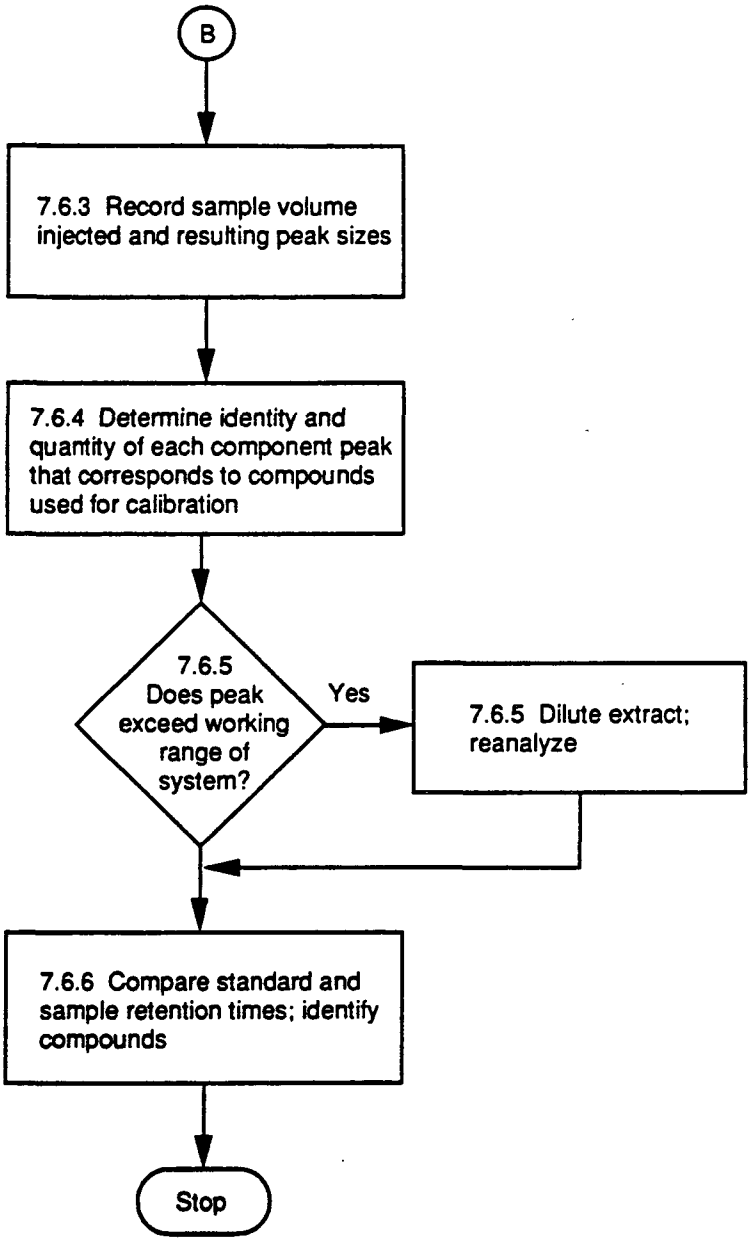


Figure 1. GC/ECD chromatograms of a composite phthalate esters standard (concentration 10 ng/µL per compound) analyzed on a DB-5 and a DB-1701 fused-silica open tubular column. Temperature program: 150°C (0.5 min hold) to 220°C at 5°C/min, then to 275°C (13 min hold) at 3°C/min.

METHOD 8061—PHTHALATE ESTERS (FLOW CHART)




A
ESD 426-89
7.4.1 Set conditions for Columns 1 and 2
7.4.2 Refer to Table 1 for retention times and MDLs; refer to Figure 1 for example of chromatograms
7.5.1 Refer to Method 8000 for calibration techniques; select lowest point on calibration curve
7.5.2 Choose and execute internal calibration (refer to Method 8000)
7.6.1 Add internal standard if necessary
7.6.2 Establish daily retention time windows, analysis sequence, dilutions, and identification criteria
B


B
7.6.3 Record sample volume injected and resulting peak sizes
7.6.4 Determine identity and quantity of each component peak that corresponds to compounds used for calibration
7.6.5 Does peak exceed working range of system?
Yes
7.6.5 Dilute extract; reanalyze
7.6.6 Compare standard and sample retention times; identify compounds
Stop

APPENDIX C

GC/MS CHROMATOGRAMS AND MASS SPECTRA (PLOT AND LIST)[a] FOR METHOD 8060 COMPOUNDS

[a]To identify a particular mass spectrum in this appendix, refer to Table 1 in this appendix which gives compound name, scan number, three most intense ions and their relative intensities. The GC/MS operating conditions are given in footnote "a" of Table 1.

TABLE 1. RETENTION TIMES (SCAN NUMBER) AND THREE MOST INTENSE PEAKS IN THE MASS SPECTRA OF METHOD 8060 COMPOUNDS[a]

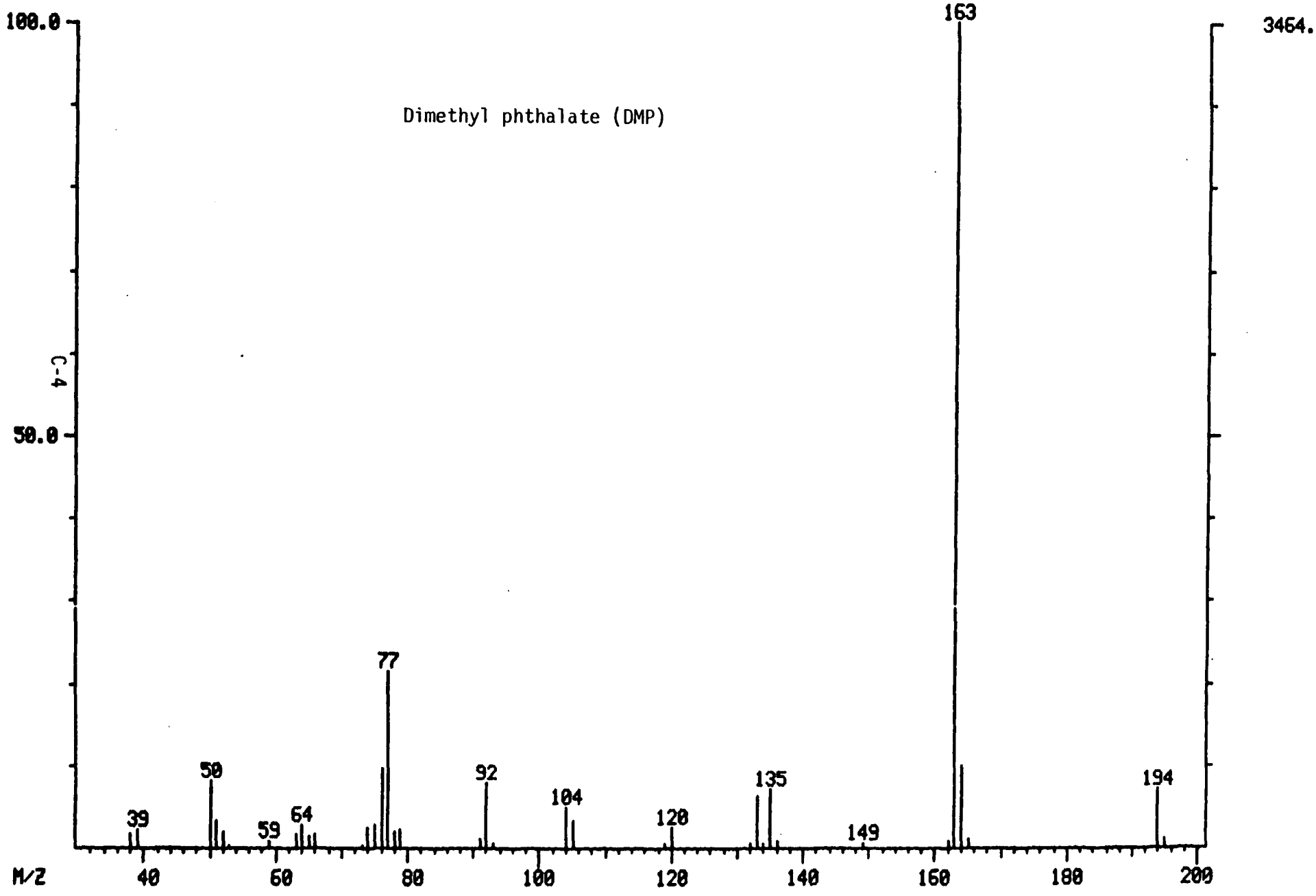
Compound no.	Compound name	Scan number	Mass spectrum m/z (relative intensity)		
1	DMP	1128	163 (100),	77 (21),	164 (10)
2	DEP	1264	149 (100),	177 (23),	150 (12)
3	DIBP	1499	149 (100),	57 (28),	41 (13)
4	DBP	1573	149 (100),	41 (9.2),	150 (8.9)
5	BMEP	1602	59 (100),	58 (73),	149 (13)
6	BMPP	1662	149 (100),	85 (66),	43 (66)
7	BEEP	1687	45 (100),	72 (94),	73 (92)
8	DAP	1714	149 (100),	43 (19),	150 (8.8)
9	HEHP	1737	149 (100),	57 (19),	55 (12)
10	DHP	1844	149 (100),	43 (21),	41 (8.4)
11	BBP	1851	149 (100),	91 (69),	206 (26)
12	BBEP	1928	57 (100),	56 (82),	45 (80)
13	DCP	1962	149 (100),	167 (34),	55 (24)
14	DEHP	1973	149 (100),	57 (39),	167 (36)
15	DOP	2082	149 (100),	43 (14),	57 (12)
16	DNP	2191	149 (100),	43 (18),	150 (9.8)
Benzyl benzoate (IS)		1397	105 (100),	91 (43),	77 (28)
Diphenyl phthalate (SU)		1959	225 (100),	77 (39),	226 (15)
Diphenyl isophthalate (SU)		2057	225 (100),	76 (27),	104 (23)
Diphenyl terephthalate (SU)		2061	225 (100),	104 (44),	76 (20)
Dibenzyl phthalate (SU)		2087	107 (100),	91 (81),	149 (70)
Dioctyl isophthalate (SU)		2127	167 (100),	279 (41),	149 (21)

[a]The GC operating conditions are as follows: 30 m x 0.25 mm ID DB-5 fused-silica capillary column, 45 to 300°C at 8°C/min.

MASS SPECTRUM
02/02/88 23:04:00 + 18:48
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1128
CALI: ESTERSTD #2

BASE M/Z: 163
RIC: 7688.



Mass List Data: ESTERSTD #112B Base m/z: 163
02/02/88 23:04:00 + 18:48 Cali: ESTERSTD # 2 RIC: 7688.
Sample:
!#
#
#(#3

Dimethyl phthalate (DMP)

Conds.:
Enhanced (S 15B 2N OT)

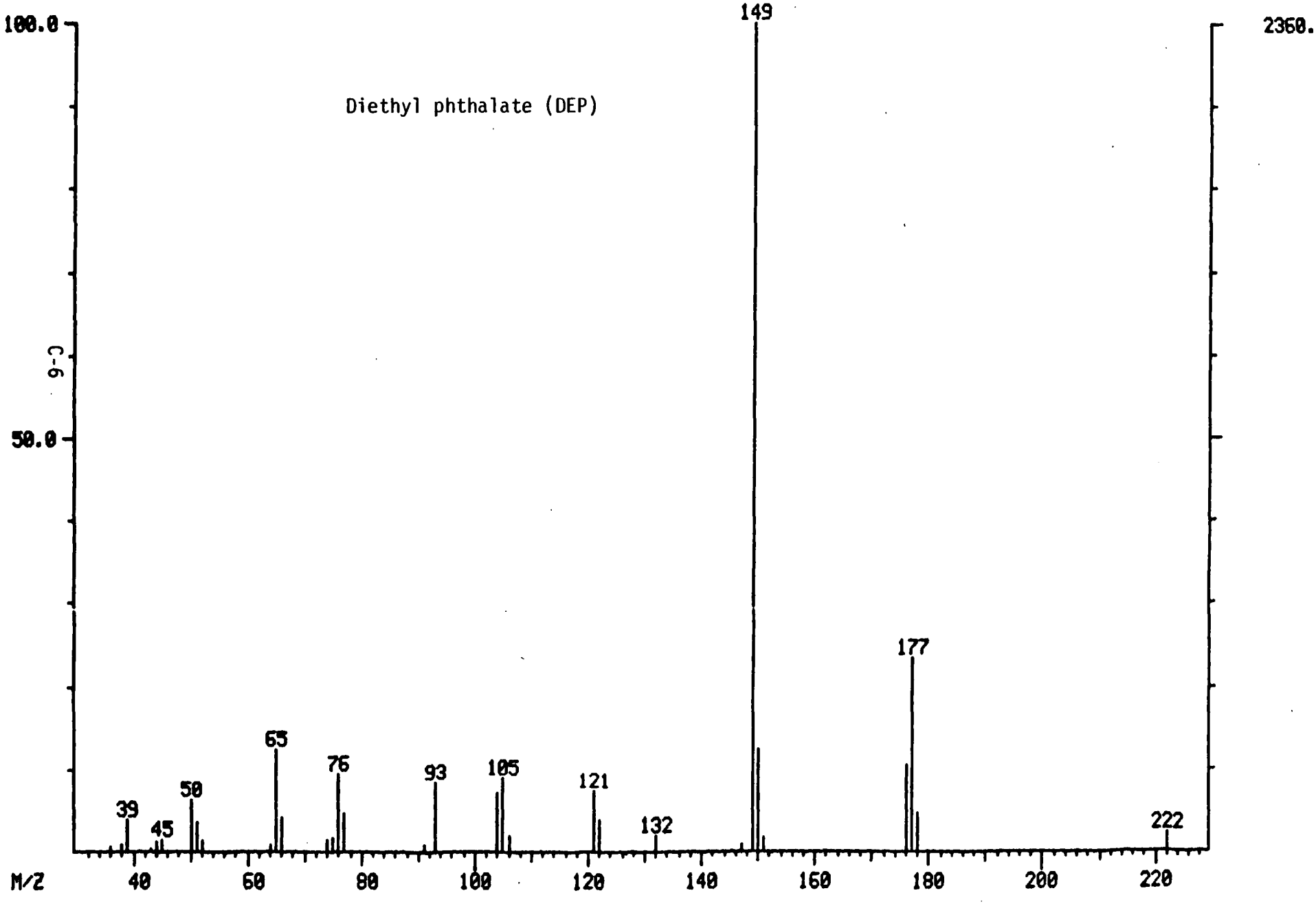
38 0.00 0. Minima Min Inten: 0.
195 Maxima # 0

Mass	% RA	Inten.
38?	1.53	53.
39?	2.05	71.
50	7.94	275.
51	3.20	111.
52	1.79	62.
53	0.40	14.
59	0.92	32.
63	1.65	57.
64	2.80	97.
65	1.21	42.
66	1.67	58.
73	0.38	13.
74	2.42	84.
75	2.66	92.
76	9.56	331.
77	21.39	741.
78	1.79	62.
79	2.25	78.
91	1.10	38.
92	7.82	271.
93	0.43	15.
104	4.76	165.
105	3.20	111.
119	0.49	17.
120	2.54	88.
132	0.43	15.
133	6.09	211.
134	0.64	22.
135	7.02	243.
136	0.87	30.
149	0.43	15.
162	0.92	32.
163	100.00	3464.
164	9.82	340.
165	1.15	40.
194	6.87	238.
195	0.95	33.

MASS SPECTRUM
02/02/88 23:04:00 + 21:04
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1264
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 5856.



