DIMETHYL PHTHALATE (DMP)
DIETHYL PHTHALATE (DEP)
DIBUTYL PHTHALATE (DBP)
DI-2-ETHYLHEXYL PHTHALATE (DEHP)
DI-*n*-OCTYL PHTHALATE (DNOP)

Method number: 104

Matrix: Air

	DMP	DEP	DBP	DEHP	DNOP
Target concentration:	5 mg/m^3 TWA	5 mg/m^3 TWA	5 mg/m^3 TWA	5 mg/m^3 TWA	5 mg/m^3 TWA
OSHA PEL:	5 mg/m^3 TWA	None	5 mg/m^3 TWA	5 mg/m^3 TWA	None
ACGIH TLV:	5 mg/m^3 TWA	5 mg/m^3 TWA	5 mg/m^3 TWA	5 mg/m^3 TWA 10 mg/m^3 STEL	None

Procedure: Samples are collected by drawing known volumes of air through OVS-Tenax sampling tubes. Samples are desorbed with toluene and analyzed by GC using a flame ionization detector (FID).

Recommended air volume and sampling rate: 240 L at 1.0 L/min

	DMP	DEP	DBP	DEHP	DNOP
Reliable quantitation limits:	90 µg/m^3	68 µg/m^3	34 µg/m^3	55 µg/m^3	45 µg/m^3
Standard errors of estimate:	6.8%	6.7%	5.6%	5.4%	5.5%

Status of method: Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: August 1994

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1. General Discussion

1.1 Background

1.1.1 History

Airborne phthalates have been collected in ethylene glycol (Ref. 5.1), on mixed cellulose ester membrane filters (Ref. 5.2), and on Tenax GC adsorbent (Ref. 5.3). The analytical methods include GC/FID, GC/MS, GC/ECD, and HPLC/UV. An OSHA stopgap method specifies collection on OVS-2 (OSHA Versatile Sampler), desorption with carbon disulfide and analysis by GC/FID (Ref. 5.4). OVS samplers, with a glass fiber filter in front to stop droplets and sorbent behind to adsorb vapor, are ideal for collecting contaminants that may be present as both aerosol and vapor. The author of the stopgap study found that most of the phthalates spiked on the glass fiber filters migrated to the resin bed after 60 L of air had been drawn through them, indicating that filters alone would not be sufficient. However, XAD-2 resin used in the OVS-2 is difficult to work with. During the transfer of the resin from the sample tube to a vial, many resin beads cling to the glass wall and are impossible to dislodge. For these reasons OVS-Tenax was selected for the collection of airborne phthalates.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

Dimethyl phthalate (DMP). DMP is of low to moderate toxicity, but when accidentally ingested in large amounts it may cause gastrointestinal irritation, central nervous system depression with coma, and hypotension. It is an irritant to the eyes and the mucous membranes. It is not irritant to the skin and is not absorbed. DMP is not known to cause cancer in humans or animals. (Ref. 5.5)

Diethyl phthalate (DEP). Adverse effects on humans from exposure to DEP have not been reported. DEP has caused death in animals given very high doses by mouth, but brief oral exposures to lower doses caused no harmful effects. The only effect found in animals that ate high doses of DEP for long periods of time was a decrease in weight gain because they ate less food. DEP is not known to cause cancer in humans or animals. DEP does not appear to affect the ability of male animals to sire offspring. However, a decrease occurred in the number of live offspring born to female animals that were exposed to DEP throughout their lives. Some birth defects occurred in newborn rats whose mothers received high doses (approximately 3 g/kg) of DEP by injection during pregnancy. DEP can be mildly irritating when applied to the skin of animals. It can also be slightly irritating when put directly into the eyes of animals. (Ref. 5.6)

Dibutyl phthalate (DBP). Adverse effects on humans from exposure to DBP have not been reported. In animals, eating large amounts of DBP can affect their ability to reproduce. DBP can cause death of unborn animals. In male animals, sperm production can decrease after eating large amounts of DBP. However, when exposure to DBP stops, sperm production seems to return to near normal levels. Exposure to high levels of DBP might cause similar effects in humans as in animals, but this is not known. There is no evidence that DBP causes cancer, but this has not been thoroughly studied. (Ref. 5.7)

Di-2-ethylhexyl phthalate (DEHP). From animal studies, breathing DEHP does not appear to have serious harmful effects. Studies in rats have shown that DEHP in the air has no effect on lifespan or the ability to reproduce. However, eating high doses of DEHP for a long time resulted in liver cancer in rats and mice. The U.S. Department of Health and Human Services has determined that DEHP may reasonably be anticipated to be a carcinogen. (Ref. 5.8) IARC designated DEHP to Group 2B (possibly carcinogenic to humans) (Ref. 5.9). Short-term exposures to DEHP interfered with sperm formation in mice and rats. These effects were reversible, but the process of sexual maturation was

delayed when the animals were exposed before puberty. Short-term exposures appeared to have no effect on male fertility. After long-term exposures, fertility of both male and female rats was decreased. Studies of pregnant mice and rats exposed to DEHP resulted in effects on the development of the fetus, including malformation of fetus and reduction in neonatal weights and survival. Long-term exposure of animals to DEHP resulted in structural and functional changes in the kidney. (Ref. 5.8)

Di-*n*-octyl phthalate (DNOP) . DNOP may cause irritation to the skin and may cause severe irritation and possible corneal damage to the eyes. Ingestion may cause central nervous system depression with nausea, vomiting, dizziness, weakness, headache, and difficult respiration. A large dose is required to cause death in animals. (Ref. 5.10)

1.1.3 Workplace exposure

DMP is used as a solvent and plasticizer for cellulose acetate and cellulose acetate-butyrate formulations. During World War II it was used effectively as a mosquito and insect repellant. Occupational exposure may occur in industrial facilities where DMP is manufactured or used in its various applications. No data on the extent of workplace exposure were found. (Ref. 5.5)

DEP is used as a plasticizer for cellulose ester plastic films and sheets (photographic, blister packaging, and tape applications) and molded and extruded articles (consumer articles such as toothbrushes, automotive components, tool handles, and toys). DEP was reported as an ingredient in 67 cosmetic formulations at concentrations ranging from <0.1% to 25-50%. These cosmetics included bath preparations (oils, tablets, and salts), eye shadows, toilet waters, perfumes and other fragrance preparations, hair sprays, wave sets, nail polish and enamel removers, nail extenders, nail polish, bath soaps, detergents, aftershave lotions, and skin care preparations. In addition, DEP is used as a component in insecticide sprays and mosquito repellents, as a camphor substitute, as a plasticizer in solid rocket propellants, as a wetting agent, as a dye application agent, as an ingredient in aspirin coatings, as a diluent in polysulfide dental impression materials, and in adhesives, plasticizers, and surface lubricants used in food and pharmaceutical packaging. Human exposure to DEP can result from breathing contaminated air, eating foods into which DEP has leached from packaging materials, eating contaminated seafood, drinking contaminated water, or as a result of medical treatment involving the use of PVC tubing (e.g., dialysis patients). The use of DEP in consumer products, however, is likely to be the primary source of human exposure. DEP has been detected in adipose tissue samples taken from people (including children) nationwide. Occupational exposure may occur in industrial facilities where DEP is used in the manufacture of plastics or consumer products. (Ref. 5.6)

