



## *Project Summary*

# Determination of Phthalates in Industrial and Municipal Wastewaters

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This report is one of a series investigating the analytical behavior of selected priority pollutants and suggests a suitable test procedure for their measurement.

The specific compounds studied in this effort were:

1. Dimethyl Phthalate (DMP)
2. Diethyl Phthalate (DEP)
3. Dibutyl Phthalate (DBP)
4. Benzyl Butyl Phthalate (BBP)
5. Diethylhexyl Phthalate (DEHP)
6. Dioctyl Phthalate (DOP)

It was desirable that common sample treatment for the various categories be employed, where possible, to minimize cost of analysis of unrelated compounds in any given water sample. The efforts reported under the following performance headings were designed to provide information relative to this common purpose.

The study was conducted in two phases. In Phase I, work was conducted with clean water and was intended to provide information which would give direction to Phase II work conducted on actual wastewaters, and to serve as a basis for comparison for the information developed.

*This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the*

*same title (see Project Report ordering information at back).*

### Introduction

#### *Literature Search*

The literature search as conducted yielded over 150 references. Examination of titles, and in many cases, abstracts, drastically reduced the number to five as being of interest to this program. The papers of G. S. Giam and his coworkers at Texas A and M are of particular interest. The paper by Giam, et al., entitled "Sensitive Method for Determination of Phthalate Ester Plasticizers in Open-Ocean Biota Samples" (*Anal. Chem.*, Vol. 47, No. 13, November 1975) was probably the most important product of the literature search. The authors reported several possible laboratory sources of phthalate esters which can/could result in contamination of samples. They also reported the necessity of deactivation of Florisil to prevent loss of DEHP when column chromatography employing Florisil is used in a sample clean-up procedure.

#### *Gas Chromatography*

All six phthalates have been chromatographed on two columns. The primary column (Column 1) is 1.8-m x 4-mm ID glass tubing packed with 1.5-percent SP-2250 plus 1.95-percent SP-2401 on 100/120 mesh Supelcoport. The sec-

ondary column (Column 2) has 3-percent OV-1 as its liquid phase but is otherwise the same as Column 1.

Initial investigations with Column 1 indicated that all six phthalates could be resolved at a column temperature of 200°C. However, the retention time for DOP was excessive at 34 minutes and the early eluting phthalates would be difficult to quantitate due to the proximity of the solvent peak. This would be even more critical on extracts of wastewater where the early eluters would be more likely to co-elute with interferences. Therefore, the six phthalates were divided into two groups of three for chromatography. The "low" temperature (160°C) group includes DMP (eluting in 1.9 minutes) DEP (2.9 minutes), DBP (12.6 minutes), while the "high" temperature (225°C) group includes BBP (4.1 minutes) DEHP (5.1 minutes), and DOP (9.0 minutes). Investigations with Column 2 gave comparable results, leaving little basis for recommending either column over the other.

At the beginning of this work, the electron capture detector was considered to be the primary detector for the analysis of phthalates, and the flame ionization detector the alternate detector, but experimentation confirmed that the electron capture detector is preferred over the flame ionization detector on the bases of the greater sensitivity and selectivity.

The response of the electron capture detector was not linear for DMP and DEP, and it was necessary to establish and use calibration curves for these two phthalates and to limit the amounts injected to not more than 1-2 nanograms. The electron capture response to DBP, BBP, DEHP, and DOP was not linear over several orders of magnitude but was sufficiently linear over a limited range to be used for quantitation purposes.

### Extraction Study

The extraction study was initiated to determine the recoveries of the six phthalates of interest from clean water at pH 2, 7, and 10 using 15 percent dichloromethane (DCM) in hexane and 100 percent DCM as the extracting solvents.

The water used in the extraction study was a naturally buffered well water obtained from the Southwest Research Institute supply line prior to chlorination.

The water was found to be very low in electron capture sensitive materials as determined through comparison of an extract of the water with a glassware blank.

The one liter samples of water were dosed while in one-liter Erlenmeyer flasks, then poured into two-liter separatory funnels for extraction with three 60-mL aliquots of either 15 percent DCM in hexane or 100 percent DCM. Three dosed samples were extracted at pH 2 and 10 with each solvent. At pH 7, four dosed samples were extracted with each solvent.

Essentially all the DCM must be removed prior to analysis when the extracting solvent is 100 percent DCM. This was done by taking the extract to a volume of 10 to 15 mL, adding 75 to 100 mL of hexane, and then reconcentrating to the final volume. The DCM extracts usually produced a wider "solvent" peak than those produced by 15 percent DCM in hexane. This peak broadening

was not reduced when the amount of hexane added before reconcentration was increased in amounts up to 200 mL, nor was it a serious problem.