Mass List Data: ESTERSTD #1264 Base m/z: 149
02/02/88 23:04:00 + 21:04 Cali: ESTERSTD # 2 RIC: 5856.
Sample:
!#
#
#(#3

Diethyl phthalate (DEP)

Conds.:
Enhanced (S 15B 2N OT)

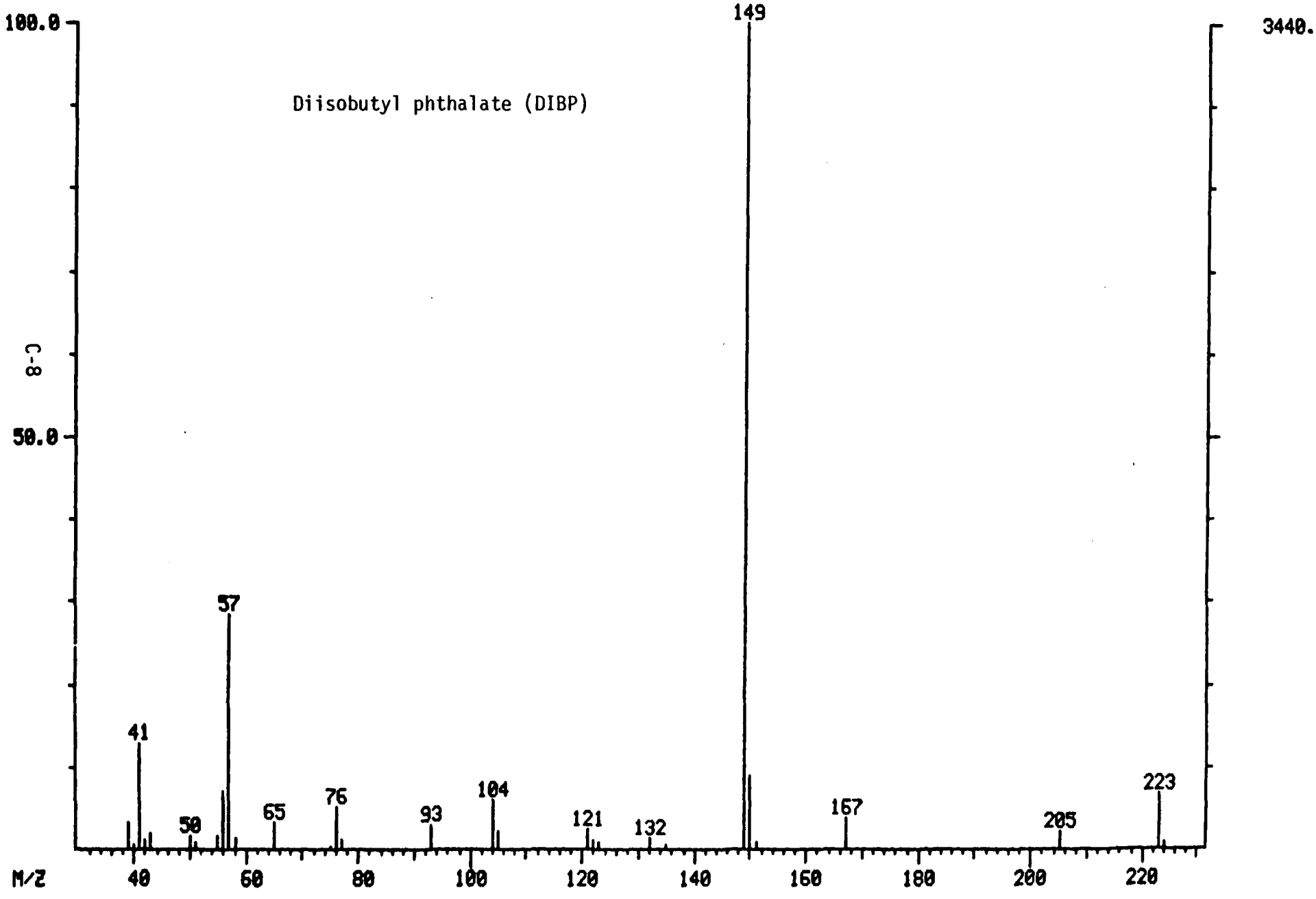
36	0.00	0.	Minima	Min	Inten:	0.
222			Maxima	#	0	

Mass	% RA	Inten.
36?	0.51	12.
38?	0.68	16.
39?	3.90	92.
43	0.38	9.
44	1.10	26.
45	1.27	30.
50	6.19	146.
51	3.39	80.
52	1.36	32.
64	0.93	22.
65	12.29	290.
66	4.03	95.
74	1.40	33.
75	1.74	41.
76	9.32	220.
77	4.70	111.
91	0.72	17.
93	8.26	195.
104	6.95	164.
105	8.94	211.
106	1.86	44.
121	7.16	169.
122	3.69	87.
132	1.78	42.
147	0.89	21.
149	100.00	2360.
150	12.46	294.
151	1.48	35.
176	10.42	246.
177	23.43	553.
178	4.49	106.
222	2.12	50.

MASS SPECTRUM
02/02/88 23:04:00 + 24:59
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1499
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 7256.



Mass List Data: ESTERSTD #1499 Base m/z: 149
02/02/88 23:04:00 + 24:59 Cali: ESTERSTD # 2 RIC: 7256.
Sample:
!#
#
#(#3

Diisobutyl phthalate (DIBP)

Conds.:
Enhanced (S 15B 2N OT)

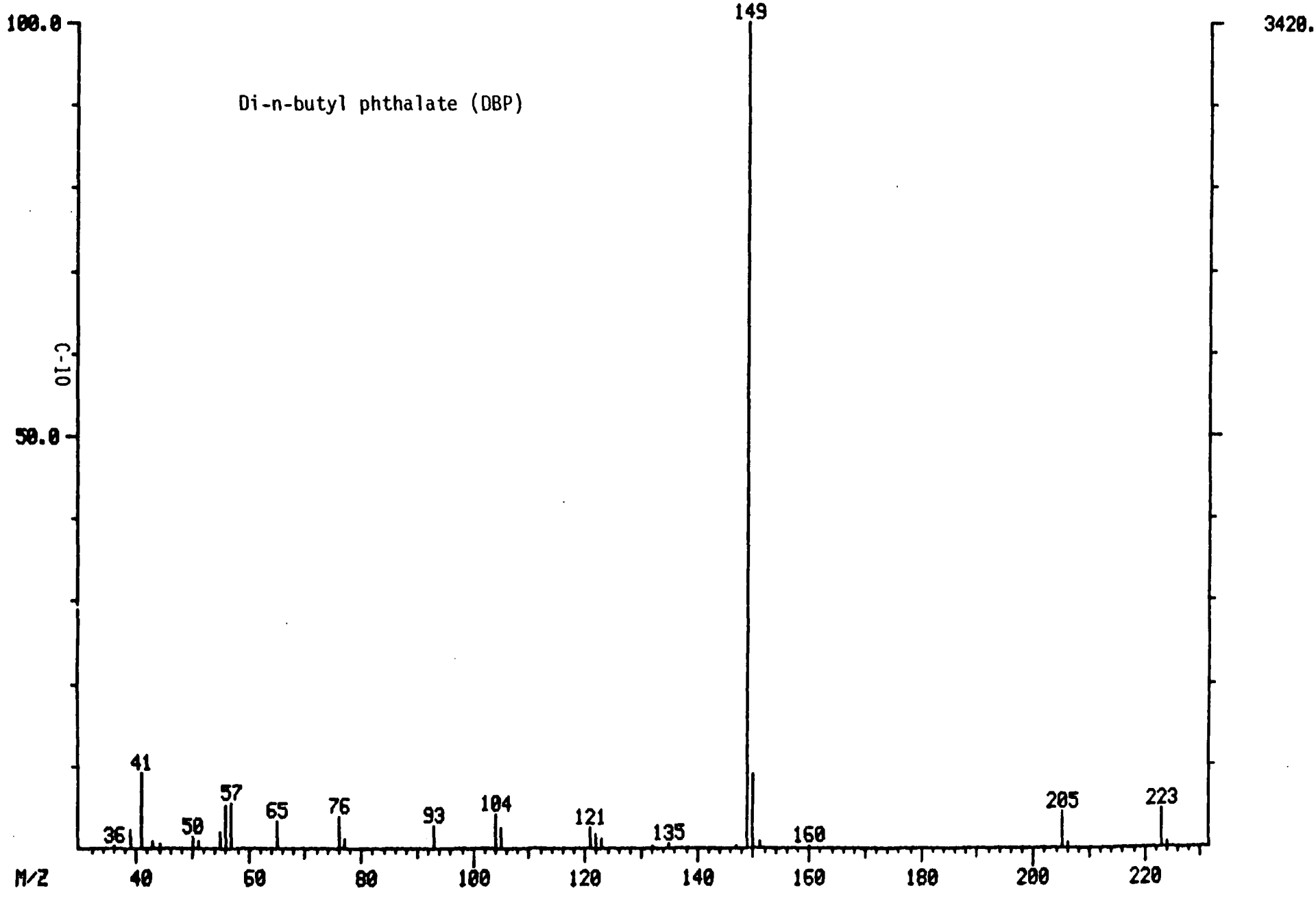
39 0.00 0. Minima Min Inten: 0.
224 Maxima # 0

Mass	% RA	Inten.
39?	3.11	107.
40	0.67	23.
41	12.88	443.
42	0.99	34.
43	2.01	69.
50	1.69	58.
51	0.78	27.
55	1.54	53.
56	6.92	238.
57	28.37	976.
58	1.31	45.
65	3.17	109.
75	0.38	13.
76	5.00	172.
77	1.19	41.
93	2.97	102.
104	5.78	199.
105	2.03	70.
121	2.38	82.
122	1.16	40.
123	0.87	30.
132	1.31	45.
135	0.41	14.
149	100.00	3440.
150	8.98	309.
151	0.90	31.
167	3.72	128.
205	2.21	76.
223	6.69	230.
224	0.81	28.

MASS SPECTRUM
02/02/88 23:04:00 + 26:13
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1573
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 5888.



Mass List
02/02/88 23:04:00 + 26:13
Sample:
!#
#
#(#3
Di-n-butyl phthalate (DBP)

Data: ESTERSTD #1573
Cali: ESTERSTD # 2

Base m/z: 149
RIC: 5888.

Conds.:
Enhanced (S 15B 2N OT)

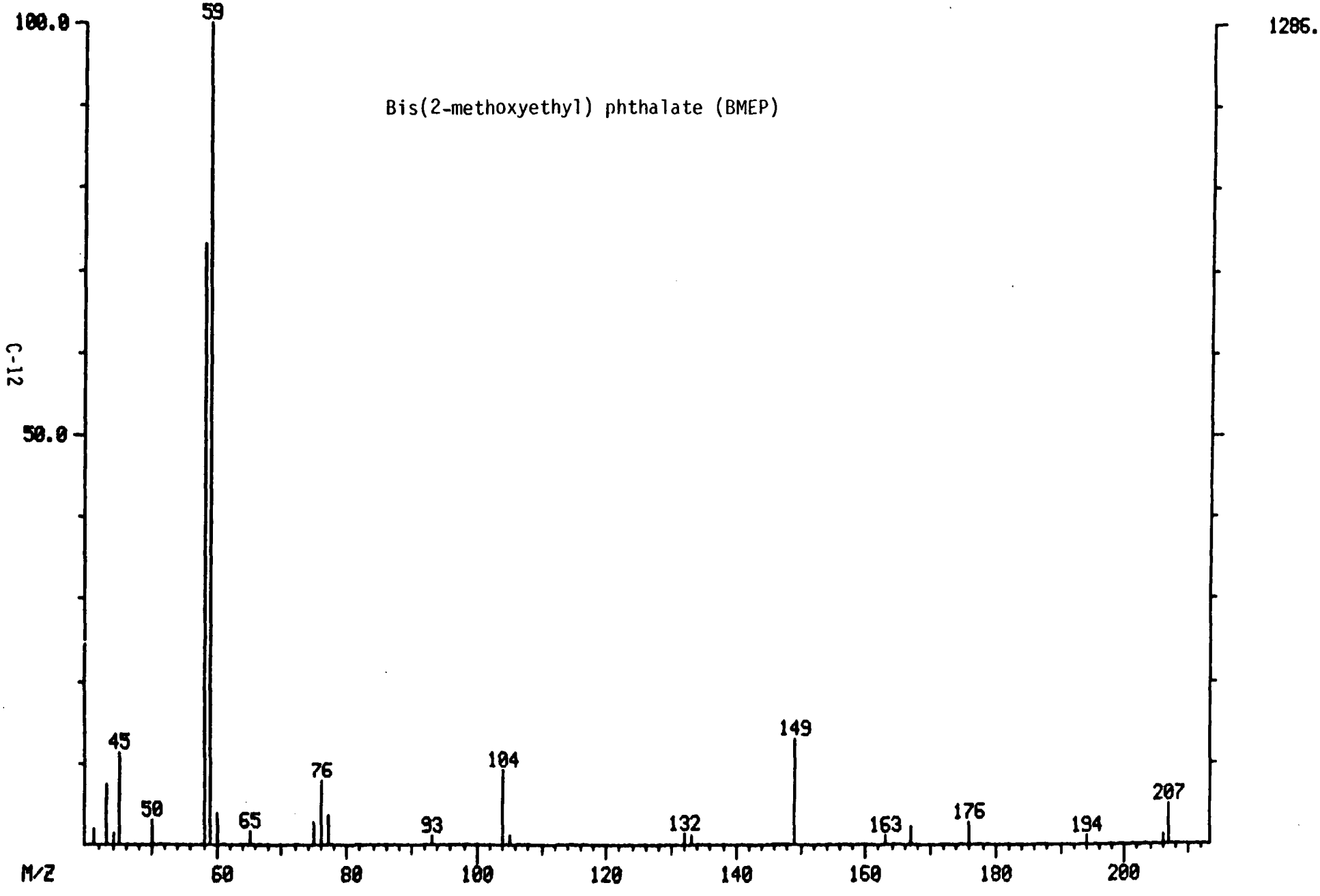
36	0.00	0.	Minima	Min Inten:		0.
224			Maxima	#	0	

Mass	% RA	Inten.
36?	0.18	6.
39?	2.25	77.
41	9.18	314.
43	0.85	29.
44	0.58	20.
50	1.35	46.
51	0.79	27.
55	1.90	65.
56	5.09	174.
57	5.50	188.
65	3.30	113.
76	3.77	129.
77	1.20	41.
93	2.81	96.
104	4.09	140.
105	2.54	87.
121	2.54	87.
122	1.55	53.
123	1.02	35.
132	0.38	13.
135	0.41	14.
147	0.38	13.
149	100.00	3420.
150	8.89	304.
151	0.76	26.
160	0.38	13.
205	4.36	149.
206	0.44	15.
223	4.59	157.
224	0.44	15.

MASS SPECTRUM
02/02/88 23:04:00 + 26:42
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1602
CALI: ESTERSTD #2

BASE M/Z: 59
RIC: 3316.



Mass List Data: ESTERSTD #1602 Base m/z: 59
02/02/88 23:04:00 + 26:42 Cali: ESTERSTD # 2 RIC: 3316.
Sample:
!#
#
#(#3

Bis(2-methoxyethyl) phthalate (BMEP)
Conds.:
Enhanced (S 15B 2N OT)

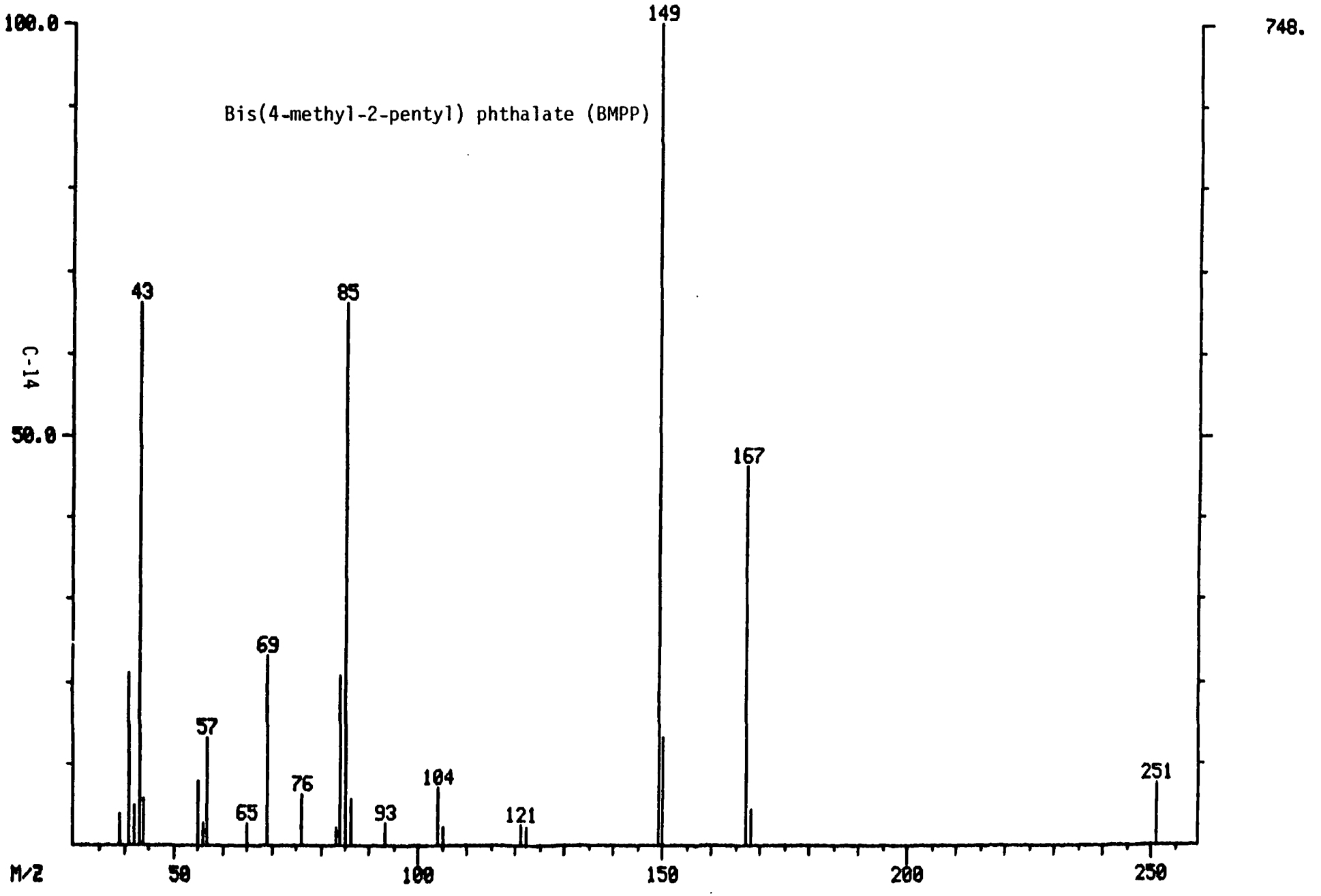
41	0.00	0.	Minima	Min Inten:		0.
207			Maxima	#	0	

Mass	% RA	Inten.
41	1.79	23.
43	7.39	95.
44	1.48	19.
45	11.20	144.
50	2.95	38.
58	73.09	940.
59	100.00	1286.
60	3.89	50.
65	1.56	20.
75	2.57	33.
76	7.85	101.
77	3.58	46.
93	1.01	13.
104	9.18	118.
105	1.09	14.
132	1.32	17.
133	1.01	13.
149	12.91	166.
163	1.09	14.
167	2.10	27.
176	2.80	36.
194	1.01	13.
206	1.17	15.
207	4.82	62.