DBP is used primarily as a specialty plasticizer for nitrocellulose, polyvinyl acetate, and polyvinyl chloride. It has been used in plastisol formulations for carpet back coating and other vinyl compounds. DBP has also been used as an adjusting agent for lead chromate pigments, as a concrete additive, as an insect repellant for the impregnation of clothing, as a solvent for perfume oils, and as a stabilizer in rocket propellants. DBP is widespread in the environment and has been identified at low levels in air, water, and soil. Therefore, humans may be exposed to DBP by inhalation of air or by ingestion of water or food containing DBP. Individuals who manufacture or use specialty plasticizers would have the highest potential for exposure to DBP. No data were located on typical exposure levels in the workplace. (Ref. 5.7)

DEHP is principally used as a plasticizer in the production of polyvinyl chloride (PVC) and vinyl chloride resins. Estimates are that at least 95% of the DEHP produced ends up in these uses. PVC is flexible and is used in many common items such as toys, vinyl upholstery, shower curtains, adhesives, coatings, and as components of paper and paperboard. PVC is also used to produce disposable medical examination and surgical gloves, the flexible tubing used to administer parenteral solutions, and the tubing used in

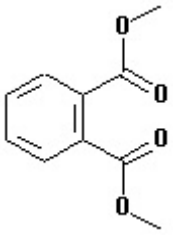
hemodialysis treatment. Non-plasticizer uses include the use of DEHP as a solvent in erasable ink; as an acaricide in orchards; as an inert ingredient in pesticide products, cosmetics, and vacuum pump oil; as a component of dielectric fluids in electrical capacitors; to detect leaks in respirators; and to test air filtration systems. DEHP is a ubiquitous environmental contaminant. The principal route of human exposure to DEHP is ingestion of contaminated food, especially fish, seafood, or fatty foods, with an estimated daily dose of about 0.25 mg. The highest exposures to DEHP result from medical procedures such as blood transfusions or hemodialysis, during which DEHP may leach from plastic equipment into biological fluids. Workers in industries manufacturing or using DEHP plasticizer may be frequently exposed to above average levels of this compound. (Ref. 5.8)

DNOP is used as a plasticizer in the production of polyvinyl chloride and vinyl chloride resins. Occupational exposure may occur in the workplace where this compound is used. No data on the extent of workplace exposure were found. (Ref. 5.10)

1.1.4 Physical properties and other descriptive information (Ref. 5.11)

Dimethyl phthalate

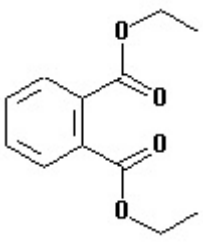
CAS no.: 131-11-3
synonyms: 1,2-benzenedicarboxylic acid, dimethyl ester; phthalic acid, dimethyl ester; dimethyl 1,2-benzenedicarboxylate; dimethyl *o*-phthalate; Avolin; DMP; Fermine; Palitinol M; Unimoll DM; RCRA U102
structural formula:



molecular wt: 194.19
boiling point: 284°C
melting point: 0 - 2°C
appearance: colorless to pale yellow oily liquid
odor: slight aromatic odor
specific gravity: 1.1905
vapor pressure: less than 1.3 Pa (0.01 mmHg) at 25°C
flash point: 146°C (closed-cup)
solubility: soluble in benzene, alcohol, ether, chloroform; slightly soluble in mineral oil; practically insoluble in petroleum ether and other paraffin hydrocarbons

Diethyl phthalate

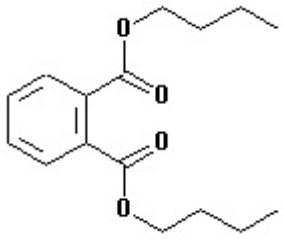
CAS no.: 84-66-2
synonyms: diethyl 1,2-benzenedicarboxylate; ethyl phthalate; Neantine; Palatinol A; *o*-benzenedicarboxylic acid diethyl ester; Placidol E; 1,2-benzenedicarboxylic acid, diethyl ester; phthalic acid, diethyl ester; phthalol; DEP; "Kodaflex" DEP Plasticizer; RCRA U088
structural formula:



molecular wt: 222.24
boiling point: 298°C
melting point: −41°C
appearance: colorless liquid
odor: odorless
specific gravity: 1.1175
vapor pressure: 1.9 kPa (14 mmHg) at 163°C, 0.22 Pa (1.65×10^{-3} mmHg) at 25°C
flash point: 140°C (open cup)
solubility: soluble in alcohol, ether, acetone, benzene; moderately soluble in aliphatic solvents

Dibutyl phthalate

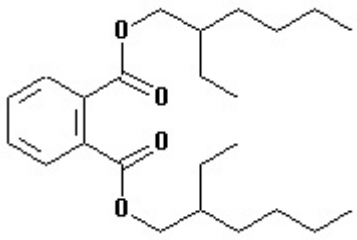
CAS no.: 84-74-2
synonyms: phthalic acid, dibutyl ester; di-*n*-butyl phthalate; butyl phthalate; *o*-benzenedicarboxylic acid, dibutyl ester; dibutyl 1,2-benzenedicarboxylate; dibutyl phthalate ester; benzene-*o*-dicarboxylic acid, di-*n*-butyl ester; DBP; Celluflex DBP; Elanol; Polycizer DBP; PX 104; Staflex DBP; bis-*n*-butyl phthalate; *n*-butyl phthalate; dibutyl *o*-phthalate
structural formula:



molecular wt: 278.35
boiling point: 340°C
melting point: −35°C
appearance: colorless to faint yellow oily liquid
odor: weak aromatic odor
specific gravity: 1.047
vapor pressure: less than 1.3 Pa (0.01 mmHg) at 20°C
flash point: 157°C (closed-cup); 171°C (open cup)
solubility: soluble in acetone, alcohol, ether, benzene, and other common organic solvents

Di-(2-ethylhexyl) phthalate

CAS no.: 117-81-7
synonyms: bis-(2-ethylhexyl) phthalate; 1,2-benzenedicarboxylic acid, bis-(2-ethylhexyl) ester; DEHP; octyl phthalate; ethylhexyl phthalate; Bisoflex 81; phthalic acid, dioctyl ester; phthalic acid, bis-(2-ethylhexyl) ester; diethylhexyl phthalate; dioctyl phthalate; di-(ethylhexyl) phthalate; 2-ethylhexyl phthalate; Fleximel; Flexol DOP; Kodaflex DOP; Octoil; RCRA U028
structural formula:

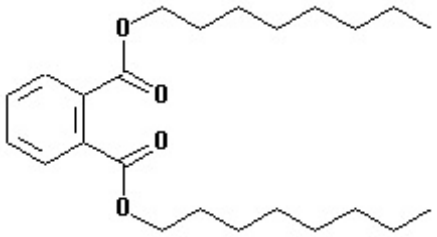


molecular wt: 390.6

boiling point: 384°C
melting point: −55°C
appearance: colorless to pale yellow oily liquid
odor: almost odorless
specific gravity: 0.981
vapor pressure: 0.18 kPa (1.32 mmHg) at 200°C
flash point: 215°C (open cup)
solubility: soluble in hexane, mineral oil

Di-*n*-octyl phthalate

CAS no.: 117-84-0
synonyms: phthalic acid, dioctyl ester; *o*-benzenedicarboxylic acid, dioctyl ester; 1,2-benzenedicarboxylic acid, dioctyl ester; DNOP; Dinopol NOP; di-*n*-octyl phthalate; dioctyl *o*-phthalate; octyl phthalate; *n*-octyl phthalate; Vinicizer 85; RCRA U107
structural formula:



molecular wt: 390.6
boiling point: 220°C at 0.67 kPa (5 mmHg)
melting point: −30°C
appearance: light-colored liquid
odor: odorless
specific gravity: 0.9861
vapor pressure: less than 27 Pa (0.2 mmHg) at 150°C
flash point: 209°C (closed-cup)
solubility: soluble in mineral oil, dimethyl sulfoxide, ethanol, benzene

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The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters.