The data acquired in the extraction study are presented in Tables 1 and 2. The data have not been corrected for blank extractions.

No clear tendency can be detected for one solvent system to produce superior recoveries or for the recoveries to be influenced by the pH of the water. The principal differences occurred when 100 percent DCM was used and a particular pH gave unacceptable results, especially in the cases of DEP and DBP. When 15 percent DCM in hexane was used as the extraction solvent, no differences were detected among the pHs. Another factor in the evaluation is that the 15 percent DCM-hexane solvent system produced more consistent results with fewer of the apparent contaminations and none of the low recoveries. It can be concluded, then,

Table 1. Extraction Study Results - 100% DCM % Recovery

pH	Extract	DMP	DEP	DBP	BBP	DEHP	DOP
2	1	96	89	63	88	102	94
	2	125	98	81	88	92	90
	3	67	71	40	90	101	96
	Mean	96	86	61	89	98	93
7	1	135	103	97	118	104	99
	2	143	106	95	110	99	97
	3	144	103	95	109	98	96
	4	115	99	94	98	98	94
Mean	134	103	95	109	100	97	
10	1	108	100	96	91	100	90
	2	119	115	00	91	99	95
	3	113	111	88	90	112	94
	Mean	113	109	95	91	104	93

Table 2. Extraction Study Results - 15% DCM in Hexane % Recovery

pH	Extract	DMP	DEP	DBP	BBP	DEHP	DOP
2	1	107	104	100	93	99	95
	2	105	101	87	92	96	95
	3	100	99	87	84	127	91
	Mean	104	101	91	90	107	94
7	1	116	101	104	—	—	91
	2	111	101	—	90	101	92
	3	109	103	104	85	104	91
	4	104	101	97	94	98	93
Mean	110	102	102	90	101	92	
10	1	110	104	95	98	105	97
	2	110	103	93	94	102	96
	3	113	104	95	98	112	99
	Mean	111	104	94	97	110	97

— data not available - contamination (?)

that 15 percent DCM-hexane should be used for extracting the wastewater and no adjustment of the pH need be made. The mean recoveries obtained with 15 percent DCM-hexane at the three pHs are shown at the bottom of the summary table to indicate the recovery obtained.

### Preservation Study

The preservation study was conducted to determine the effects of a 7 day storage period at various conditions on the recovery of the six phthalate esters of interest from dosed water samples. Each sample consisted of one quart of water dosed with six phthalates, as in the extraction study (see Table 3). Two replicates for each of twelve conditions of pH, temperature, and residual chlorine were prepared as shown in the following model:

	4°C	
	0 ppm Cl	2 ppm Cl
pH 2	2	2
pH 7	2	2
pH 10	2	2

  

	24°C	
	0 ppm Cl	2 ppm Cl
pH 2	2	2
pH 7	2	2
pH 10	2	2

The 2 ppm residual chlorine level was obtained, where required, by adding 160 microliters of Mallinckrodt sodium hydrochlorite analytical reagent (5 percent minimum available Cl).

After storage, the samples were extracted with 15 percent DCM-hexane without pH adjustment. Data obtained in the preservation study are presented in Table 3.

The results for dimethyl phthalate showed that the best conditions for DMP was storage at neutral conditions with basic conditions clearly unacceptable. The better temperature for storage was 4°C with an average recovery of 95.8 percent versus 82.2 percent at room temperature. The three pHs produced distinct means for BBP, with storage at pH 2 giving the best results, 93.8 percent recovery, followed by pH 7 and pH 10 (72.8 and 60.3 percent recovery, respectively). Higher results were obtained on average when storage was at 4°C as opposed to room temperature, with mean recoveries of 84.3 percent and 67.0 percent, respectively.