MASS SPECTRUM
02/02/88 23:04:00 + 27:42
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1662
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 3292.



Mass List Data: ESTERSTD #1662 Base m/z: 149
02/02/88 23:04:00 + 27:42 Cali: ESTERSTD # 2 RIC: 3292.
Sample:
!#
#
#(#3

Bis(4-methyl-2-pentyl) phthalate (BMPP)

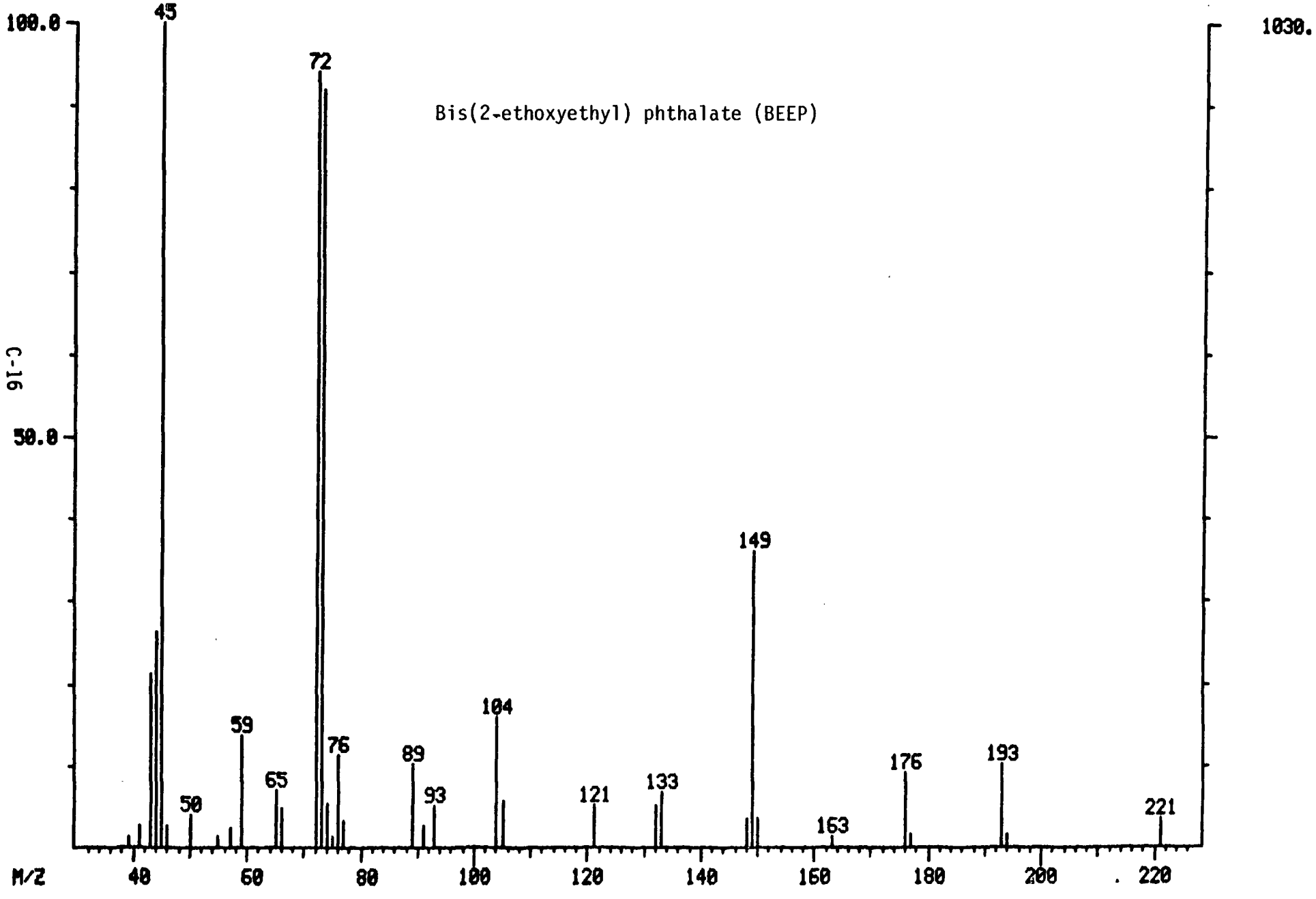
Conds.:
Enhanced (S 15B 2N OT)

39	0.00	0.	Minima	Min Inten:		0.
251			Maxima	#	0	
Mass	% RA	Inten.				
39?	3.74	28.				
41	20.99	157.				
42	4.81	36.				
43	66.04	494.				
44	5.61	42.				
55	7.89	59.				
56	2.81	21.				
57	13.10	98.				
65	2.81	21.				
69	22.99	172.				
76	6.15	46.				
83	2.14	16.				
84	20.59	154.				
85	66.18	495.				
86	5.75	43.				
93	2.67	20.				
104	6.95	52.				
105	2.27	17.				
121	2.54	19.				
122	2.27	17.				
149	100.00	748.				
150	13.24	99.				
167	46.12	345.				
168	4.41	33.				
251	7.49	56.				

MASS SPECTRUM
02/02/88 23:04:00 + 28:07
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1687
CALI: ESTERSTD #2

BASE M/Z: 45
RIC: 5392.



Mass List Data: ESTERSTD #1687 Base m/z: 45
02/02/88 23:04:00 + 28:07 Cali: ESTERSTD # 2 RIC: 5392.
Sample:
!#
#
#(#3

Bis(2-ethoxyethyl) phthalate (BEEP)
Conds.:
Enhanced (S 15B 2N OT)

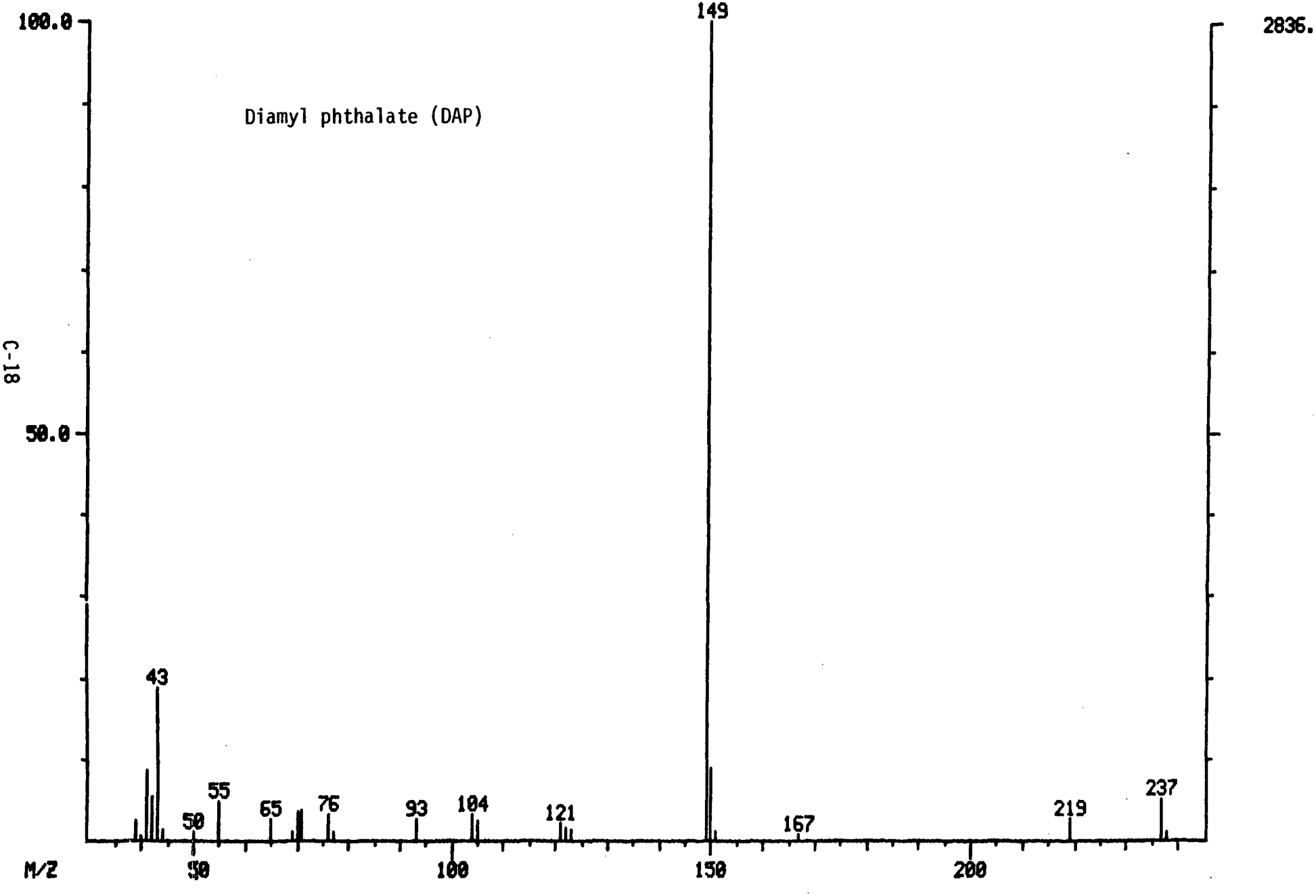
39 0.00 0. Minima Min Inten: 0.
221 Maxima # 0

Mass	% RA	Inten.
39?	1.36	14.
41	2.72	28.
43	21.36	220.
44	26.41	272.
45	100.00	1030.
46	2.72	28.
50	3.98	41.
55	1.26	13.
57	2.33	24.
59	13.59	140.
65	6.99	72.
66	4.95	51.
72	93.98	968.
73	92.04	948.
74	5.44	56.
75	1.36	14.
76	11.26	116.
77	3.11	32.
89	10.19	105.
91	2.62	27.
93	5.15	53.
104	15.73	162.
105	5.53	57.
121	5.05	52.
132	5.24	54.
133	6.80	70.
148	3.50	36.
149	36.12	372.
150	3.40	35.
163	1.46	15.
176	9.13	94.
177	1.65	17.
193	10.19	105.
194	1.55	16.
221	3.59	37.

MASS SPECTRUM
02/02/88 23:04:00 + 28:34
SAMPLE: \###(#3
CONDS.:
ENHANCED (5 150 2N 0T)

DATA: ESTERSTD #1714
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 5456.



Mass List
02/02/88 23:04:00 + 28:34
Sample:
!#
#
#(#3

Data: ESTERSTD #1714
Cali: ESTERSTD # 2

Base m/z: 149
RIC: 5456.

Diamyl phthalate (DAP)

Conds.:
Enhanced (S 15B 2N OT)

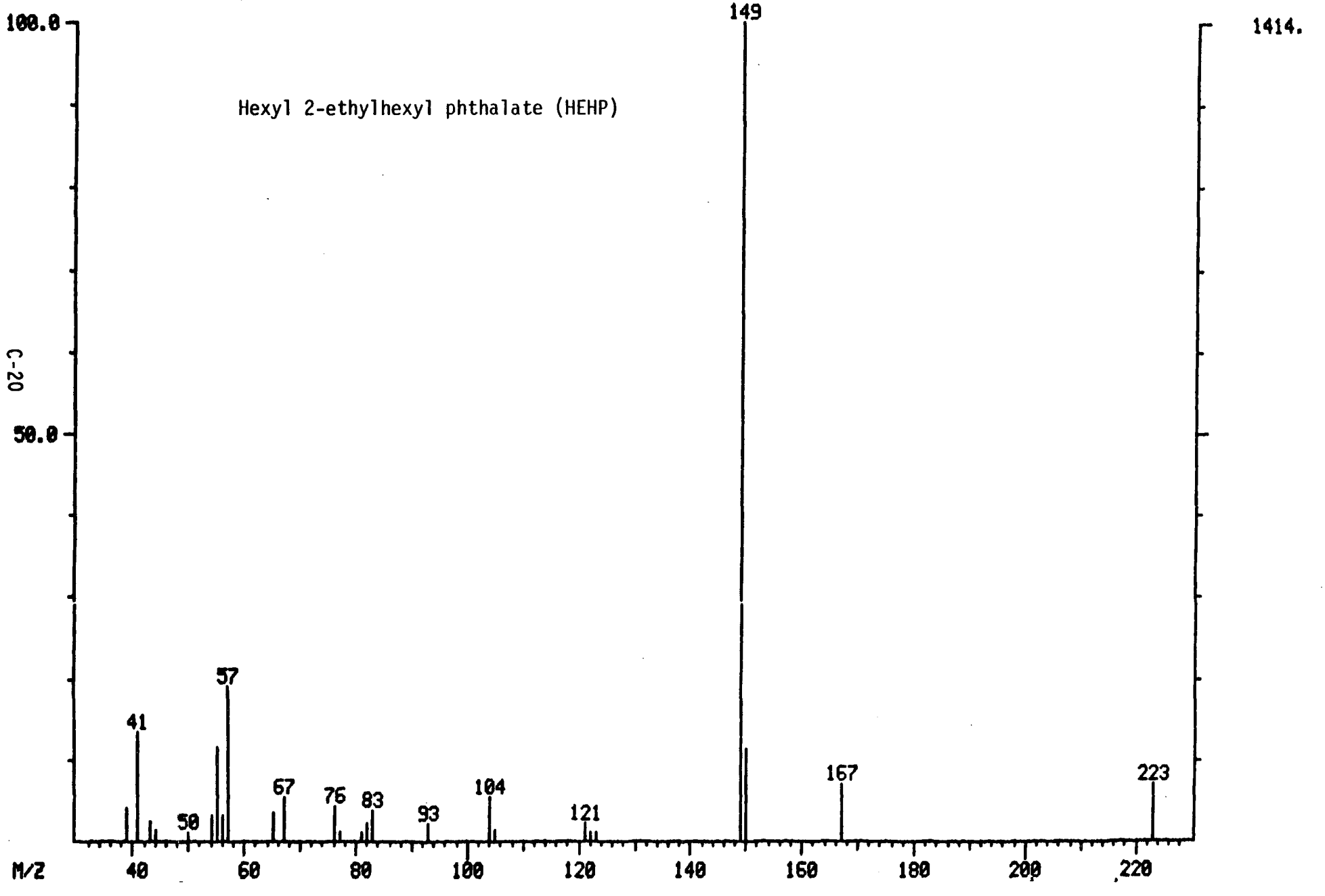
39	0.00	0.	Minima	Min Inten:	0.
238			Maxima	# 0	

Mass	% RA	Inten.
39?	2.50	71.
40	0.49	14.
41	8.64	245.
42	5.50	156.
43	18.86	535.
44	1.38	39.
50	1.09	31.
55	4.94	140.
65	2.79	79.
69	1.20	34.
70	3.60	102.
71	3.67	104.
76	3.24	92.
77	1.20	34.
93	2.64	75.
104	3.21	91.
105	2.40	68.
121	2.15	61.
122	1.52	43.
123	1.27	36.
149	100.00	2836.
150	8.78	249.
151	1.20	34.
167	0.92	26.
219	2.72	77.
237	5.22	148.
238	0.95	27.