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limits of the analytical procedure are 0.16, 0.13, 0.10, 0.09, and 0.10 ng for DMP, DEP, DBP, DEHP, and DNOP, respectively. These are the amounts of analytes that will give responses that are significantly different from the background responses of reagent blanks. (Sections 4.1 and 4.2)

1.2.2 Detection limit of the overall procedure

The detection limits of the overall procedure are 6.5, 4.8, 2.4, 3.9, and 3.3 µg per sample (27, 20, 10, 16, and 14 µg/m^3) for DMP, DEP, DBP, DEHP, and DNOP, respectively. These are the amounts of analyte spiked on the sampler that will give responses that are significantly different from the background responses of sampler blanks. (Sections 4.1 and 4.3)

1.2.3 Reliable quantitation limit

The reliable quantitation limits are 21.7, 16.2, 8.1, 13.1, and 10.9 µg per sample (90, 68, 34, 55, and 45 µg/m^3) for DMP, DEP, DBP, DEHP, and DNOP, respectively. These are the amounts of analyte spiked on a sampler that will give signals that are considered the lower limits for precise quantitative measurements. (Section 4.4)

1.2.4 Precision (analytical procedure)

The precisions of the analytical procedure, measured as the pooled relative standard deviations over a concentration range equivalent to 0.5 to 2 times the target concentration, are 0.35%, 0.54%, 0.45%, 1.15%, and 1.57% for DMP, DEP, DBP, DEHP, and DNOP, respectively. (Section 4.5)

1.2.5 Precision (overall procedure)

The precisions of the overall procedure at the 95% confidence level for the ambient temperature 15-day storage tests (at the target concentration) are ±13.4%, ±13.0%, ±10.9%, ±10.6%, and ±10.8% for DMP, DEP, DBP, DEHP, and DNOP, respectively (Section 4.6). These include additional 5% for sampling error.

1.2.6 Recovery

The recovery of phthalates from samples used in 15-day storage tests remained above 99.6%, 93.1%, 99.1%, 99.8%, and 99.6% for DMP, DEP, DBP, DEHP, and DNOP, respectively, when the samples were stored at ambient temperature. (Section 4.7)

1.2.7 Reproducibility

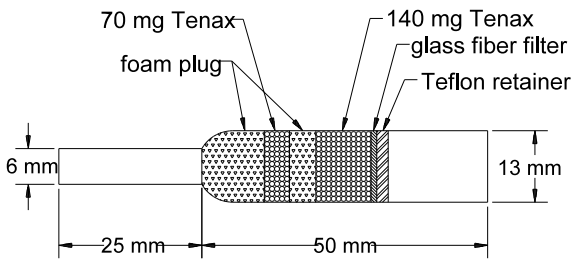
Twelve samples collected from controlled test atmospheres of mixed phthalates, and a draft copy of this procedure, were submitted to an SLTC organic service branch for analysis. The samples were analyzed after 13 days of storage at ambient temperature. No individual sample result deviated from its theoretical value by more than the precisions reported in Section 1.2.5. (Section 4.8)

2. Sampling Procedure

2.1 Apparatus

2.1.1 A personal sampling pump, calibrated to ±5% of the recommended flow rate with the sampling device attached.

2.1.2 OVS-Tenax sampling tube. The sampling tubes used in this study were obtained from SKC (catalog number 226-56 (OVS)). The tube contains a glass fiber filter and two sections of Tenax adsorbent separated by a foam plug.



2.2 Reagents

None required.

2.3 Technique

2.3.1 Attach the sampler to the sampling pump with a piece of flexible tubing and place it in the worker's breathing zone. Air should enter the larger end of the tube.

2.3.2 Air should not pass through any hose or tubing before entering the sampling tube.

2.3.3 After sampling replace the plastic caps. Wrap each sample with a Form OSHA-21 seal.

2.3.4 Record air volume for each sample.

2.3.5 Submit at least one blank with each set of samples. Blanks should be handled in the same manner as samples, except no air is drawn through them.

2.3.6 List any compounds that could be considered potential interferences.

2.4 Sampler capacity

Sampling capacity is determined by measuring how much air can be sampled before breakthrough occurs. Breakthrough is considered to occur when the effluent from the sampler contains a concentration of analyte that is 5% of the upstream concentration (5% breakthrough). The sampler capacity for DMP was determined to be over 305 L at a sampling rate of 1.0 L/min with DMP concentration of 10 mg/m^3 (2 times the target concentration). The sampler capacities for the other four phthalates exceeded 300 L. (Section 4.9)

2.5 Desorption efficiency

2.5.1 The average desorption efficiencies for phthalates from the OVS-Tenax, over the range of 0.5 to 2.0 times the target concentration, were 98.4%, 99.3%, 99.8%, 99.5%, and 98.6% for DMP, DEP, DBP, DEHP, and DNOP, respectively. (Section 4.10.1)

2.5.2 The desorption efficiencies at 0.05, 0.1, and 0.2 times the target concentration (TC) are listed below. (Section 4.10.1)

Table 2.5.2
Desorption efficiencies (%) at 0.05, 0.1, and 0.2 times the target concentration

	DMP	DEP	DBP	DEHP	DNOP
0.05× TC	91.3	99.9	101.4	98.3	99.4
0.1 × TC	91.4	98.8	97.6	95.5	92.2
0.2 × TC	95.1	100.2	100.1	99.8	94.9

2.5.3 Desorbed samples remain stable for at least 24 h. (Section 4.10.2)

2.6 Recommended air volume and sampling rate

2.6.1 For TWA samples, the recommended air volume is 240 L at 1.0 L/min.

2.6.2 For STEL samples, the recommended air volume is 15 L at 1.0 L/min.

2.6.3 With short-term samples, the air concentration equivalents to the reliable quantitation limits necessarily become larger. For example, the reliable quantitation limit is 0.87 mg/m^3 for DEHP when 15 L is collected.

2.7 Interferences (sampling)

2.7.1 Generally the presence of other organic contaminants in the air will reduce the capacity of the sampler to collect these phthalates.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions (sampling)

2.8.1 The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2 All safety practices that apply to the work area being sampled should be followed.

3. Analytical Procedure

3.1 Apparatus

3.1.1 A GC equipped with an FID. A Hewlett-Packard 5890 GC equipped with an FID and a 7673 autosampler were used in this evaluation.

3.1.2 A GC column capable of separating DMP, DEP, DBP, DEHP, DNOP, the internal standard, and any interferences. A 5-m HP-1 (0.53-mm i.d., 2.65-µm film) column was used in this evaluation.

3.1.3 An electronic integrator or other suitable means of measuring detector response. A Waters 860 Networking Computer System was used in this evaluation.

3.1.4 Glass vials, 4.5-mL, with poly(tetrafluoroethylene)-lined caps for desorbing samples. WISP vials were used in this study.

3.1.5 A dispenser capable of delivering 4.0 mL of desorbing solvent.

3.2 Reagents

3.2.1 Dimethyl phthalate. Dimethyl phthalate, 99%, was obtained from Aldrich.

3.2.2 Diethyl phthalate. Diethyl phthalate, 99%, was obtained from Kodak.

3.2.3 Dibutyl phthalate. Di-*n*-butyl phthalate, 99%, was obtained from Kodak.

3.2.4 Di-2-ethylhexyl phthalate. Di-2-ethylhexyl phthalate, 98%, was obtained from Aldrich.

3.2.5 Di-*n*-octyl phthalate. Di-*n*-octyl phthalate, EP grade, was obtained from Tokyo Kasei.

3.2.6 Toluene. Toluene, Optima grade, was obtained from Fisher.

3.2.7 1-Phenyldodecane. 1-Phenyldodecane, 99%, was obtained from Aldrich.