On the basis of the trends shown, the recommended conditions for storage of

**Table 3. Results of Preservation Study - DMP, DEP, DBP, BBP, DEHP, DOP (Percent Recovery - 7 - Day Storage Period)**

pH	Temperature °C	Chlorine ppm	Replicate	DMP	DEP	DBP	BBP	DEHP	DOP		
2	4	0	1	*	*	*	105	108	107		
			2	103	97	79	88	91	90		
		2	2	1	104	95	89	98	96	99	
				2	104	94	89	93	96	95	
		7	24	0	1	110	103	86	88	101	93
					2	109	99	90	91	118	91
2	2			1	116	100	91	85	88	92	
				2	115	103	89	103	104	95	
10	4			0	1	93	98	85	78	89	94
					2	92	97	84	67	86	90
		2	2	1	97	100	91	77	88	92	
				2	94	100	88	77	84	90	
		2	24	0	1	112	100	92	73	99	69
					2	*	*	*	*	*	*
10	4	2	1	100	98	89	70	85	95		
			2	100	100	105	68	104	91		
		2	2	1	94	100	90	79	86	83	
				2	90	97	94	87	92	88	
		2	24	0	1	89	97	95	84	84	83
					2	87	103	94	79	75	75
2	2	2	1	30	85	74	40	89	81		
			2	32	85	81	41	94	89		
2	2	2	1	26	80	68	37	93	88		
			2	25	78	71	35	94	87		

\* data not available - contamination (?)

phthalate esters as a class would specify an adjustment of the water to acidic conditions, and storage at a temperature of 4°C. Under these conditions, no interference can be expected from residual chlorine up to the 2 ppm level.

Adjustment of wastewater samples to pH 2 may not be practical under field conditions and may be avoided with minimal effect on the determination of phthalate esters, provided the samples are stored at 4°C.

### Liquid-Solid Column Chromatography

Two column chromatographic approaches were developed to clean up extracts for phthalate analysis. Deactivated Florisil and alumina were both examined for their ability to quantitatively elute the six phthalate esters.

The clean-up procedures using Florisil and alumina were evaluated as to the recoveries that could be obtained when

doses of the six phthalates were applied to columns of these adsorbents. The recoveries for all six test phthalates from both materials appear to be very good, averaging 90 percent or better.

### Wastewater Application

With the assistance and approval of the project officer, five wastewaters were procured and analyzed. All samples were put in clean, one gallon bottles and shipped unrefrigerated via air to Southwest Research Institute laboratories. All of the wastewater from a particular source with the exception of Wastewater 2, were pooled, adjusted to pH 5-7 if necessary, returned to the bottles in which they were shipped, and stored in the dark at 4°C until used. Due to the high acid content of Wastewater 2 which required approximately 48 g/L NaOH to neutralize, it was stored at 4°C as received.

In order to develop method improvements and to provide base data for

dosing and recovery experiments and for the accuracy and precision evaluations to follow, each wastewater was analyzed in triplicate for each substance of interest in this program.

One liter of wastewaters was extracted three times using 60 mL DCM for each extraction. The combined extract was dried with  $\text{Na}_2\text{SO}_4$  and placed in a Kuderna-Danish (K-D) evaporator. The DCM extract was concentrated to 5-10 mL, 90 mL of hexane was added, and the extract was concentrated to slightly less than 10 mL in the K-D. The sample was then transferred to a small vial and concentrated to 2 mL. This 2 mL concentrated extract was then subjected to the Florisil clean-up procedure as previously described. One procedural change, used only with Wastewaters 3, 4, and 5, was attempted and with some success. In the Florisil clean-up procedure, instead of collecting a single fraction of 100 mL of eluting solvent containing all the phthalate esters of interest, a two-fraction collection was made. Fraction 1, which consisted of the first 60 mL contained nearly all of the DOP and DEHP, most of the DBP and BBP and, in some instances, much of the early GC-eluting material. Fraction 2, the next 40 mL, contained all the DMP, most of the DEP, some DEP and BBP and, in some instances, reduced amounts of early GC-eluting material(s) which otherwise interfere with detection of the DMP and DEP.

## Accuracy and Precision

### Approach

The accuracy and precision assessment for the method was of a limited nature due to the number and types of analytical results obtained. According to the design of the program three replicates of each of five wastewaters were to be dosed for the compounds of interest and analyzed, both at a zero time and after seven days storage at 4°C.

## Results

### Wastewater 1

Neither the DMP nor the DEP was dosed into Wastewater 1, either at time zero or after storage due to interferences. Consistent results were obtained for the other four compounds studied, however, with recoveries from 70 percent for DEHP to 81 percent for DBP. In each of these cases, the precision of the analyses was good, with ranges of 2, 0,

4, and 2 percent recovery for DBP, BBP, DEHP, and DOP, respectively.

The preservation recoveries were generally good for the four higher-boiling phthalates, but more variable than the zero day analyses. The recoveries were from a low of 94 percent to a high of 106, with ranges of 6, 7, 9, and 18. The 106 average for DBP was influenced by a single value of 118, and the indication is that recovery for these compounds was not affected by the storage conditions in this wastewater.