MASS SPECTRUM
02/02/88 23:04:00 + 28:57
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1737
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 3108.



Mass List
02/02/88 23:04:00 + 28:57
Sample:
!#
#
#(#3

Data: ESTERSTD #1737
Cali: ESTERSTD # 2

Base m/z: 149
RIC: 3108.

Hexyl 2-ethylhexyl phthalate (HEHP)

Conds.:
Enhanced (S 15B 2N OT)

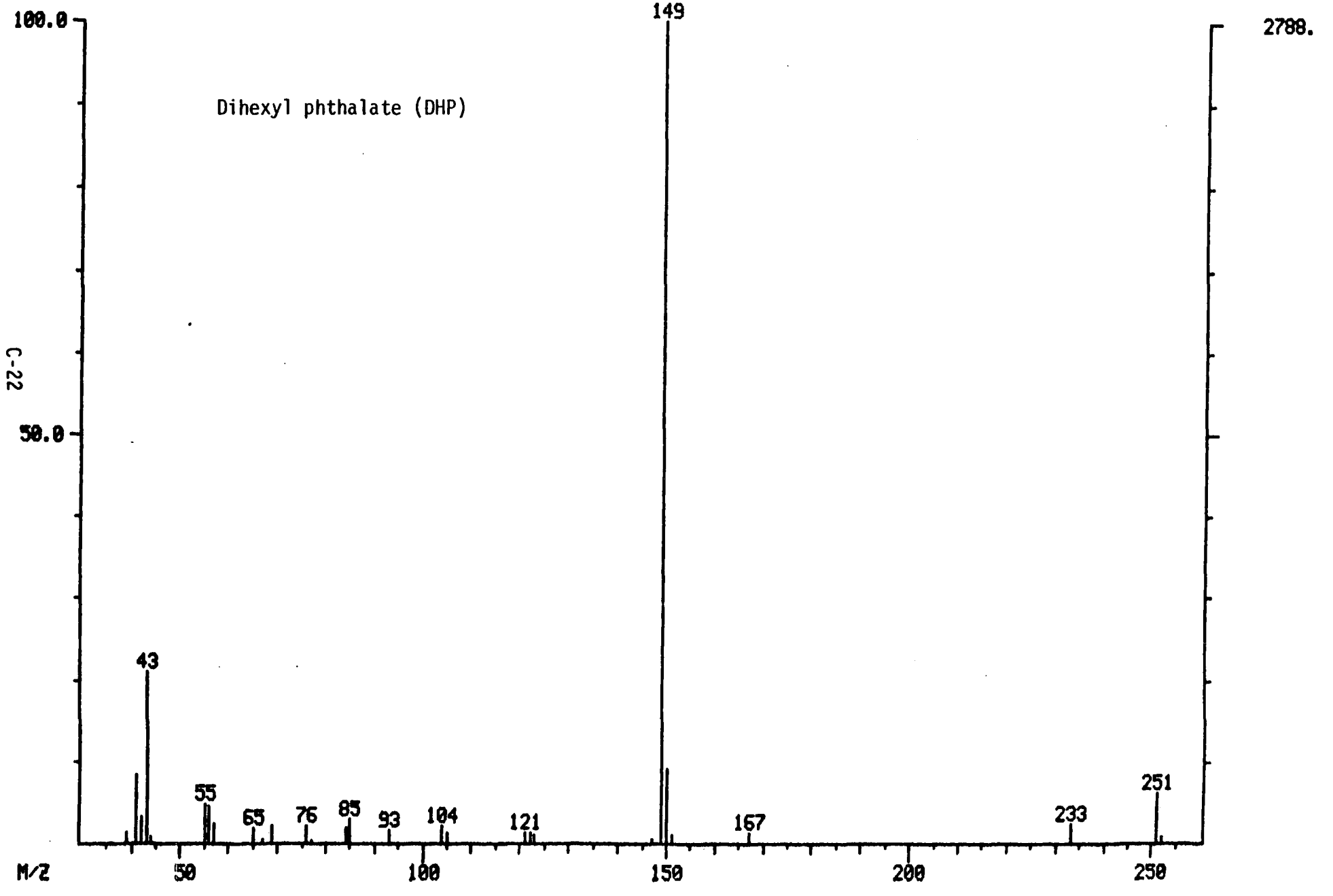
39	0.00	0.	Minima	Min Inten:	0.
223			Maxima	# 0	

Mass	% RA	Inten.
39?	4.03	57.
41	13.44	190.
43	2.33	33.
44	1.34	19.
50	1.13	16.
54	3.11	44.
55	11.53	163.
56	3.32	47.
57	18.95	268.
65	3.61	51.
67	5.37	76.
76	4.17	59.
77	1.06	15.
81	0.99	14.
82	2.19	31.
83	3.82	54.
93	2.19	31.
104	5.37	76.
105	1.34	19.
121	2.19	31.
122	1.20	17.
123	1.13	16.
149	100.00	1414.
150	11.24	159.
167	6.93	98.
223	7.07	100.

MASS SPECTRUM
02/02/88 23:04:00 + 30:44
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1844
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 5272.



Mass List
02/02/88 23:04:00 + 30:44
Sample:
!#
#
#(#3

Data: ESTERSTD #1844
Cali: ESTERSTD # 2

Base m/z: 149
RIC: 5272.

Dihexyl phthalate (DHP)

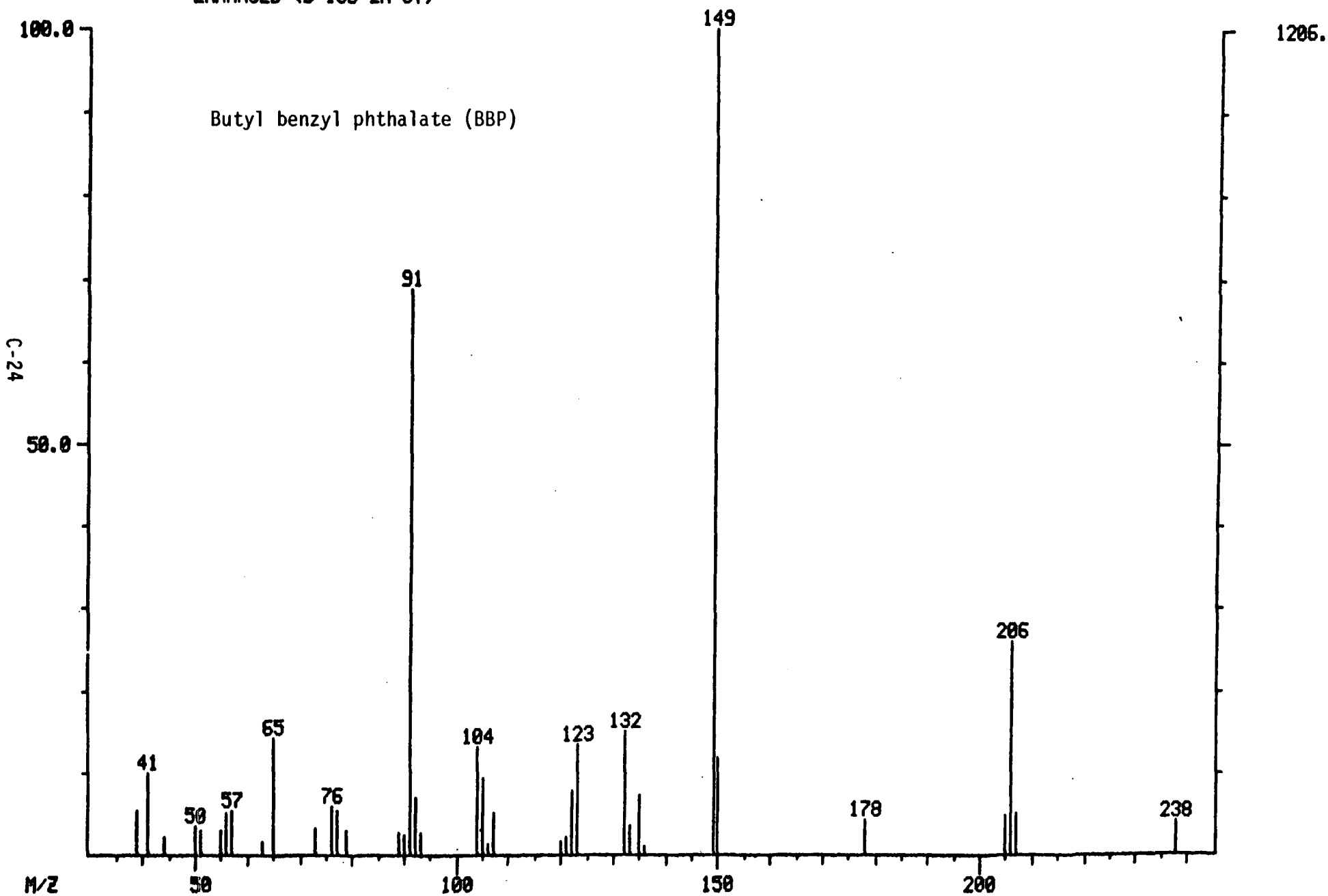
Conds.:
Enhanced (S 15B 2N OT)

39	0.00	0.	Minima	Min Inten:	0.
252			Maxima	# 0	
Mass	% RA	Inten.			
39?	1.40	39.			
41	8.43	235.			
42	3.19	89.			
43	20.95	584.			
44	0.82	23.			
55	4.73	132.			
56	4.56	127.			
57	2.40	67.			
65	1.79	50.			
67	0.57	16.			
69	2.08	58.			
76	2.19	61.			
77	0.25	7.			
84	1.79	50.			
85	2.91	81.			
93	1.54	43.			
104	2.08	58.			
105	1.47	41.			
121	1.43	40.			
122	1.22	34.			
123	1.15	32.			
147	0.47	13.			
149	100.00	2788.			
150	9.18	256.			
151	1.15	32.			
167	1.33	37.			
233	2.51	70.			
251	6.28	175.			
252	0.68	19.			

MASS SPECTRUM
02/02/88 23:04:00 + 30:51
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1851
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 4752.



Mass List
02/02/88 23:04:00 + 30:51
Sample:
1#
#
#(#3
Butyl benzyl phthalate (BBP)

Data: ESTERSTD #1851
Cali: ESTERSTD # 2

Base m/z: 149
RIC: 4752.

Conds.:
Enhanced (S 15B 2N OT)

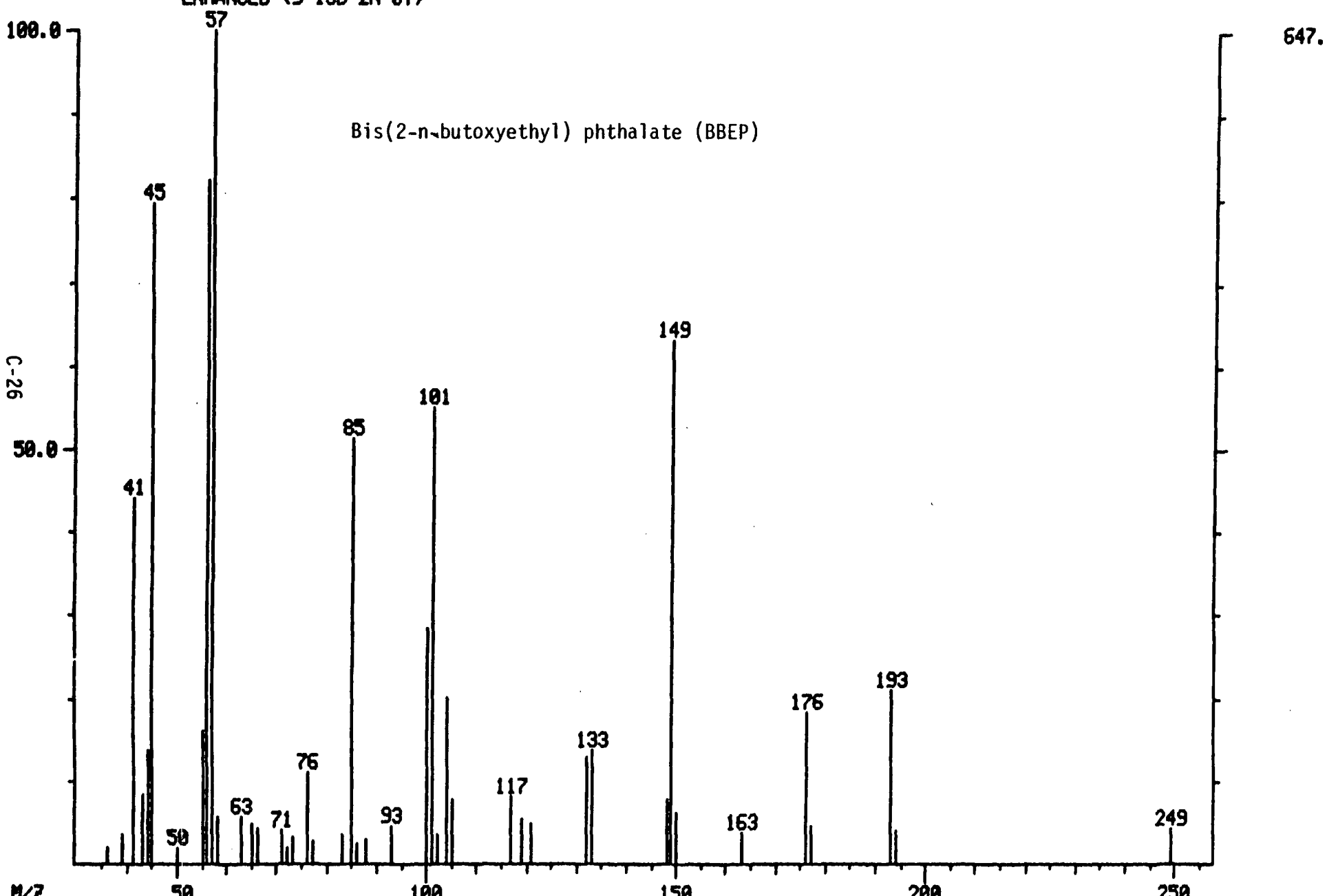
39 0.00 0. Minima Min Inten: 0.
238 Maxima # 0

Mass	% RA	Inten.
39?	5.39	65.
41	9.95	120.
44	2.16	26.
50	3.57	43.
51	2.99	36.
55	2.90	35.
56	5.14	62.
57	5.31	64.
63	1.58	19.
65	14.34	173.
73	3.32	40.
76	5.97	72.
77	5.47	66.
79	2.90	35.
89	2.82	34.
90	2.40	29.
91	68.91	831.
92	6.97	84.
93	2.57	31.
104	13.18	159.
105	9.54	115.
106	1.33	16.
107	4.98	60.
120	1.66	20.
121	2.24	27.
122	7.79	94.
123	13.43	162.
132	15.09	182.
133	3.48	42.
135	7.38	89.
136	1.16	14.
149	100.00	1206.
150	11.94	144.
178	4.39	53.
205	4.89	59.
206	26.20	316.
207	5.22	63.
238	4.15	50.

MASS SPECTRUM
02/02/88 23:04:00 + 32:08
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1928
CALI: ESTERSTD #2

BASE M/Z: 57
RIC: 4880.