3.2.8 Desorbing solvent with internal standard. Dissolve 0.36 mL of 1-phenyldodecane in 1 L of toluene.

3.3 Standard preparation

3.3.1 Prepare stock standards by diluting weighed amounts of phthalate in desorbing solvent.

3.3.2 Prepare analytical standards by diluting the stock standards with desorbing solvent. For each phthalate, a 300 µg/mL standard solution corresponds to the target concentration.

3.3.3 Prepare a sufficient number of analytical standards to generate a calibration curve. Analytical standard concentrations must bracket sample concentrations.

3.4 Sample preparation

3.4.1 Transfer the glass fiber filter, Tenax resin of the front section, **and the middle foam plug** to a WISP vial.

3.4.2 Transfer the Tenax resin of the back section and the back foam to another WISP vial.

3.4.3 Add 4.0 mL of the desorbing solvent to each vial.

3.4.4 Cap the vials and shake them on a mechanical shaker for 30 min.

3.5 Analysis

3.5.1 GC conditions

column:	HP-1 (5 m, 0.53-mm i.d., 2.65-µm film)	
zone temp:	column	1 min at 75°C, ramp to 270°C at 15°C/min, 1 min at 270°C
	injector	270°C
	detector	275°C
gas flow:	column (He)	5.53 mL/min
	auxiliary (N_2)	30 mL/min
	hydrogen	32 mL/min
	air	395 mL/min
	split vent	53 mL/min (split ratio 10:1)
injection volume:	1 µL	
retention times:	DMP	6.0 min
	DEP	7.1 min
	1-phenyldodecane	9.3 min (ISTD)
	DBP	9.6 min
	DEHP	12.9 min
	DNOP	13.8 min

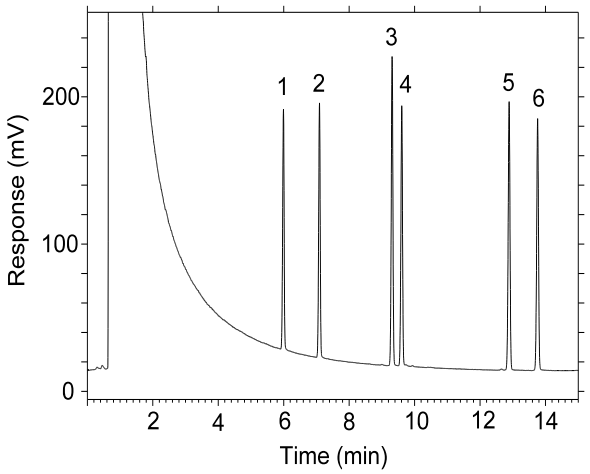


Figure 3.5.1. Chromatogram at target concentration.
Key: 1 = DMP, 2 = DEP, 3 = 1-phenyldodecane (ISTD), 4 = DBP, 5 = DEHP, 6 = DNOP.

3.5.2 Measure peak areas by an electronic integrator or other suitable means.

3.5.3 Use an internal standard (ISTD) calibration method. Prepare a calibration curve by plotting micrograms per sample versus ISTD-corrected response of standards. Bracket the samples with analytical standards.

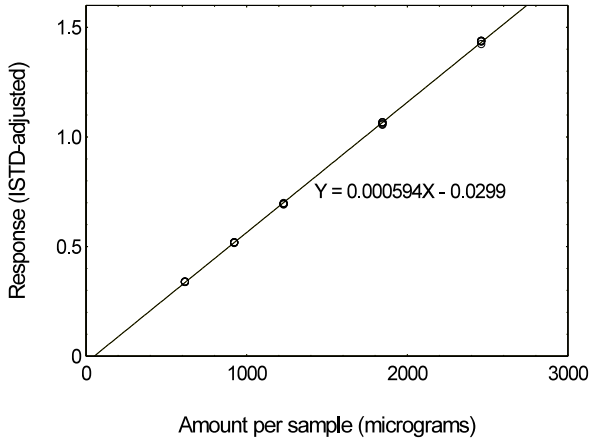


Figure 3.5.3.1 Calibration curve of DMP.

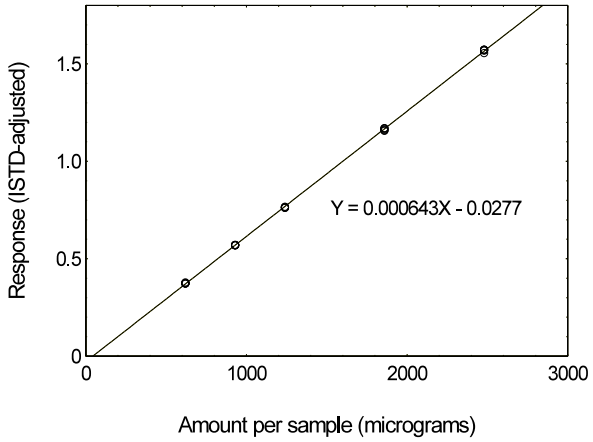


Figure 3.5.3.2. Calibration curve of DEP.

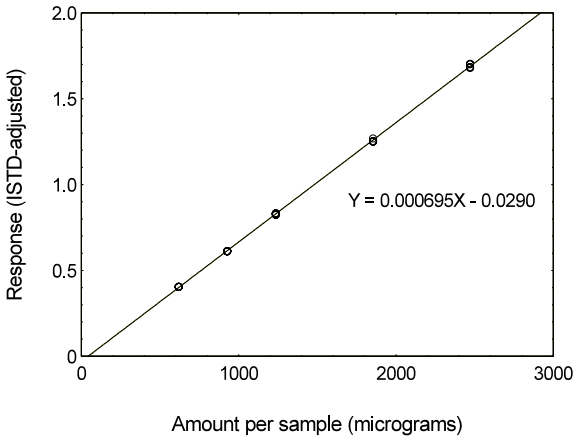


Figure 3.5.3.3. Calibration curve of DBP.

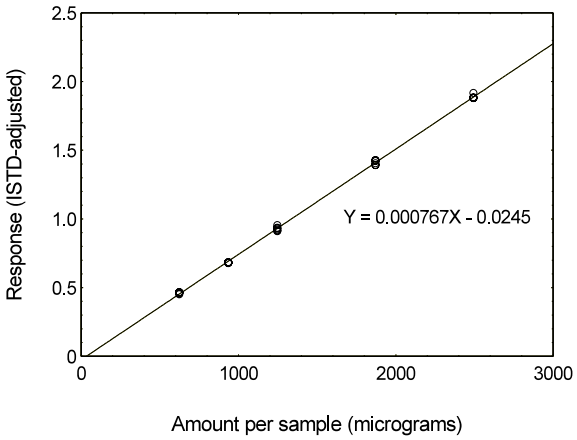


Figure 3.5.3.4. Calibration curve of DEHP.