### Wastewater 2

Wastewater 2 was a particularly difficult sample. The pH of this sample was not adjusted at the time of sampling. The initial analysis of this wastewater indicated large interferences making qualitative estimations almost impossible. Upon further storage in the cold room, the sample darkened and considerable black precipitate was formed. Considering the problems encountered, no attempt was made to establish recovery or preservation data on Wastewater 2. Very likely Wastewater 2 was a process water and the clean-up procedure was inadequate.

### Wastewater 3

The analyses on this wastewater produced results which ranged from low to very good, depending upon the particular compound. Results for both DMP and DEP were very good, with triplicate analyses indicating 100 percent recovery of the spike. The recovery of DBP was 91 percent, on average, but with a range of 10 percent recovery. The results for the remaining phthalates were not good in this wastewater, however. The average recovery of BBP was 104 percent, but the individual recoveries had a range of 27 percent (93-120). DEHP and DOP were recovered at 65 and 66 percent, respectively, of the dose level with ranges of 16 and 20 percent recovery.

The preservation data were also inconsistent from one compound to the next. For the six compounds studied, the average recovery relative to the zero day analyses went from 68 percent for DBP to 109 percent for DEHP. These analyses were more variable than the zero day analyses in the cases of DMP and DBP, equivalent for DEP, and considerably less variable for the remainder. The ranges of the triplicate analyses at zero time were 27, 16, and 20 for DBP, DEHP, and DOP, respectively, at the

initial analyses compared to 9, 6, and 10 for these compounds after seven days' storage.

### Wastewater 4

The analysis on Wastewater 4 for DMP and DEP produced good recovery, 88 and 82 percent, respectively, with ranges of 3 and 2 percent. Recovery of 91 percent on average was noted for DBP but more variability was also noted with a range of 10 percent recovery. Lower recoveries were obtained for the remaining three phthalates, with average percent recoveries of 76, 50, and 50 for BBP, DEHP, and DOP, respectively with ranges of 10, 9, and 8.

The preservation data were good for the first four compounds, going from 96 to 107 percent recovery. For the DEHP and DOP analyses, however, the average recoveries were 140 and 139 percent with ranges of 9 and 11, respectively. These recoveries are comparable to 70 and 69 percent, respectively, of the original dosed amount and indicate a problem with the initial analyses.

### Wastewater 5

The results for both DMP and DEP were good in this wastewater, with average recoveries of 97 and 92 percent, respectively, and ranges of 6 and 4 percent recovery. The DBP and BBP results were low and variable, with average recoveries of 41 and 63 and ranges of 16 and 13 percent recovery, respectively. The DEHP and DOP values were consistent but only 71 percent of the dose was recovered on the DEHP, while 93 percent was recovered on the DOP. For both of these compounds there was a zero range, with all three analyses showing the same recovery.

The preservation recoveries were fairly consistent for all of the compounds, with ranges of recovery of 0 to 9 percent. However, the level of recovery could be broken down into three groups: DMP-DEP, DBP-BBP, DEHP-DOP. The recovery after storage was 95 to 100 for the first pair, 61 to 65 for the second, and 78 to 79 for the third. The 61 percent recovery represents only 25 percent of the initial dosed amount remaining after seven days and indicates that storage in this wastewater would not be recommended for these analyses.

## Summary

The accuracy and precision evaluations on phthalate esters in wastewater lead to the following conclusions: Acceptable recovery was obtained for

phthalate esters using this methodology when the background of electron capture sensitive materials was low. When interferences were present, as in the case of Wastewater 1 in the DMP and DEP region, the clean-up procedures did not remove them sufficiently to allow these substances to be quantitated in  $\mu\text{g}/\text{l}$  concentrations. In the case of Wastewater 2, believed to be a process wastewater as opposed to a final treated effluent, excessive interferences could not be removed by the clean-up procedures to allow quantitative estimation of the analytes of interest. The recoveries that can be expected for the compounds studied ranged from 40 to 100 percent, depending upon the compound and the wastewater studied. In general, the precision of the analyses was acceptable to good, with ranges of less than 10 percent recovery common.

The overriding conclusion is that the recovery and the ability to store the water for later analysis are a function of the wastewater. Storage frequently resulted in significant losses of the study materials and in less precise determinations. Therefore, storage cannot be recommended as a general rule.

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*The complete report, entitled "Determination of Phthalates in Industrial and Municipal Wastewaters," (Order No. PB 81-232 167; Cost: \$9.50, subject to change) will be available only from:*

*National Technical Information Service  
5285 Port Royal Road  
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*The EPA Project Officer can be contacted at:  
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