Mass List Data: ESTERSTD #1928 Base m/z: 57
02/02/88 23:04:00 + 32:08 Cali: ESTERSTD # 2 RIC: 4880.
Sample:
!#
#
#(#3

Bis(2-n-butoxyethyl) phthalate (BBEP)

Conds.:
Enhanced (S 15B 2N OT)

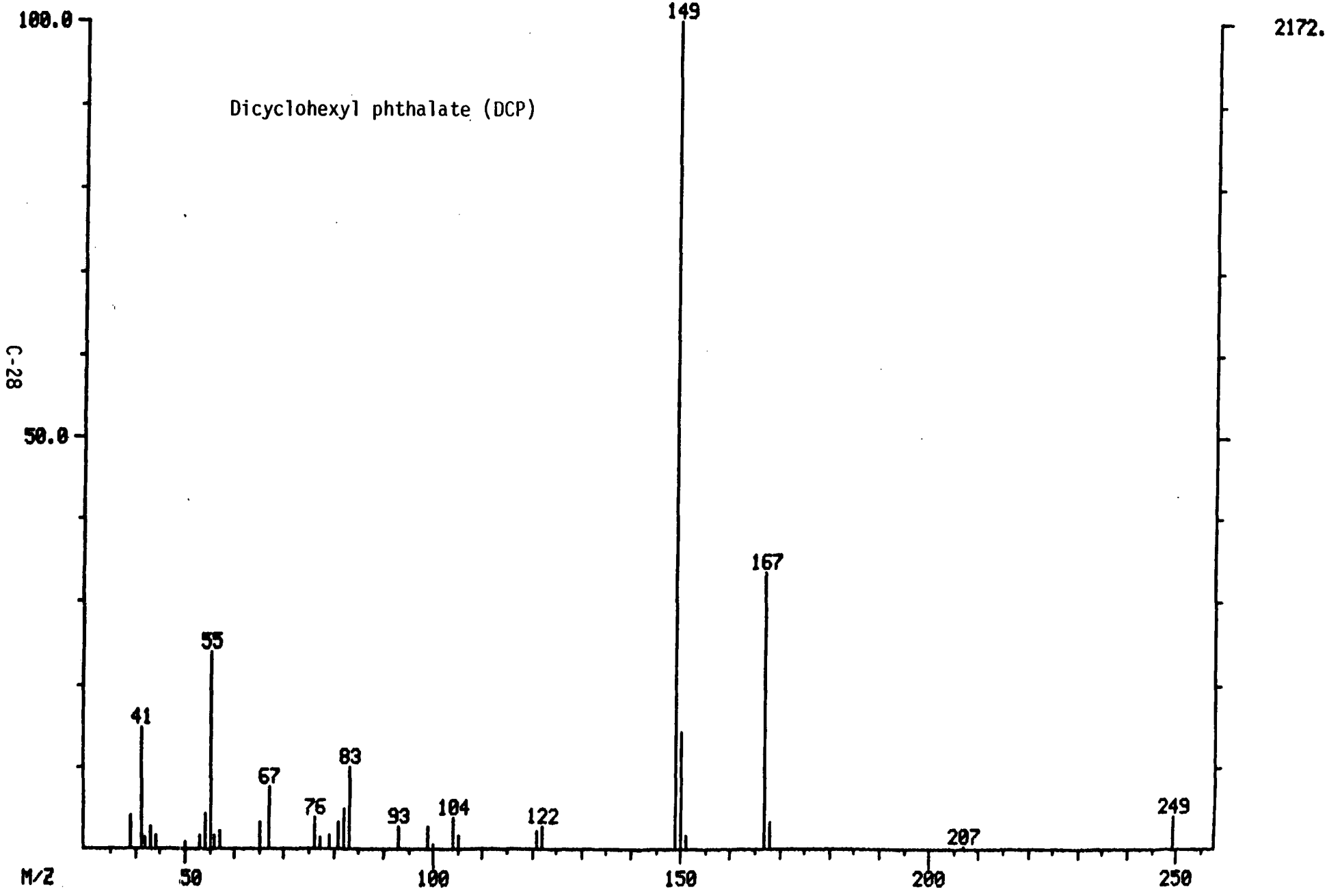
36 0.00 0. Minima Min Inten: 0.
249 Maxima # 0

Mass	% RA	Inten.
36?	2.01	13.
39?	3.40	22.
41	44.05	285.
43	8.35	54.
44	13.60	88.
45	79.60	515.
50	2.01	13.
55	16.07	104.
56	82.23	532.
57	100.00	647.
58	5.56	36.
63	5.56	36.
65	4.95	32.
66	4.17	27.
71	4.02	26.
72	2.01	13.
73	3.25	21.
76	10.97	71.
77	2.63	17.
83	3.40	22.
85	51.31	332.
86	2.32	15.
88	3.09	20.
93	4.64	30.
100	28.59	185.
101	55.18	357.
102	3.40	22.
104	20.25	131.
105	7.73	50.
117	8.19	53.
119	5.41	35.
121	4.95	32.
132	12.98	84.
133	13.60	88.
148	7.88	51.
149	63.21	409.
150	6.18	40.
163	3.86	25.
176	18.39	119.
177	4.48	29.
193	20.87	135.
194	4.02	26.
249	4.17	27.

MASS SPECTRUM
02/02/88 23:04:00 + 32:42
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1962
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 5832.



Mass List Data: ESTERSTD #1962 Base m/z: 149
02/02/88 23:04:00 + 32:42 Cali: ESTERSTD # 2 RIC: 5832.
Sample:
!#
#
#(#3
Dicyclohexyl phthalate (DCP)

Conds.:
Enhanced (S 15B 2N OT)

39	0.00	0.	Minima	Min Inten:		0.
249			Maxima	#	0	
Mass	% RA	Inten.				

Mass	% RA	Inten.
39?	3.96	86.
41	14.87	323.
42	1.43	31.
43	2.62	57.
44	1.70	37.
50	0.87	19.
53	1.52	33.
54	4.28	93.
55	24.03	522.
56	1.61	35.
57	2.03	44.
65	3.36	73.
67	7.41	161.
76	3.78	82.
77	1.29	28.
79	1.70	37.
81	3.22	70.
82	4.83	105.
83	9.85	214.
93	2.76	60.
99	2.62	57.
100	0.60	13.
104	3.73	81.
105	1.70	37.
121	2.16	47.
122	2.81	61.
149	100.00	2172.
150	14.36	312.
151	1.57	34.
167	33.70	732.
168	3.36	73.
207	0.28	6.
249	4.01	87.

Mass List Data: ESTERSTD #1962 Base m/z: 149
02/02/88 23:04:00 + 32:42 Cali: ESTERSTD # 2 RIC: 5832.
Sample:
!#
#
#(#3
Dicyclohexyl phthalate (DCP)

Conds.:
Enhanced (S 15B 2N OT)

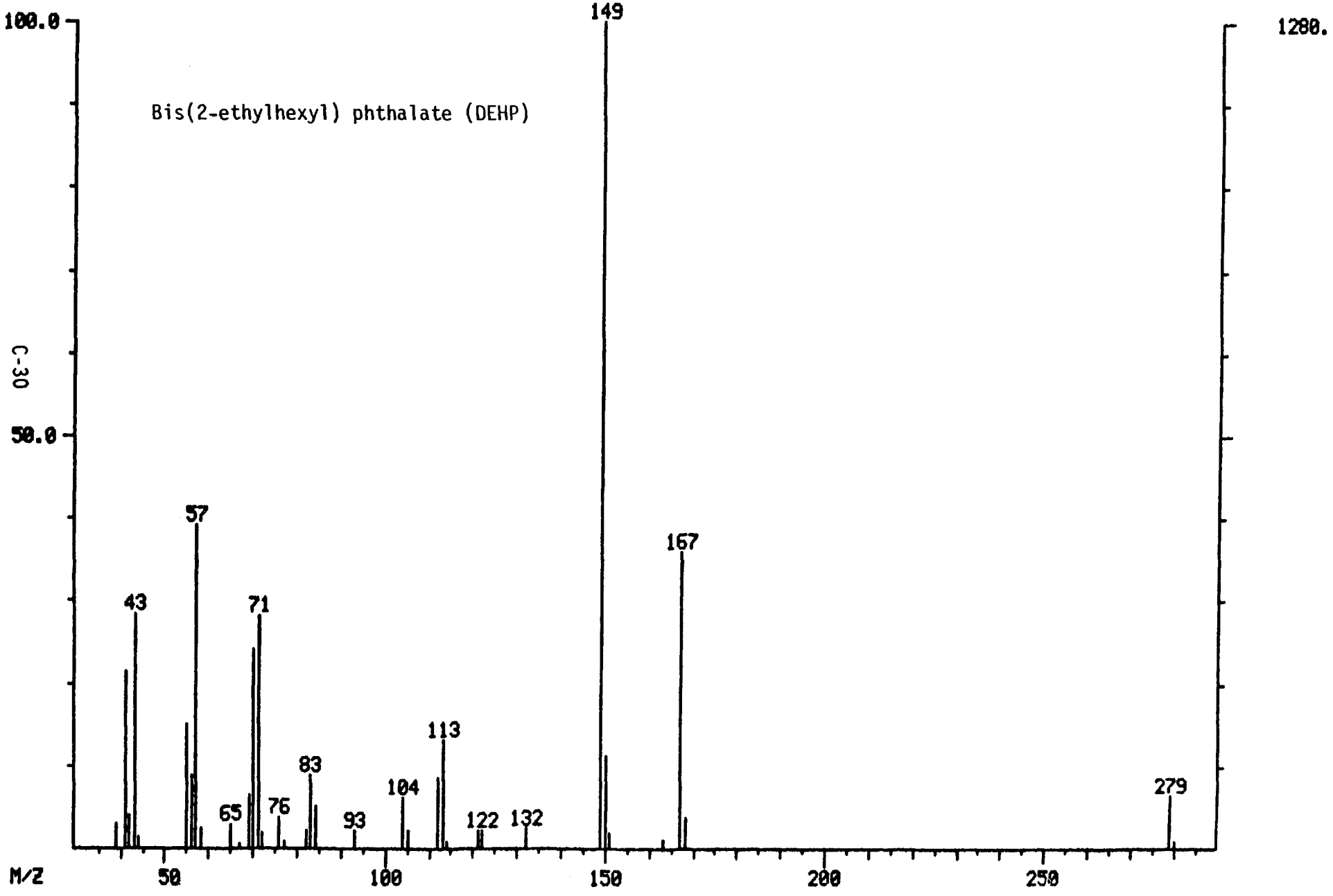
39	0.00	0.	Minima	Min Inten:		0.
249			Maxima	#	0	
Mass	% RA	Inten.				

Mass	% RA	Inten.
39?	3.96	86.
41	14.87	323.
42	1.43	31.
43	2.62	57.
44	1.70	37.
50	0.87	19.
53	1.52	33.
54	4.28	93.
55	24.03	522.
56	1.61	35.
57	2.03	44.
65	3.36	73.
67	7.41	161.
76	3.78	82.
77	1.29	28.
79	1.70	37.
81	3.22	70.
82	4.83	105.
83	9.85	214.
93	2.76	60.
99	2.62	57.
100	0.60	13.
104	3.73	81.
105	1.70	37.
121	2.16	47.
122	2.81	61.
149	100.00	2172.
150	14.36	312.
151	1.57	34.
167	33.70	732.
168	3.36	73.
207	0.28	6.
249	4.01	87.

MASS SPECTRUM
02/02/88 23:04:00 + 32:53
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #1973
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 5248.



Mass List Data: ESTERSTD #1973 Base m/z: 149
02/02/88 23:04:00 + 32:53 Cali: ESTERSTD # 2 RIC: 5248.
Sample:
!#
#
#(#3

Bis(2-ethylhexyl) phthalate (DEHP)

Conds.:
Enhanced (S 15B 2N OT)

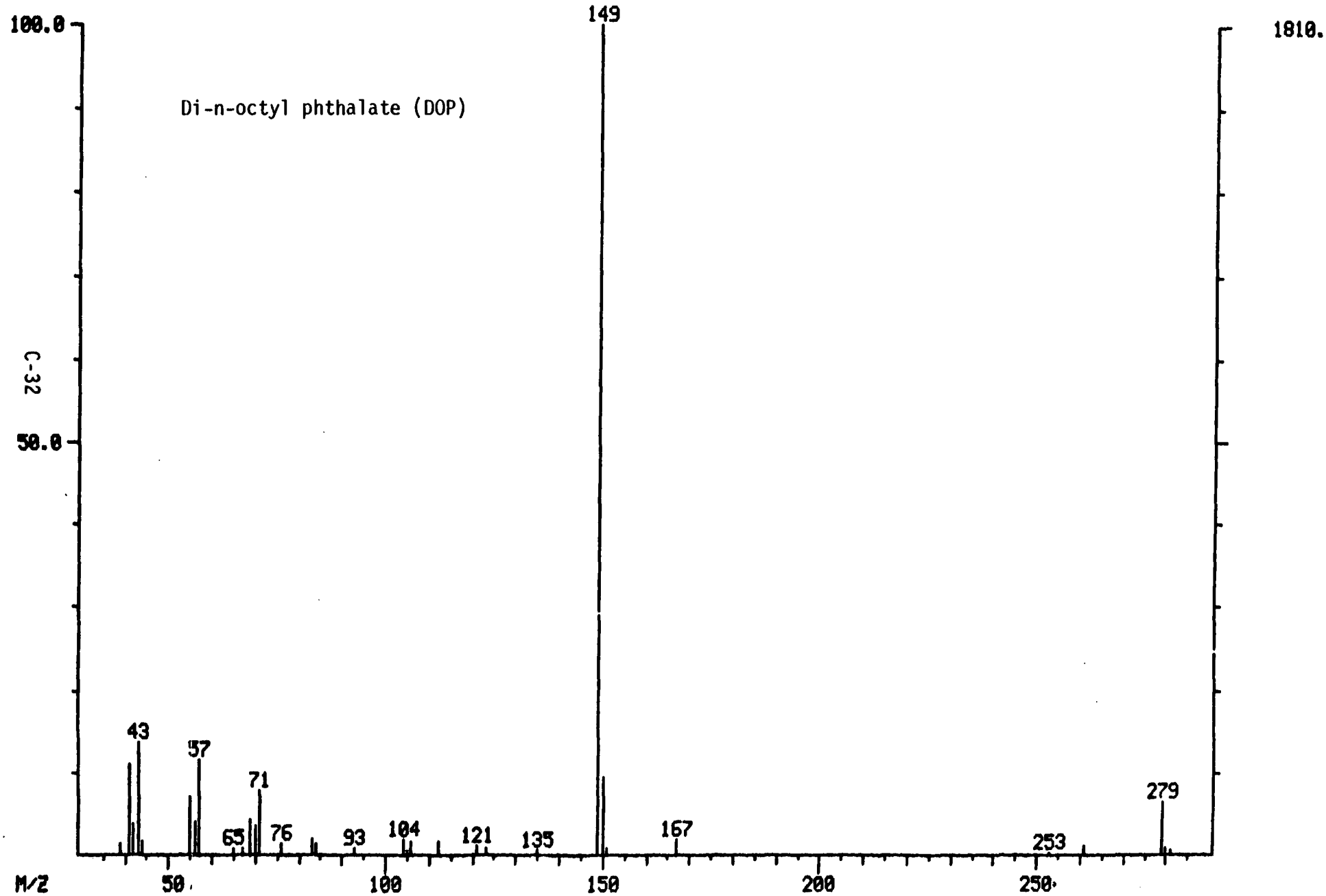
39	0.00	0.	Minima	Min Inten:	0.
280			Maxima	# 0	

Mass	% RA	Inten.
39?	3.05	39.
41	21.41	274.
42	4.06	52.
43	28.44	364.
44	1.33	17.
55	15.00	192.
56	8.91	114.
57	39.30	503.
58	2.42	31.
65	2.97	38.
67	0.62	8.
69	6.33	81.
70	24.06	308.
71	28.36	363.
72	1.95	25.
76	3.75	48.
77	0.70	9.
82	2.19	28.
83	8.98	115.
84	5.00	64.
93	2.11	27.
104	6.25	80.
105	2.03	26.
112	8.52	109.
113	13.12	168.
114	0.70	9.
121	2.03	26.
122	2.11	27.
132	2.42	31.
149	100.00	1280.
150	11.25	144.
151	1.80	23.
163	1.09	14.
167	36.09	462.
168	3.75	48.
279	6.48	83.
280	0.70	9.

MASS SPECTRUM
02/02/88 23:04:00 + 34:42
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #2082
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 3744.