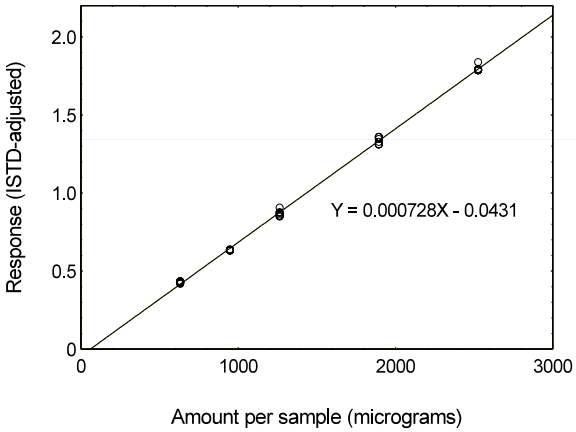


Figure 3.5.3.5. Calibration curve of DNOP.

3.6 Interferences (analytical)

3.6.1 Any compound that produces an FID response and has a similar retention time as any of the analytes or internal standard is a potential interference. If any potential interferences were reported, they should be considered before samples are desorbed. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed with additional analytical data (Section 4.11).

3.7 Calculations

The amount (in micrograms) of a phthalate per sample is obtained from the appropriate calibration curve. The back section is analyzed primarily to determine the extent of breakthrough. If any analyte is found on the back section, it is added to the amount found on the front section. This total amount is then corrected by subtracting the total amount (if any) found in the blank. The air concentration is calculated using the following formula.

$$\text{mg/m}^3 = \frac{\text{micrograms of phthalate per sample}}{\text{liters of air sampled} \times \text{desorption efficiency}}$$

3.8 Safety precautions (analytical)

3.8.1 Adhere to the rules set down in your Chemical Hygiene Plan.

3.8.2 Avoid skin contact and inhalation of all chemicals.

3.8.3 Wear safety glasses and a lab coat at all times while in the lab area.

4. Backup Data

4.1 Determination of detection limits

Detection limits (DL), in general, are defined as the amount (or concentration) of analyte that gives a response (Y_{DL}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DL} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvenient and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of analytical standards or samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for DL:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total no. of data points
k = 2 for a linear regression curve

At point Y_{DL} on the regression curve

$$Y_{DL} = A(DL) + Y_{BR}$$

A = analytical sensitivity (slope)

therefore

$$DL = \frac{(Y_{DL} - Y_{BR})}{A}$$

Substituting 3(SEE) + Y_{BR} for Y_{DL} gives

$$DL = \frac{3(SEE)}{A}$$

4.2 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as the mass of analyte actually introduced into the chromatographic column. Ten analytical standards whose concentrations were equally spaced from 0 to 12.5 µg/mL were prepared. The standard containing 12.5 µg/mL represented approximately 10 times the baseline noise for all analytes. These solutions were analyzed with the recommended analytical parameters (1 µL injection with 10:1 split). The data obtained were used to determine the required parameters (A and SEE) for the calculation of the DLAP. These parameters and the calculated DLAP's for the five phthalates are listed below.

Table 4.2.2
Detection Limit of the Analytical Procedure for DMP

concentration (µg/mL)	mass on column (ng)	ISTD-adjusted response
0.00	0.000	0.000000
1.23	0.123	0.000000
2.46	0.246	0.006172
3.69	0.369	0.007495
4.92	0.492	0.009049
6.15	0.615	0.011572
7.38	0.738	0.013412
8.61	0.861	0.018499
9.84	0.984	0.019438
11.07	1.107	0.022577
12.30	1.230	0.025851

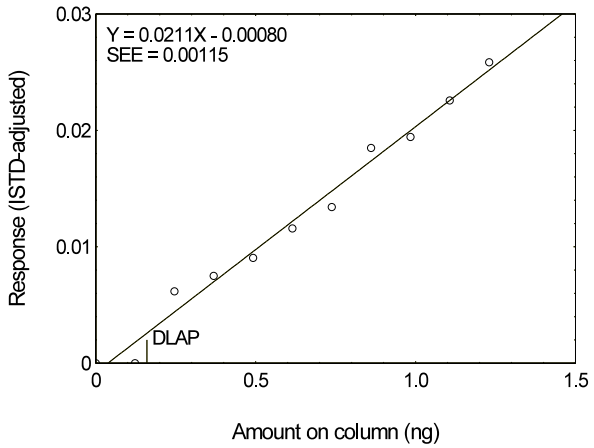


Figure 4.2.2. Plot of the data for determining the DLAP of DMP.

Table 4.2.3
Detection Limit of the Analytical Procedure for DEP

concentration (µg/mL)	mass on column (ng)	ISTD-adjusted response
0.00	0.000	0.000000
1.24	0.124	0.003659
2.48	0.248	0.008365
3.72	0.372	0.011870
4.96	0.496	0.014416
6.20	0.620	0.015966
7.44	0.744	0.020705
8.68	0.868	0.023028
9.92	0.992	0.025402
11.16	1.116	0.031727
12.40	1.240	0.032579

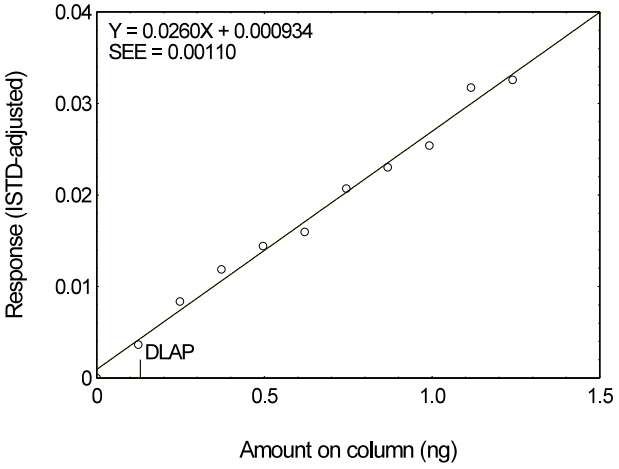


Figure 4.2.3. Plot of the data used for determining the DLAP of DEP.

Table 4.2.4
Detection Limit of the Analytical Procedure for DBP

concentration (µg/mL)	mass on column (ng)	ISTD-adjusted response
0.00	0.000	0.000000
1.24	0.124	0.003495
2.47	0.247	0.006206
3.71	0.371	0.009197
4.94	0.494	0.012034
6.18	0.618	0.014716
7.41	0.741	0.020491
8.65	0.865	0.021137
9.88	0.988	0.023602
11.12	1.112	0.027755
12.36	1.236	0.030736

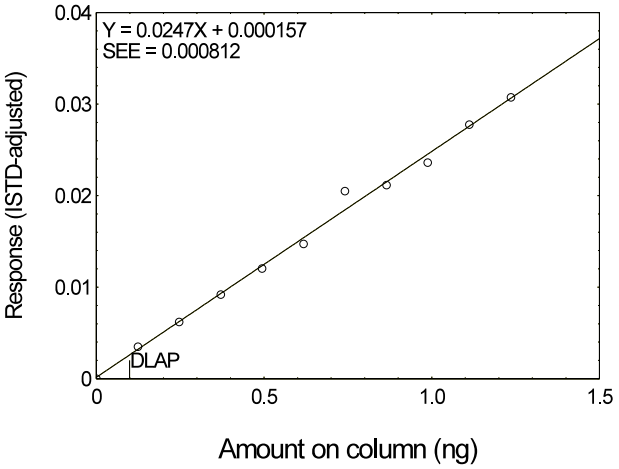


Figure 4.2.4. Plot of the data used for determining the DLAP of DBP.