Mass List Data: ESTERSTD #2082 Base m/z: 149
02/02/88 23:04:00 + 34:42 Cali: ESTERSTD # 2 RIC: 3744.
Sample:
!#
#
#(#3

Di-n-octyl phthalate (DOP)

Conds.:
Enhanced (S 15B 2N OT)

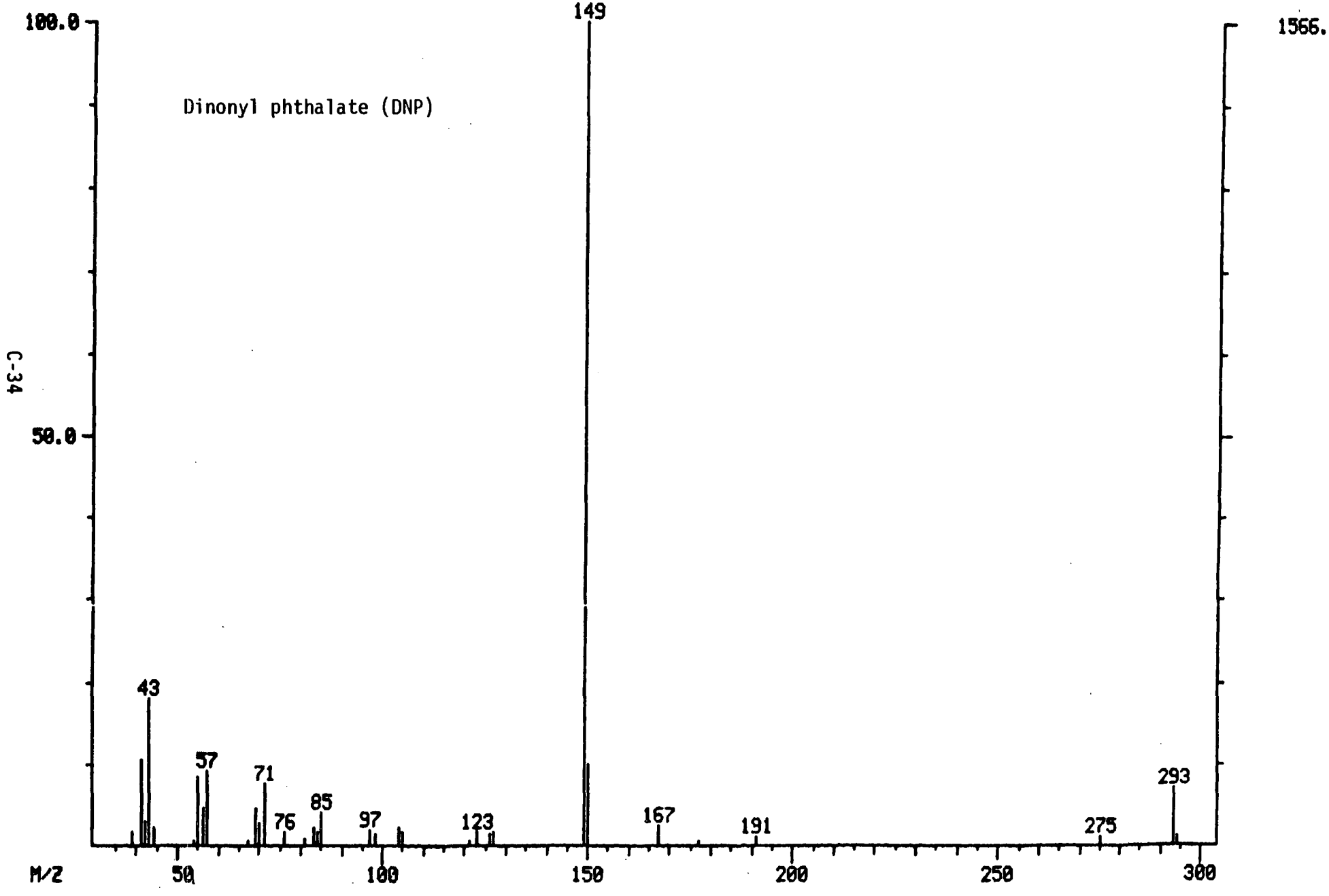
39 0.00 0. Minima Min Inten: 0.
281 Maxima # 0

Mass	% RA	Inten.
39?	1.38	25.
41	10.94	198.
42	3.87	70.
43	13.76	249.
44	1.49	27.
55	7.07	128.
56	4.09	74.
57	11.66	211.
65	0.88	16.
67	0.88	16.
69	4.25	77.
70	3.37	61.
71	7.73	140.
76	1.44	26.
83	1.82	33.
84	1.38	25.
93	0.77	14.
104	1.88	34.
105	0.50	9.
106	1.55	28.
112	1.66	30.
121	1.05	19.
123	0.88	16.
135	0.50	9.
149	100.00	1810.
150	9.28	168.
151	0.83	15.
167	1.82	33.
253	0.39	7.
261	1.10	20.
279	6.57	119.
280	0.77	14.
281	0.61	11.

MASS SPECTRUM
02/02/88 23:04:00 + 36:31
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: ESTERSTD #2191
CALI: ESTERSTD #2

BASE M/Z: 149
RIC: 3428.



Mass List
02/02/88 23:04:00 + 36:31
Sample:
!#
#
#(#3

Data: ESTERSTD #2191
Cali: ESTERSTD # 2

Base m/z: 149
RIC: 3428.

Dinonyl phthalate (DNP)

Conds.:
Enhanced (S 15B 2N OT)

39 0.00 0.
294

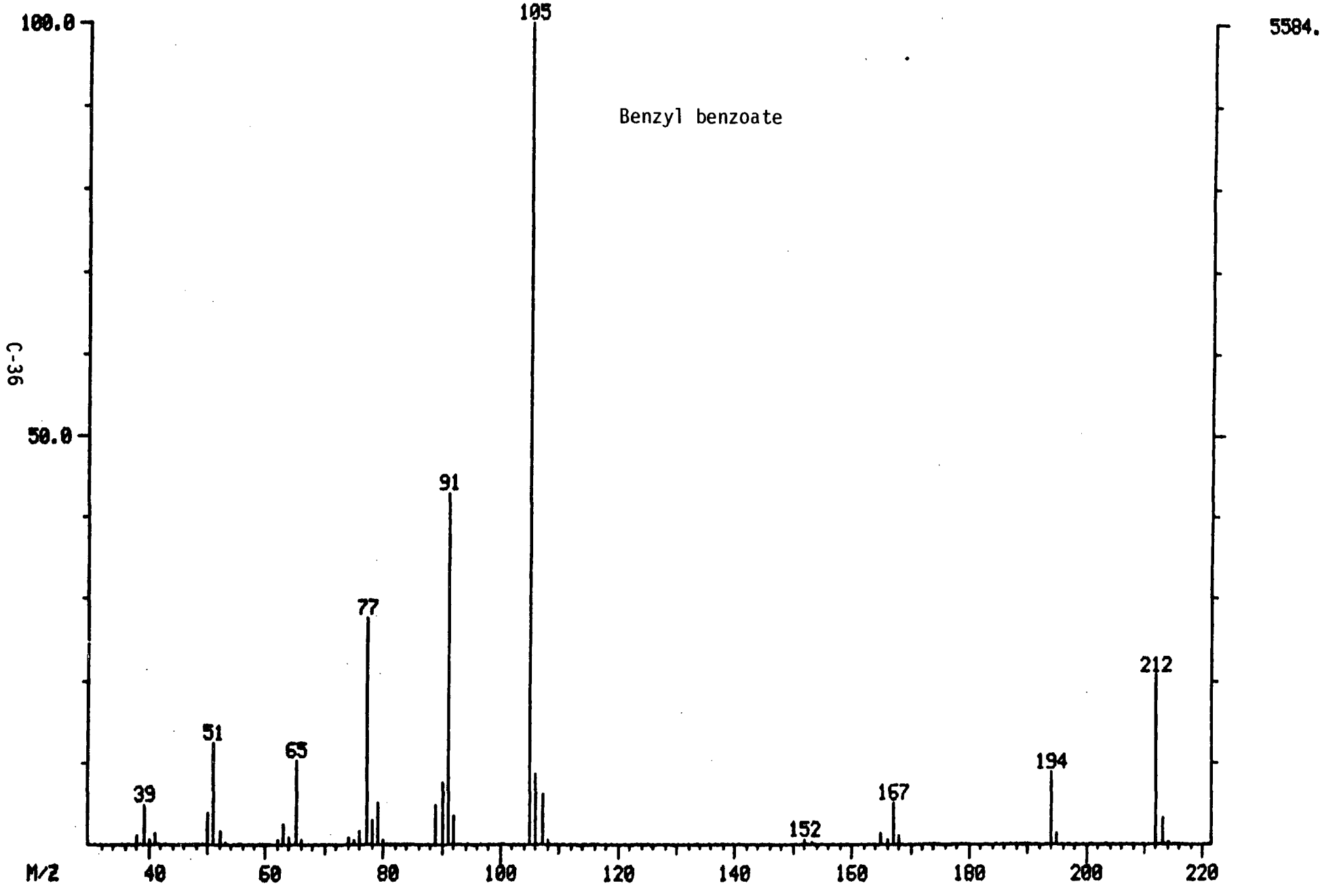
Minima Min Inten: 0.
Maxima # 0

Mass	% RA	Inten.
39?	1.60	25.
41	10.54	165.
42	2.94	46.
43	17.94	281.
44	2.04	32.
54	0.57	9.
55	8.30	130.
56	4.60	72.
57	9.26	145.
67	0.57	9.
69	4.53	71.
70	2.62	41.
71	7.60	119.
76	1.53	24.
81	0.83	13.
83	2.23	35.
84	1.53	24.
85	4.15	65.
97	1.79	28.
98	1.34	21.
104	2.11	33.
105	1.66	26.
121	0.57	9.
123	1.53	24.
126	1.47	23.
127	1.53	24.
149	100.00	1566.
150	9.83	154.
167	2.36	37.
177	0.57	9.
191	1.15	18.
275	0.96	15.
293	6.96	109.
294	1.02	16.

MASS SPECTRUM
02/04/88 0:23:00 + 23:17
SAMPLE: PHTHALATE STD A 100NG/UL
CONDS.: FINN4500
ENHANCED (S 15B 2N 0T)

DATA: R0203STDA #1397
CALI: R0203STDA #2

BASE M/Z: 105
RIC: 16640.



Mass List Data: R0203STDA #1397 Base m/z: 105
02/04/88 0:23:00 + 23:17 Cali: R0203STDA # 2 RIC: 16640.
Sample: PHTHALATE STD A 100NG/UL
Conds.: FINN4500
Enhanced (S 15B 2N OT)

38	0.00	0.	Minima	Min Inten:		0.
214			Maxima	#	0	

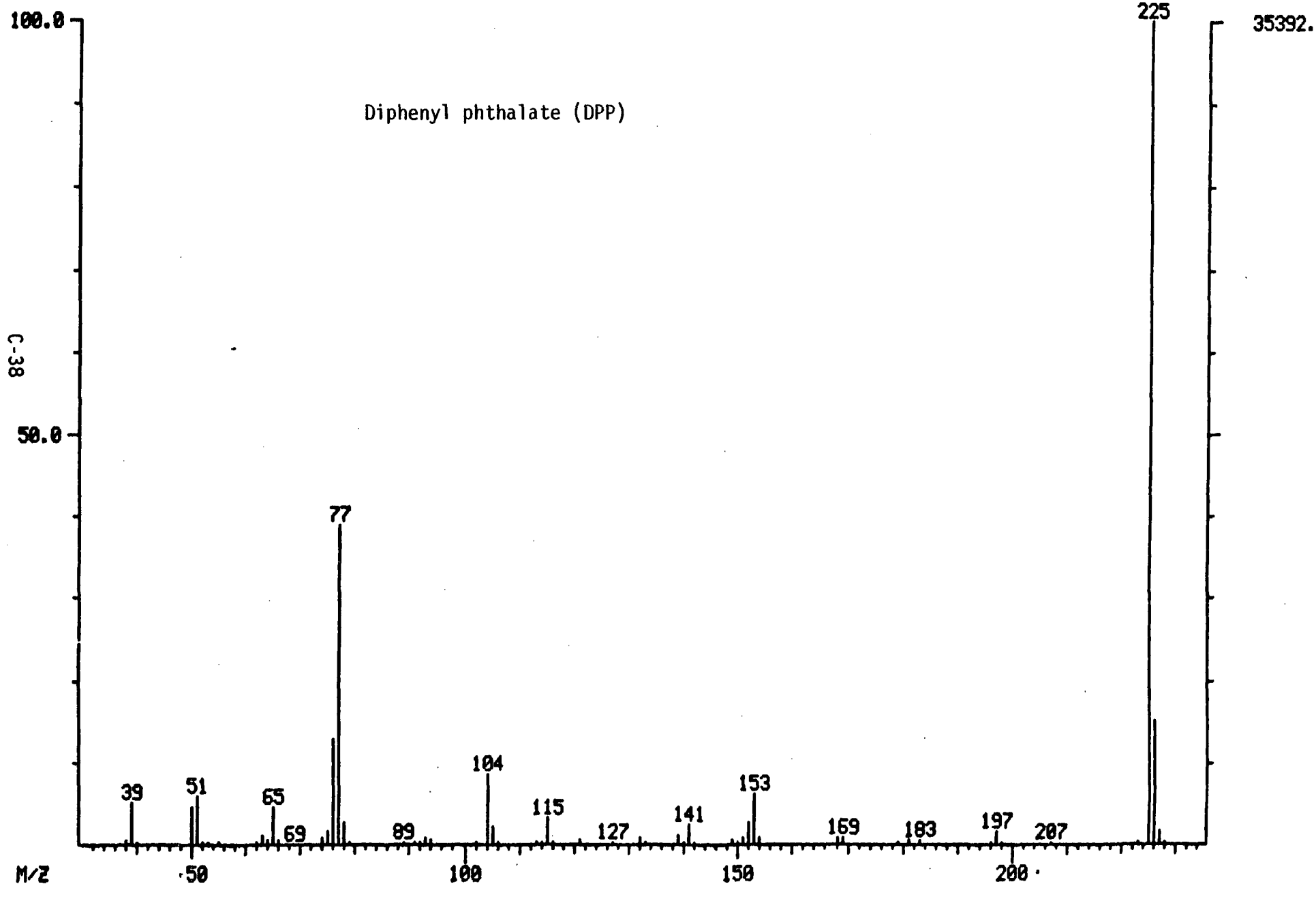
Mass	% RA	Inten.
38?	1.02	57.
39?	4.92	275.
40	0.43	24.
41	1.41	79.
50	3.64	203.
51	12.46	696.
52	1.59	89.
53	0.16	9.
62	0.61	34.
63	2.53	141.
64	0.88	49.
65	10.30	575.
66	0.64	36.
74	0.75	42.
75	0.64	36.
76	1.61	90.
77	27.79	1552.
78	2.97	166.
79	5.07	283.
80	0.43	24.
89	4.94	276.
90	7.40	413.
91	42.91	2396.
92	3.38	189.
105	100.00	5584.
106	8.70	486.
107	6.23	348.
108	0.48	27.
152	0.56	31.
153	0.27	15.
165	1.40	78.
166	0.59	33.
167	5.21	291.
168	1.13	63.
194	8.86	495.
195	1.47	82.
212	20.59	1150.
213	3.22	180.
214	0.25	14.

Benzyl benzoate

MASS SPECTRUM
02/04/88 1:16:00 + 32:39
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: R0203STDB #1959
CALI: R0203STDB #2

BASE M/Z: 225
RIC: 84736.