Table 4.2.5
Detection Limit of the Analytical Procedure for DEHP

concentration (µg/mL)	mass on column (ng)	ISTD-adjusted response
0.00	0.000	0.009830
1.25	0.125	0.012161
2.49	0.249	0.015005
3.74	0.374	0.016568
4.99	0.499	0.020997
6.23	0.623	0.022298
7.48	0.748	0.025840
8.73	0.873	0.029510
9.97	0.997	0.031756
11.22	1.122	0.035372
12.47	1.247	0.038701

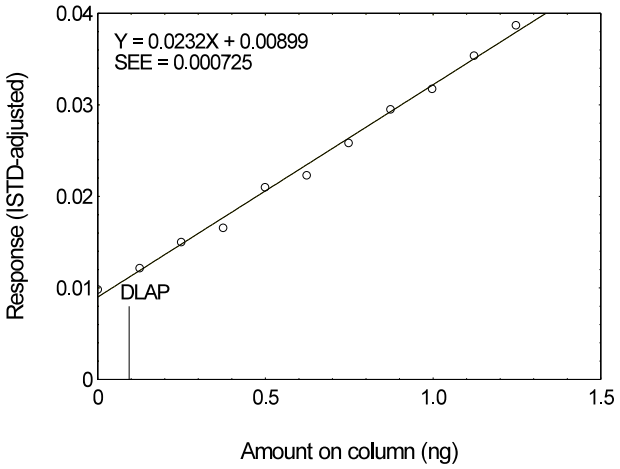


Figure 4.2.5. Plot of the data used for determining the DLAP of DEHP.

Table 4.2.6
Detection Limit of the Analytical Procedure for DNOP

concentration (µg/mL)	mass on column (ng)	ISTD-adjusted response
0.00	0.000	0.016174
1.26	0.126	0.017594
2.53	0.253	0.020140
3.79	0.379	0.022811
5.05	0.505	0.024236
6.31	0.631	0.028774
7.58	0.758	0.030987
8.84	0.884	0.033952
10.10	1.010	0.035165
11.36	1.136	0.038195
12.63	1.263	0.040625

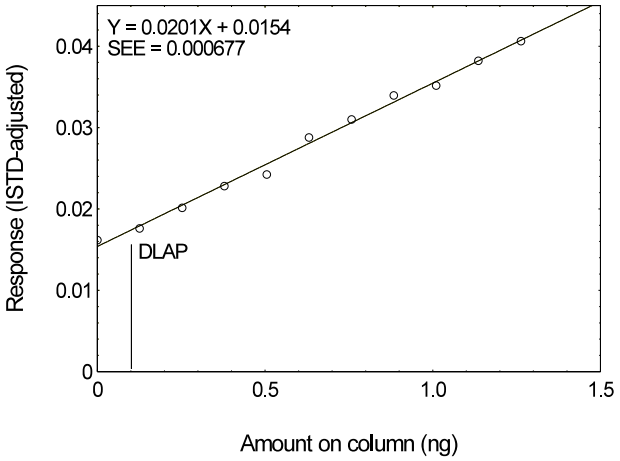


Figure 4.2.6. Plot of the data used for determining the DLAP of DNOP.

4.3 Detection limit of the overall procedure (DLOP)

The DLOP is measured as mass per sample and expressed as equivalent air concentration, based on the recommended sampling parameters. Ten OVS-Tenax samplers were spiked with amounts of phthalates equally spaced from 0 to 50 µg/sample. The latter amount, when spiked on a sampler, would produce a peak approximately 10 times the baseline noise for a sample blank. These spiked samples were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (A and SEE) for the calculation of the DLOP. The parameters obtained and the calculated DLOP's for the five phthalates are listed below.

Figure 4.3.1
Summary of the calculated A, SEE, and DLOP

	DMP	DEP	DBP	DEHP	DNOP
A (μg^{-1})	0.000498	0.000631	0.000616	0.000605	0.000491
SEE	0.00108	0.00102	0.000499	0.000790	0.000536
DLOP (µg)	6.5	4.8	2.4	3.9	3.3

Table 4.3.2
Detection Limit of the Overall Procedure for DMP

mass per sample (µg)	ISTD-adjusted response
0.00	0.000000
4.92	0.003303
9.84	0.006687
14.76	0.005820
19.68	0.009595
24.60	0.011740
29.52	0.014777
34.44	0.015651
39.36	0.019574
44.28	0.023076
49.20	0.025336

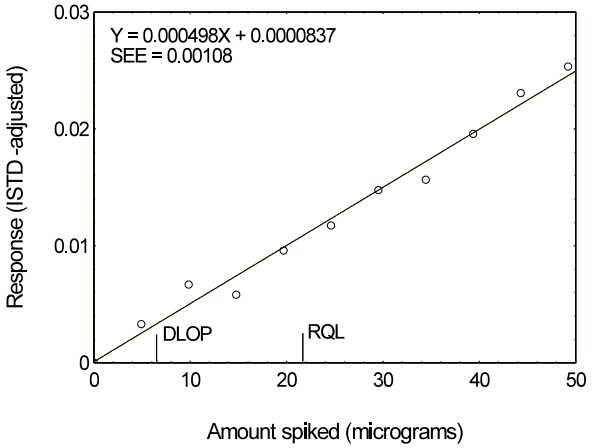


Figure 4.3.2. Plot of data used to determine the DLOP and RQL of DMP.

Table 4.3.3
Detection Limit of the Overall Procedure for DEP

mass per sample (µg)	ISTD-adjusted response
0.00	0.000000
4.96	0.005735
9.92	0.009298
14.87	0.010539
19.83	0.013962
24.79	0.017733
29.75	0.018743
34.71	0.023453
39.66	0.026416
44.62	0.030439
49.58	0.032467

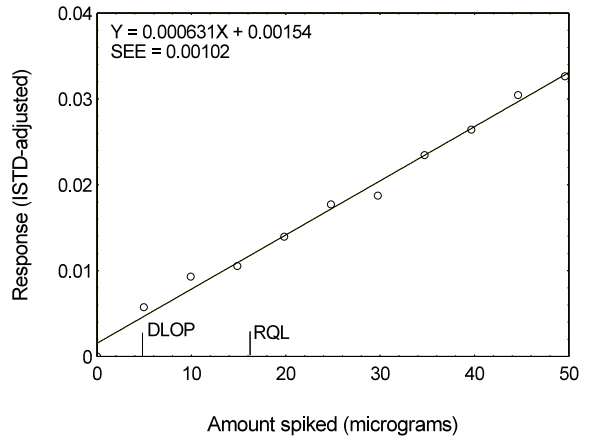


Figure 4.3.3. Plot of data used to determine the DLOP and RQL of DEP.

Table 4.3.4
Detection Limit of the Overall Procedure for DBP

mass per sample (µg)	ISTD-adjusted response
0.00	0.000000
4.94	0.003247
9.88	0.006310
14.83	0.009043
19.77	0.012165
24.71	0.014531
29.65	0.017447
34.59	0.020963
39.54	0.023689
44.48	0.027926
49.42	0.030969

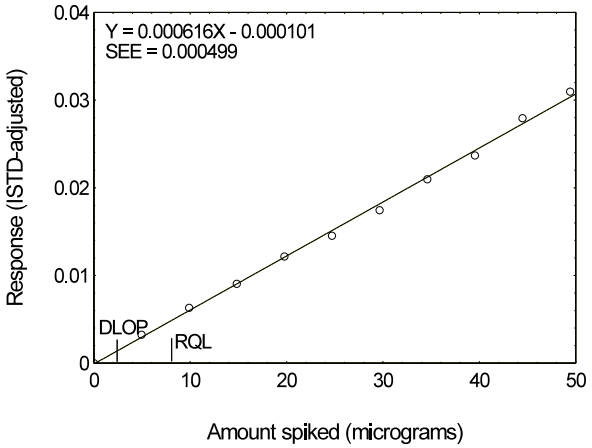


Figure 4.3.4. Plot of data used to determine the DLOP and RQL of DBP.

Table 4.3.5
Detection Limit of the Overall Procedure for DEHP

mass per sample (µg)	ISTD-adjusted response
0.00	0.008518
4.99	0.010614
9.97	0.014936
14.96	0.017956
19.94	0.020824
24.93	0.022502
29.92	0.024855
34.90	0.030300
39.89	0.032849
44.87	0.035537
49.86	0.038496

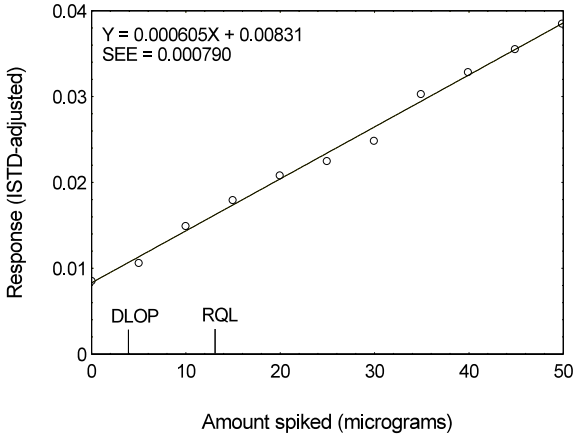


Figure 4.3.5. Plot of data used to determine the DLOP and RQL of DEHP.

Table 4.3.6
Detection Limit of the Overall Procedure for DNOP

mass per sample (µg)	ISTD-adjusted response
0.00	0.015581
5.05	0.018904
10.10	0.020513
15.15	0.023587
20.20	0.025651
25.25	0.027891
30.30	0.030478
35.35	0.034282
40.40	0.035045
45.45	0.037866
50.50	0.041035

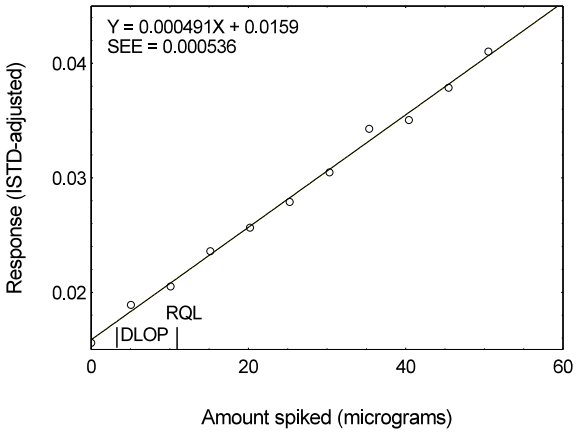


Figure 4.3.6. Plot of data used to determine the DLOP and RQL of DNOP.

4.4 Reliable quantitation limit

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line data obtained for the calculation of the DLOP (Section 4.3), providing at least 75% of the analyte is recovered. The RQL is defined as the amount of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

$$RQL = \frac{10(SEE)}{A}$$

The calculated RQL's for the five phthalates, together with the recoveries at these levels, are listed below. The recoveries are above 75%.

Table 4.4.1
Summary of the RQL's and the recoveries

	DMP	DEP	DBP	DEHP	DNOP
RQL (µg/sample)	21.7	16.2	8.1	13.1	10.9
RQL (µg/m^3)	90	68	34	55	45
Recovery (%)	100.1	99.4	100.9	103.3	100.7

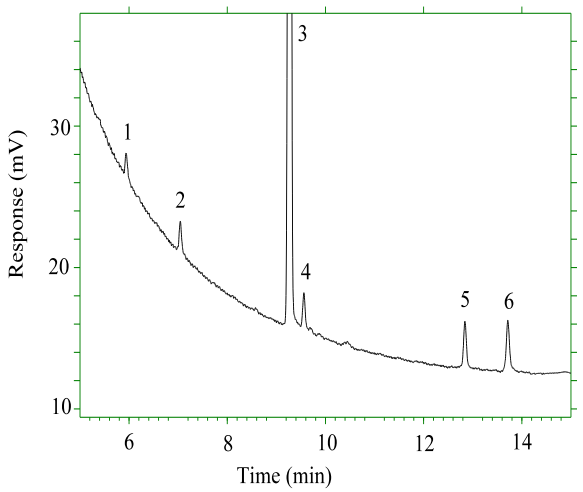


Figure 4.4.1. Chromatogram of the RQL for DMP. Key: 1 = DMP, 3 = ISTD.

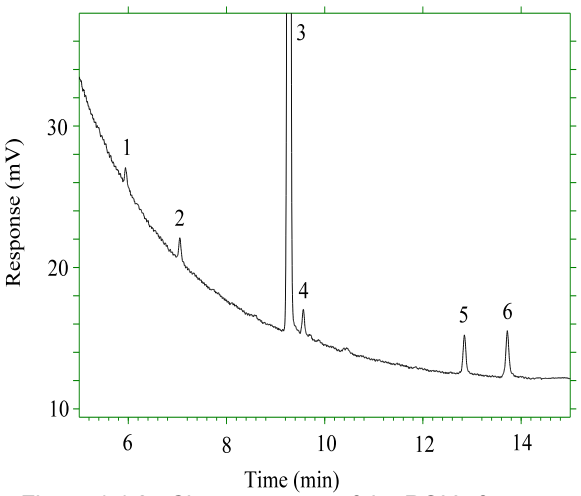


Figure 4.4.2. Chromatogram of the RQL's for DEP and DEHP. Key: 2 = DEP, 3 = ISTD, 5 = DEHP.

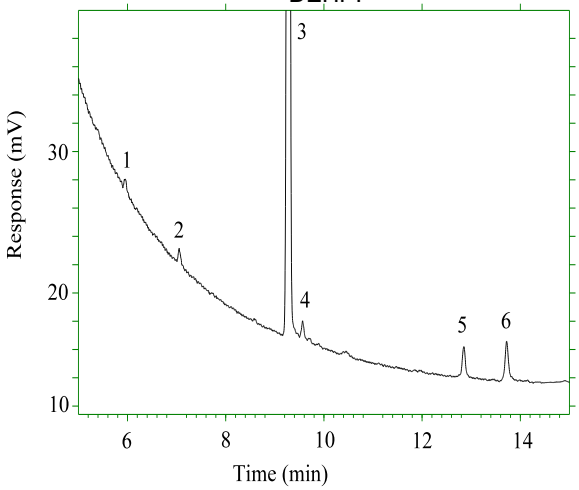


Figure 4.4.3. Chromatogram of the RQL's for DBP and DNOP. Key: 3 = ISTD, 4 = DBP, 6 = DNOP.

4.5 Precision (analytical method)

The precision of the analytical procedure is defined as the pooled relative standard deviation (RSD_p). Relative standard deviations were determined from six replicate injections of analytical standards at 0.5, 0.75, 1, 1.5, and 2 times the target concentration. After assuring that the RSDs satisfy the Cochran test for homogeneity at the 95% confidence level, RSD_p was calculated.