Mass List Data: R0203STDB #1959 Base m/z: 225
02/04/88 1:16:00 + 32:39 Cali: R0203STDB # 2 RIC: 84736.
Sample:
!#
#
#(#3

Diphenyl phthalate (DPP)

Conds.:
Enhanced (S 15B 2N OT)

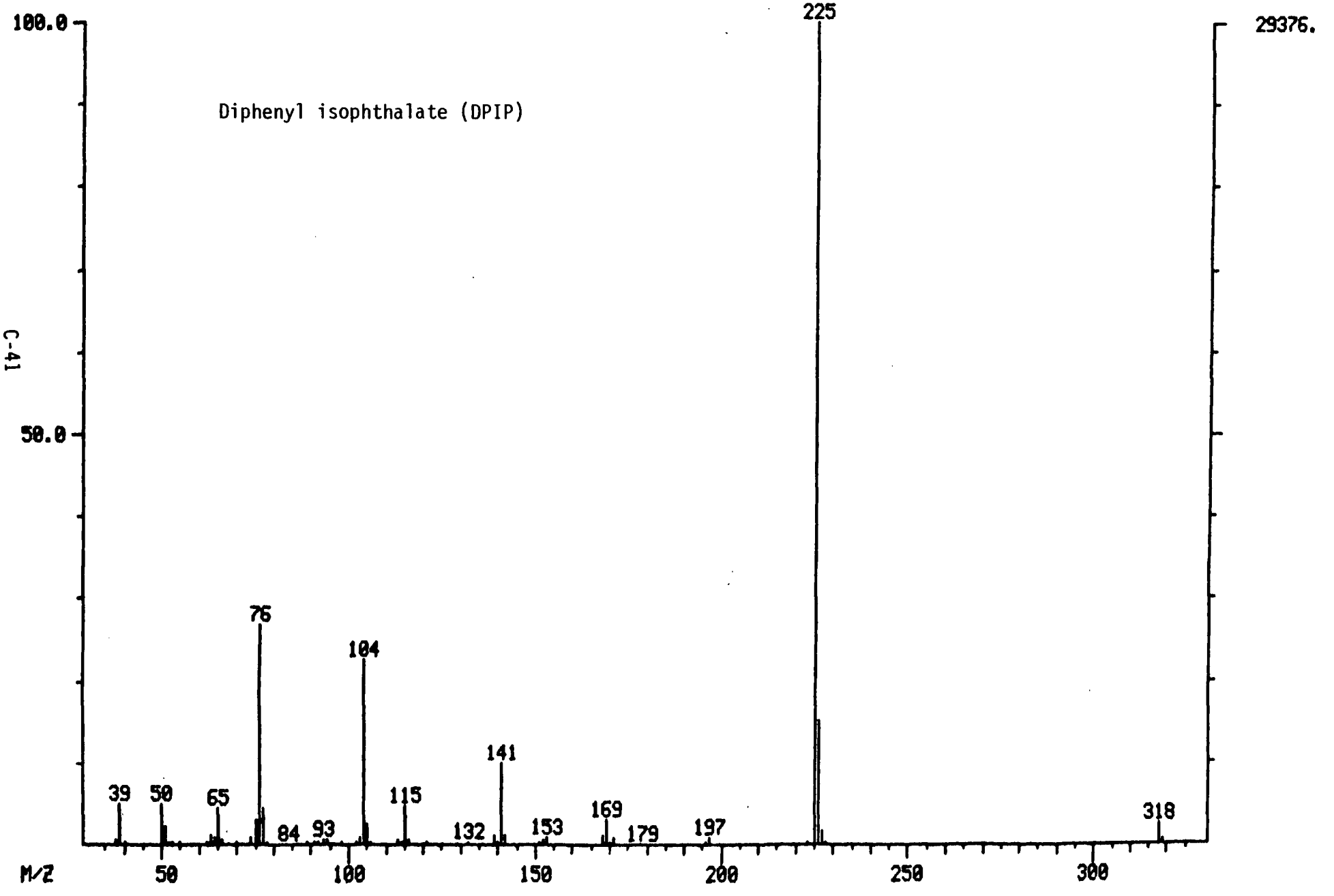
37	0.00	0.	Minima	Min Inten:	0.
228			Maxima	# 0	
Mass	% RA	Inten.	Mass	% RA	Inten.
37?	0.13	47.	140	0.33	118.
38?	0.59	210.	141	2.47	875.
39?	5.17	1830.	142	0.32	112.
40	0.30	107.	149	0.60	214.
41	0.06	22.	150	0.15	54.
49	0.05	19.	151	0.68	239.
50	4.45	1574.	152	2.60	921.
51	5.89	2084.	153	6.06	2144.
52	0.31	111.	154	0.79	279.
53	0.27	97.	155	0.06	23.
55	0.22	78.	168	0.71	253.
62	0.23	82.	169	0.82	290.
63	1.07	380.	170	0.12	44.
64	0.60	212.	179	0.19	69.
65	4.45	1574.	181	0.46	162.
66	0.46	162.	182	0.07	24.
69	0.09	31.	183	0.64	227.
70	0.05	16.	184	0.10	34.
73	0.10	36.	196	0.28	99.
74	0.80	282.	197	1.55	549.
75	1.65	583.	198	0.23	83.
76	13.02	4608.	207	0.14	51.
77	38.88	13760.	222	0.04	14.
78	2.57	911.	223	0.40	140.
79	0.24	85.	225	100.00	35392.
87	0.04	13.	226	15.01	5312.
88	0.06	23.	227	1.59	564.
89	0.28	99.	228	0.16	55.
91	0.24	85.			
92	0.28	98.			
93	0.82	289.			
94	0.47	165.			
101	0.07	25.			
102	0.14	50.			
103	0.06	22.			
104	8.54	3024.			
105	2.16	764.			
106	0.18	64.			
113	0.26	91.			
114	0.19	67.			
115	3.35	1186.			
116	0.35	125.			
119	0.11	39.			
121	0.65	230.			
126	0.06	23.			
127	0.18	63.			
128	0.02	8.			

132	0.68	242.
133	0.14	51.
139	1.21	428.

MASS SPECTRUM
02/04/88 1:16:00 + 34:17
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: R0203STDB #2057
CALI: R0203STDB #2

BASE M/Z: 225
RIC: 68480.



Mass List Data: R0203STDB #2057 Base m/z: 225
02/04/88 1:16:00 + 34:17 Cali: R0203STDB # 2 RIC: 68480.
Sample:
!#
#
#(#3

Diphenyl isophthalate (DPIP)

Conds.:
Enhanced (S 15B 2N OT)

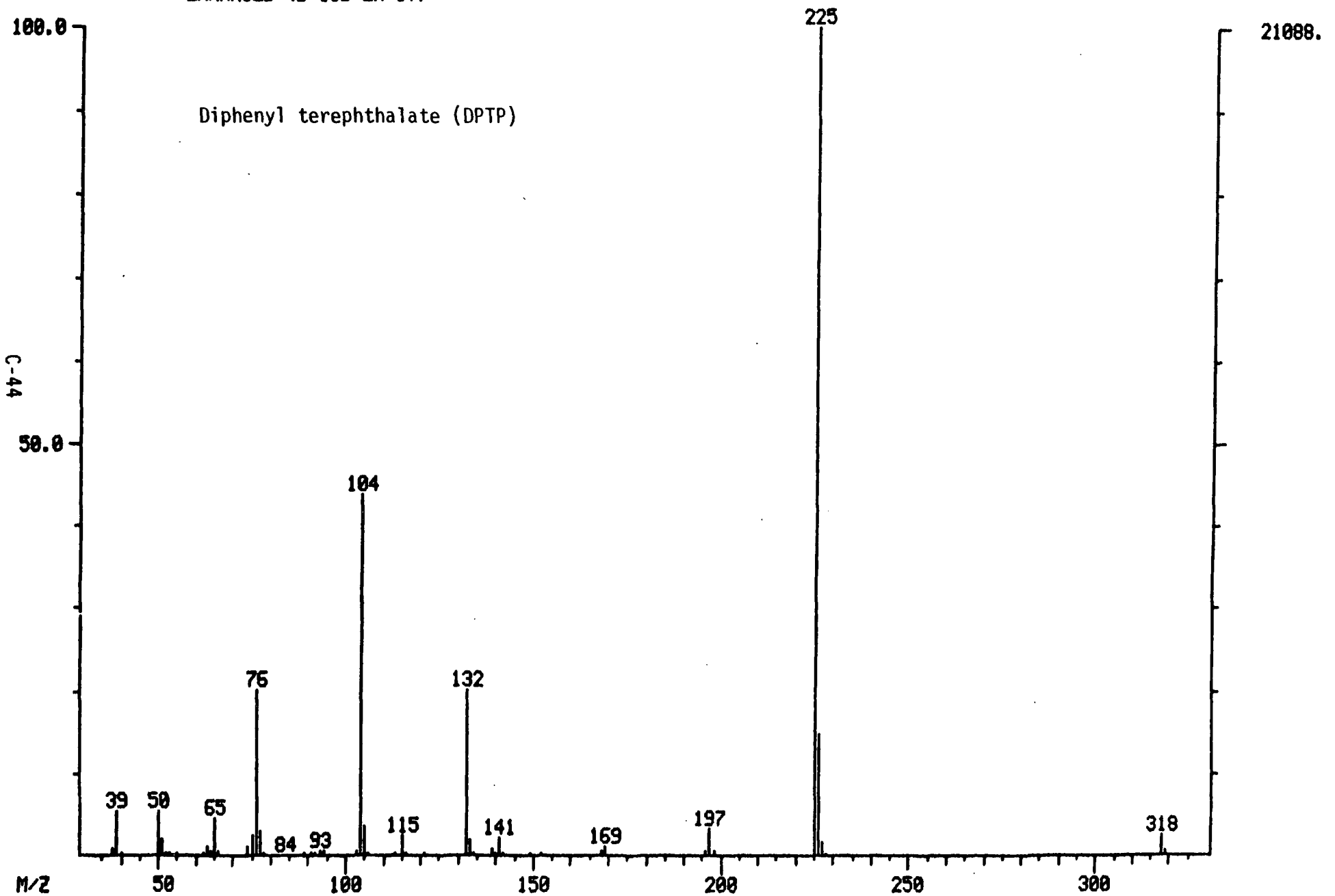
37	0.00	0.	Minima	Min Inten:		0.
320			Maxima	#	0	
Mass	% RA	Inten.	Mass		% RA	Inten.
37?	0.11	31.	143		0.10	28.
38?	0.61	178.	149		0.09	27.
39?	4.97	1460.	151		0.29	86.
40	0.31	92.	152		0.62	181.
41	0.08	24.	153		0.79	233.
50	4.91	1442.	154		0.11	33.
51	2.11	621.	167		0.04	13.
52	0.15	45.	168		1.13	331.
53	0.23	67.	169		3.02	887.
55	0.18	52.	170		0.38	112.
57	0.03	8.	171		0.80	234.
62	0.25	72.	172		0.09	27.
63	1.06	311.	179		0.13	37.
64	0.69	202.	195		0.10	28.
65	4.30	1262.	196		0.22	64.
66	0.58	170.	197		0.84	246.
69	0.12	35.	198		0.13	39.
70	0.14	40.	223		0.34	99.
73	0.07	20.	225		100.00	29376.
74	0.86	253.	226		14.92	4384.
75	3.04	892.	227		1.58	463.
76	26.82	7880.	228		0.15	44.
77	4.38	1286.	317		0.03	9.
78	0.29	85.	318		2.54	747.
84	0.08	23.	319		0.54	159.
88	0.07	22.	320		0.03	10.
89	0.19	55.				
91	0.35	104.				
92	0.25	74.				
93	0.58	169.				
94	0.51	150.				
98	0.20	59.				
102	0.14	41.				
103	0.90	263.				
104	22.58	6632.				
105	2.48	728.				
106	0.16	48.				
113	0.61	178.				
114	0.17	51.				
115	4.52	1328.				
116	0.45	132.				
119	0.13	37.				
121	0.15	44.				
127	0.08	24.				
132	0.37	110.				
133	0.11	32.				
139	1.04	306.				

140	0.37	109.
141	9.90	2908.
142	1.18	348.

MASS SPECTRUM
02/04/88 0:23:00 + 34:21
SAMPLE: PHTHALATE STD A 100NG/UL
CONDS.: FINN4500
ENHANCED (S 15B 2N 0T)

DATA: R0203STDA #2061
CALI: R0203STDA #2

BASE M/Z: 225
RIC: 53376.



Mass List Data: R0203STDA #2061 Base m/z: 225
02/04/88 0:23:00 + 34:21 Cali: R0203STDA # 2 RIC: 53376.
Sample: PHTHALATE STD A 100NG/UL
Conds.: FINN4500
Enhanced (S 15B 2N OT)

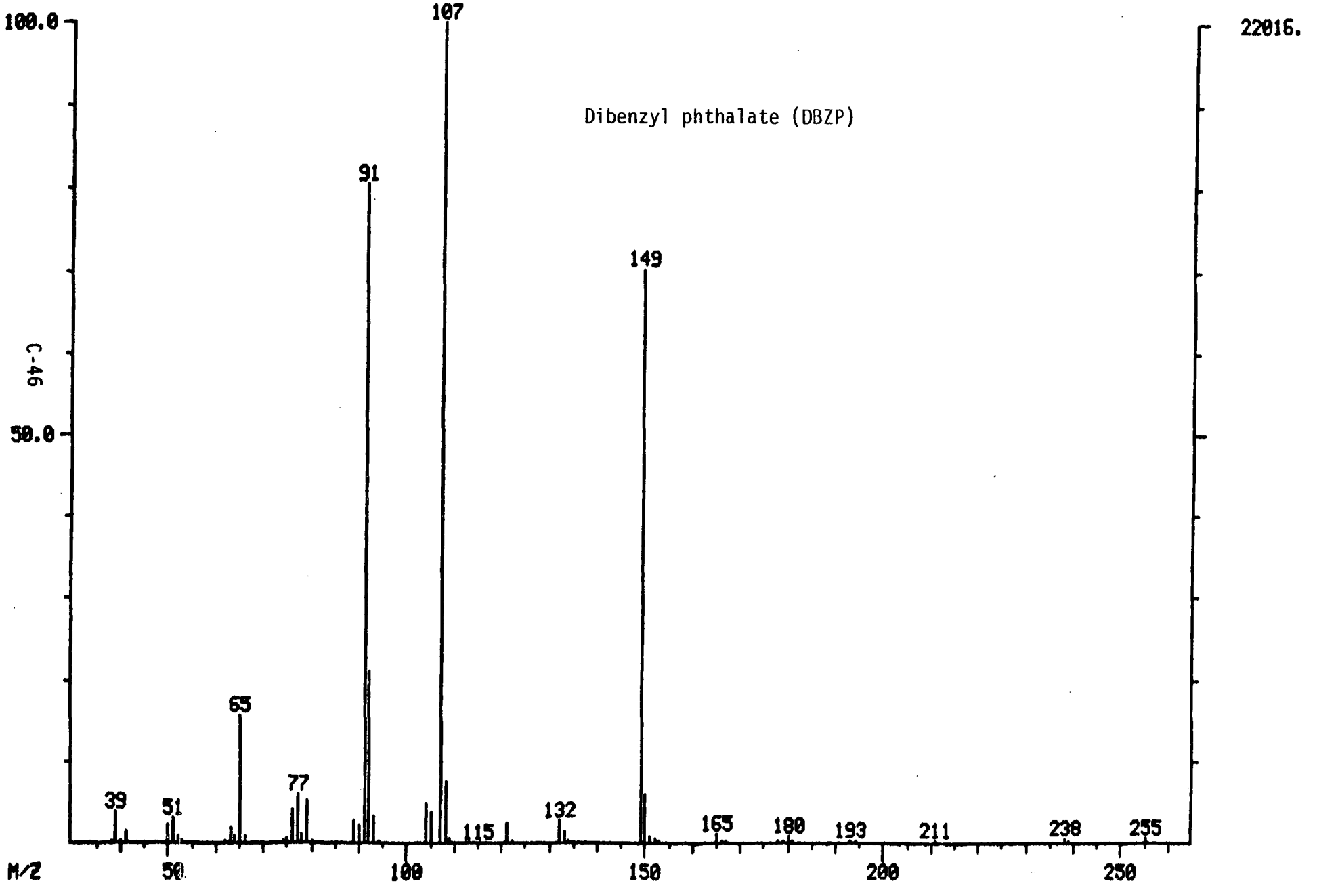
37	0.00	0.	Minima	Min Inten:	0.
320			Maxima	# 0	
Mass	% RA	Inten.	Mass	% RA	Inten.
37?	0.10	22.	169	0.98	206.
38?	0.69	145.	170	0.13	28.
39?	5.32	1122.	195	0.11	24.
40	0.34	71.	196	0.41	86.
41	0.06	13.	197	3.28	691.
50	5.43	1146.	198	0.47	99.
51	1.99	419.	225	100.00	21088.
52	0.14	29.	226	14.81	3124.
53	0.29	61.	227	1.56	329.
55	0.17	35.	228	0.14	29.
62	0.20	43.	318	2.51	529.
63	0.98	207.	319	0.52	110.
64	0.58	122.	320	0.04	9.
65	4.69	989.			
66	0.52	110.			
70	0.11	24.			
73	0.07	14.			
74	0.94	199.			
75	2.53	533.			
76	20.22	4264.			
77	2.98	629.			
78	0.20	42.			
84	0.05	10.			
89	0.16	34.			
91	0.20	43.			
92	0.17	36.			
93	0.64	136.			
94	0.49	103.			
96	0.07	15.			
98	0.08	16.			
102	0.12	26.			
103	0.46	97.			
104	43.93	9264.			
105	3.37	711.			
106	0.22	47.			
113	0.33	69.			
114	0.11	23.			
115	2.35	495.			
116	0.24	50.			
121	0.21	45.			
132	20.14	4248.			
133	1.78	375.			
134	0.14	30.			
139	0.72	151.			
140	0.21	44.			
141	2.10	443.			
142	0.25	53.			
149	0.31	65.			
152	0.18	38.			
168	0.43	90.			

Diphenyl terephthalate (DPTP)

MASS SPECTRUM
02/04/88 1:16:00 + 34:47
SAMPLE: \###(#3
CONDS.:
ENHANCED (S 15B 2N 0T)

DATA: R0203STDB #2087
CALI: R0203STDB #2

BASE M/Z: 107
RIC: 80128.



Mass List Data: R0203STDB #2087 Base m/z: 107
02/04/88 1:16:00 + 34:47 Cali: R0203STDB # 2 RIC: 80128.
Sample:
!#
#
#(#3

Dibenzyl phthalate (DBZP)

Conds.:
Enhanced (S 15B 2N OT)

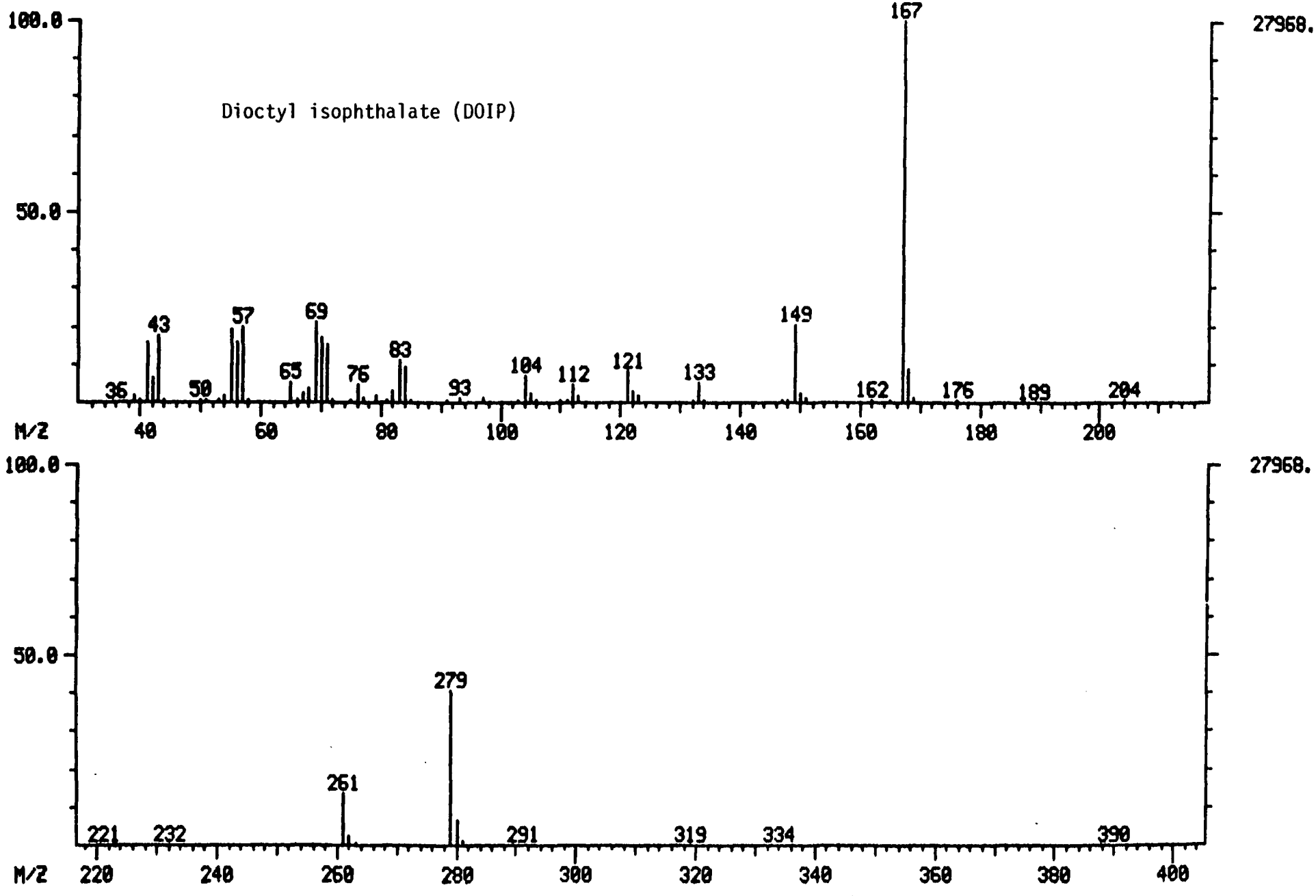
38	0.00	0.	Minima	Min Inten:	0.
256			Maxima	# 0	
Mass	% RA	Inten.	Mass	% RA	Inten.
38?	0.38	84.	166	0.35	77.
39?	3.77	829.	167	0.40	89.
40	0.32	71.	178	0.17	37.
41	1.43	314.	179	0.22	49.
44	0.10	22.	180	0.69	153.
50	2.13	469.	181	0.40	88.
51	3.05	672.	193	0.24	53.
52	0.72	159.	194	0.20	44.
53	0.30	67.	197	0.13	28.
62	0.25	54.	198	0.06	14.
63	1.77	389.	211	0.15	33.
64	0.80	177.	238	0.57	126.
65	15.72	3460.	239	0.22	49.
66	0.90	199.	240	0.04	8.
74	0.37	81.	255	0.65	143.
75	0.55	122.	256	0.11	24.
76	3.94	867.			
77	5.96	1312.			
78	0.97	214.			
79	5.01	1102.			
80	0.31	69.			
89	2.60	573.			
90	2.18	481.			
91	80.67	17760.			
92	20.93	4608.			
93	3.35	737.			
94	0.19	42.			
96	0.02	4.			
104	4.79	1054.			
105	3.85	847.			
106	0.11	25.			
107	100.00	22016.			
108	7.53	1658.			
109	0.43	94.			
115	0.12	26.			
118	0.04	9.			
119	0.07	15.			
121	2.34	515.			
122	0.37	82.			
128	0.06	14.			
132	2.80	617.			
133	1.30	287.			
134	0.15	33.			
149	70.28	15472.			
150	6.02	1326.			
151	0.77	169.			
152	0.60	132.			

153	0.28	61.
164	0.06	14.
165	1.19	262.

MASS SPECTRUM
02/04/88 0:23:00 + 35:27
SAMPLE: PHTHALATE STD A 100NG/UL
CONDS.: FINN4500
ENHANCED (S 15B 2N 0T)

DATA: R0203STDA #2127
CALI: R0203STDA #2

BASE M/Z: 167
RIC: 124416.



Mass List Data: R0203STDA #2127 Base m/z: 167
02/04/88 0:23:00 + 35:27 Cali: R0203STDA # 2 RIC: 124416.
Sample: PHTHALATE STD A 100NG/UL
Conds.: FINN4500
Enhanced (S 15B 2N OT)

Dioctyl isophthalate (DOIP)

36	0.00	0.	Minima	Min Inten:	29.
391			Maxima	# 0	
Mass	% RA	Inten.	Mass	% RA	Inten.
39?	1.87	523.	115	0.13	36.
40	0.46	128.	117	0.12	33.
41	15.47	4328.	119	0.13	36.
42	6.57	1838.	120	0.16	44.
43	17.19	4808.	121	8.25	2308.
44	0.69	193.	122	2.86	799.
45	0.11	31.	123	1.47	412.
50	0.66	185.	124	0.11	31.
51	0.33	93.	129	0.20	56.
52	0.13	35.	131	0.13	35.
53	0.77	215.	132	0.59	165.
54	1.93	539.	133	5.36	1498.
55	19.36	5416.	134	0.55	154.
56	15.50	4336.	135	0.27	76.
57	19.79	5536.	147	0.31	88.
58	0.87	243.	148	0.76	213.
65	5.48	1534.	149	20.62	5768.
66	0.66	185.	150	2.13	595.
67	2.28	637.	151	1.34	374.
68	3.39	948.	152	0.14	38.
69	20.77	5808.	162	0.55	153.
70	16.91	4728.	163	0.11	31.
71	15.07	4216.	164	0.11	32.
72	0.82	229.	165	0.37	103.
74	0.10	29.	167	100.00	27968.
75	0.79	220.	168	8.81	2464.
76	4.70	1314.	169	1.19	334.
77	1.20	335.	176	0.36	101.
78	0.15	43.	177	0.14	38.
79	1.46	409.	179	0.12	33.
80	0.15	41.	189	0.13	37.
81	0.79	222.	193	0.13	35.
82	3.12	872.	203	0.11	31.
83	11.14	3116.	204	0.30	83.
84	9.32	2608.	207	0.15	43.
85	0.73	204.	208	0.10	29.
91	0.54	150.	261	13.54	3788.
93	0.91	255.	262	2.40	672.
95	0.25	69.	263	0.33	93.
97	1.33	373.	277	0.20	57.
98	0.13	37.	279	40.50	11328.
103	0.70	196.	280	6.61	1850.
104	7.07	1976.	281	0.90	251.
105	2.31	647.	282	0.12	34.
106	0.31	86.	291	0.14	39.
110	0.30	83.	390	0.11	32.
111	0.77	216.	391	0.11	30.
112	4.78	1338.			
113	1.52	424.			
114	0.13	36.			

APPENDIX D

RESULTS OF INORGANIC ANALYSIS FOR THE ESTUARINE WATER, LEACHATE, AND GROUNDWATER

Table 1. Metals Results

Parameter	EPA Method	GROUNDWATER SAMPLE ug/L	Spike % Recov	Dup Spike RPD	Method Blank ug/L	Method Detection Limit ug/L
Aluminum	200.7	<50	NS	NS	<50	50.0
Antimony	200.7	<50	NS	NS	<50	50.0
Arsenic	200.7	<100	NS	NS	<100	100.0
Barium	200.7	79.1	NS	NS	<10	10.0
Beryllium	200.7	<5.0	NS	NS	<5	5.0
Boron	200.7	300	NS	NS	<50	50.0
Cadmium	200.7	<5.0	NS	NS	<5	5.0
Calcium	200.7	113000	NS	NS	<130	130.0
Chromium	200.7	<10	NS	NS	<10	10.0
Cobalt	200.7	<10	NS	NS	<10	10.0
Copper	200.7	<10	NS	NS	<10	10.0
Iron	200.7	31.4	NS	NS	<10	10.0
Lead	200.7	<50	NS	NS	<50	50.0
Magnesium	200.7	38000	NS	NS	<140	140.0
Manganese	200.7	45.7	NS	NS	<10	10.0
Molybdenum	200.7	<10	NS	NS	<10	10.0
Nickel	200.7	<20	NS	NS	<20	20.0
Selenium	200.7	<100	NS	NS	<100	100.0
Silicon	200.7	13100	NS	NS	<50	50.0
Silver	200.7	<10	NS	NS	<10	10.0
Sodium	200.7	51900	NS	NS	<250	250.0
Thallium	200.7	<100	NS	NS	<100	100.0
Tin	200.7	<50	NS	NS	<50	50.0
Titanium	200.7	<50	NS	NS	<50	50.0
Vanadium	200.7	<10	NS	NS	<10	10.0
Zinc	200.7	<10	NS	NS	<10	10.0

NS - Not Spiked

Table 2. General Chemical Results

Parameter	EPA Method	GROUNDWATER SAMPLE mg/L	Spike % Recov	Dup Spike RPD	Control Sample mg/L	Method Blank mg/L
Bromide	300.0 D	<0.05	104	0.06	105	<0.05
Chloride	300.0 D	79.7	114	4.0	99.0	<0.1
E.C., umhos/cm	120.1 W	910	N/A	N/A	N/A	N/A
Flouride	300.0 D	<0.05	108	6.4	NA	NA
Nitrate, as N	300.0 D	11.6	106	0.37	102	<0.1
Nitrite, as N	300.0 D	<0.1	125	0.07	NA	<0.1
pH, units of pH	150.1 M	7.4	N/A	N/A	N/A	N/A
Phosphate, as P	300.0 D	<0.2	92.7	0.34	108	<0.2
Sulfate	300.0 D	126	97.7	0.29	104	<0.3
TDS, at 180°C	160.1 G	746	N/A	0.19	N/A	N/A
TOC	415	4.0	NS	NS	NA	N/A

D - Ion Chromatography
G - gravimetric
M - electrometric
W - Wheatstone bridge conductivity meter

N/A - Not Applicable

NA - Not analyzed

NS - Not spiked

Table 3. Metals Results

Parameter	EPA Method	ESTUARINE WATER ug/L	Spike % Recov	Dup Spike ug/L	Method Blank ug/L	Method Detection Limit ug/L
Aluminum	200.7	2100	94	8.9	71.7	50
Antimony	200.7	<50	94	1.3	<50	50
Arsenic	200.7	<100	NS	NS	<100	100
Barium	200.7	<10	90	9.4	<10	10
Beryllium	200.7	<5.0	93	12	<5.0	5.0
Boron	200.7	3610	NS	NS	<20	20
Cadmium	200.7	<5.0	102	20	<5.0	5.0
Calcium	200.7	331000	97	1.0	<100	100
Chromium	200.7	<10	104	12	<10	10
Cobalt	200.7	<10	97	13	<10	10
Copper	200.7	<10	92	13	<10	10
Iron	200.7	1720	96	1.1	<20	20
Lead	200.7	<50	104	13	<50	50
Magnesium	200.7	1090000	104	0.77	<100	100
Manganese	200.7	35.5	98	7.6	<10	10
Molybdenum	200.7	38.8	NS	NS	<10	10
Nickel	200.7	<20	99	7.9	<20	20
Selenium	200.7	<200	NS	NS	<200	200
Silicon	200.7	9260	95	0.17	87.6	50
Silver	200.7	<10	87	4.5	<10	10
Sodium	200.7	8650000	106	0.37	<200	200
Thallium	200.7	<200	NS	NS	<200	200
Tin	200.7	<50	NS	NS	<50	50
Titanium	200.7	50.3	NS	NS	<50	50
Vanadium	200.7	17.8	96	11	<10	10
Zinc	200.7	<10	101	11	<10	10

NS - Not spiked

Table 4. General Chemical Results

Parameter	EPA Method	ESTUARINE WATER mg/L	LEACHATE mg/L	Spike % Recov	Dup Spike RPD	Control Sample % Recov
Bromide	300.0 D	31.4	<0.1	NA	NA	NA
Chloride	300.0 D	23900	14.5	94.3	0.72	117
Fluoride	340.2 E	0.61	<0.05	98.9	0	NA
Nitrate, as N	300.0 D	<0.1	<0.1	116	NA	108
Nitrite, as N	300.0 D	<0.1	<0.1	NA	NA	NA
pH, units of pH	150.1 M	8.0	5.5	NA	NA	NA
Phosphate, as P	300.0 D	<0.2	<0.2	103	1.6	NA
Sulfate	300.0 D	146000	<0.3	81.3	0.41	105
TDS, at 180°C	160.1 G	31100	32900	NA	4.5	NA

D - Ion Chromatography
E - ion selective electrode
G - gravimetric
M - electrometric

NA - Not analyzed

Table 5. Metals Results

Parameter	EPA Method	LEACHATE ug/L	Spike % Recov	Dup Spike RPD	Method Blank ug/L	Method Detection Limit ug/L
Antimony	200.7	<50	93	0	<50	50
Arsenic	200.7	<100	100	0	<100	100
Barium	200.7	2040	121	1.1	<10	10
Beryllium	200.7	<5.0	84	0	<5.0	5.0
Cadmium	200.7	<5.0	90	11	<5.0	5.0
Chromium	200.7	201	108	1.6	<10	10
Cobalt	200.7	76.4	85	5.3	<10	10
Copper	200.7	41.1	*	1.1	<10	10
Lead	200.7	<50	125	2.0	<50	0.2
Molybdenum	200.7	15.0	90	7.1	<10	10
Nickel	200.7	<20	89	6.9	<20	20
Selenium	200.7	<200	116	0	<200	200
Silver	200.7	11.1	82	1.2	<10	10
Thallium	200.7	<200	86	0	<200	200
Vanadium	200.7	153	90	4.7	<10	10
Zinc	200.7	81.9	*	1.9	<10	10
Aluminum	200.7	68600	NS	NS	<50	50
Boron	200.7	<20	NS	NS	<20	20
Calcium	200.7	23400	NS	NS	<100	100
Iron	200.7	51700	NS	NS	<20	20
Magnesium	200.7	13000	NS	NS	<100	100
Manganese	200.7	3030	NS	NS	<10	10
Silicon	200.7	24900	NS	NS	<50	50
Sodium	200.7	7900000	NS	NS	<200	200
Tin	200.7	<50	NS	NS	<50	50
Titanium	200.7	2330	NS	NS	<50	50

* Sample greater than 50x added spike.

NS - Not spiked