Table 4.5.1
Instrument Response to DMP

× target concn	0.5×	0.75×	1×	1.5×	2×
µg/mL	153.75	230.63	307.50	461.25	615.00
ISTD-adjusted	0.339180	0.518724	0.694646	1.06782	1.43746
response	0.339222	0.518855	0.695280	1.05593	1.42405
	0.341304	0.516464	0.697158	1.06663	1.43872
	0.339692	0.519998	0.694935	1.05802	1.43437
	0.340345	0.518792	0.699107	1.06191	1.43922
	0.338556	0.518545	0.692083	1.06777	1.43860
$\bar{x}$	0.339716	0.518563	0.695535	1.06301	1.43540
SD	0.000979	0.001151	0.002389	0.00520	0.00583
RSD (%)	0.29	0.22	0.34	0.49	0.41

Table 4.5.2
Instrument Response to DEP

× target concn	0.5×	0.75×	1×	1.5×	2×
µg/mL	154.94	232.41	309.88	464.81	619.75
ISTD-adjusted	0.374911	0.570068	0.763569	1.17061	1.57033
response	0.374138	0.569987	0.764417	1.15667	1.55567
	0.378598	0.569111	0.762847	1.16755	1.57204
	0.373550	0.568564	0.763365	1.15892	1.56837
	0.373774	0.570238	0.766802	1.16228	1.57259
	0.372888	0.571293	0.7610260	1.16811	1.57311
$\bar{x}$	0.374643	0.569877	0.763671	1.16402	1.56869
SD	0.002049	0.000948	0.001905	0.00558	0.00661
RSD (%)	0.55	0.17	0.25	0.48	0.42

Table 4.5.3
Instrument Response to DBP

× target concn	0.5×	0.75×	1×	1.5×	2×
µg/mL	154.44	231.66	308.88	463.31	617.75
ISTD-adjusted	0.405228	0.611808	0.825268	1.26829	1.68342
response	0.404333	0.611966	0.822788	1.25226	1.68432
	0.404576	0.612680	0.831174	1.25298	1.70201
	0.404915	0.611583	0.833438	1.25158	1.67908
	0.403932	0.612455	0.830629	1.25108	1.70102
	0.405790	0.611139	0.832469	1.24944	1.70313
$\bar{x}$	0.404796	0.611939	0.829294	1.25427	1.69216
SD	0.000663	0.000566	0.004269	0.00697	0.01100
RSD (%)	0.16	0.09	0.51	0.56	0.65

Table 4.5.4
Instrument Response to DEHP

× target concn	0.5×	0.75×	1×	1.5×	2×
µg/mL	155.81	233.72	311.63	467.44	623.25
ISTD-adjusted	0.464074	0.678952	0.955317	1.40557	1.88144
response	0.467006	0.682591	0.933266	1.42112	1.91779
	0.452057	0.686014	0.914818	1.39206	1.87967
	0.458669	0.682044	0.923775	1.42917	1.88589
	0.464892	0.683300	0.911533	1.42689	1.88077
	0.465609	0.682931	0.935958	1.39226	1.88146
$\bar{x}$	0.462051	0.682639	0.929111	1.41118	1.88784
SD	0.005669	0.002274	0.016079	0.01688	0.01483
RSD (%)	1.23	0.33	1.73	1.20	0.79

Table 4.5.5
Instrument Response to DNOP

× target concn	0.5×	0.75×	1×	1.5×	2×
µg/mL	157.81	236.72	315.63	473.44	631.25
ISTD-adjusted	0.428794	0.630011	0.906980	1.32827	1.78854
response	0.435110	0.633303	0.872334	1.34664	1.83870
	0.418855	0.639090	0.853098	1.31105	1.78651
	0.423316	0.635316	0.862667	1.35927	1.79472
	0.431818	0.634379	0.849245	1.35852	1.78838
	0.434664	0.635068	0.877654	1.31242	1.78544
$\bar{x}$	0.428760	0.634528	0.870330	1.33603	1.79705
SD	0.006516	0.002955	0.020982	0.02191	0.02066
RSD (%)	1.52	0.47	2.41	1.64	1.15

The Cochran test for homogeneity requires the calculation of the g statistics according to the following formula:

$$g = \frac{\text{largest RSD}^2}{RSD_{0.5\times}^2 + RSD_{0.75\times}^2 + RSD_{1\times}^2 + RSD_{1.5\times}^2 + RSD_{2\times}^2} = 0.3796$$

The *g* statistics obtained were: 0.3692, 0.3750, 0.4117, 0.4482, and 0.4696, for DMP, DEP, DBP, DEHP, and DNOP, respectively. Since these *g* statistics do not exceed the critical value of 0.5065, the RSDs within each phthalate can be considered equal and they can be pooled (RSD_P) to give an estimated RSD for the concentration range studied.

$$RSD_p = \sqrt{\frac{5(RSD_{0.5\times}^2+RSD_{0.75\times}^2+RSD_{1\times}^2+RSD_{1.5\times}^2+RSD_{2\times}^2)}{5+5+5+5+5}} = 0.53\%$$

The pooled relative standard deviations are: 0.36%, 0.40%, 0.45%, 1.15%, and 1.57%, for DMP, DEP, DBP, DEHP, and DNOP, respectively.

4.6 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data in Section 4.7. The determination of the standard error of estimate (SEE_R) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE_R is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

$$SEE_R = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

n = total no. of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed % recovery at a given time
Y_{est} = estimated % recovery from the regression line at the same given time

An additional 5% for pump error (SP) is added to the SEE_R by the addition of variances to obtain the total standard error of estimate.

$$SEE = \sqrt{(SEE_R)^2 + (SP)^2}$$

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs, as shown in Figures 4.7.1.1 to 4.7.5.2. The precisions of the overall

procedure are ±13.4%, ±13.0%, ±10.9%, ±10.6%, and ±10.8% for DMP, DEP, DBP, DEHP, and DNOP, respectively.

4.7 Storage test

Storage tests were conducted in three batches: DMP, DEP/DNOP, and DBP/DEHP. Storage samples were prepared from the controlled test atmospheres of the appropriate phthalate or phthalate mixtures. Thirty-six samples were collected. Six samples were analyzed on the day of preparation. The rest of the samples were divided into two groups: 15 were stored at 5°C, and the other 15 were stored at ambient temperature (about 22°C) in a closed drawer. At 1-4 day intervals, three samples were selected from each of the two storage sets and analyzed.

Table 4.7.1
Storage Test for DMP

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	104.5	98.3	106.1	104.5	98.3	106.1
0	99.5	100.0	91.6	99.5	100.0	91.6
1	97.6	97.4	105.2	98.1	104.3	104.6
5	98.0	105.2	104.5	96.9	95.4	104.1
8	97.7	95.7	106.2	88.5	104.5	107.0
12	98.6	102.4	104.1	97.9	89.7	97.2
15	108.5	101.3	113.0	97.9	112.4	110.5

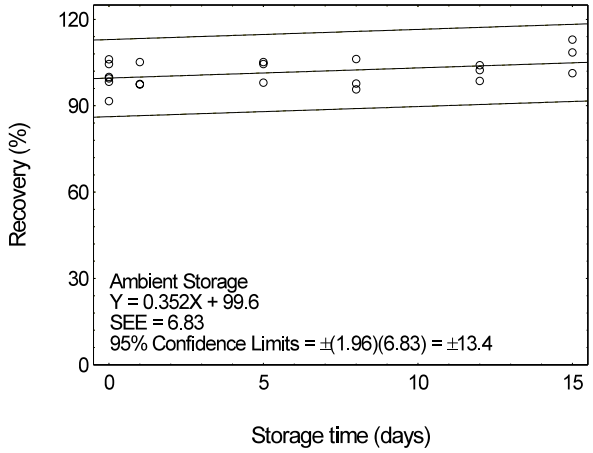


Figure 4.7.1.1. Ambient storage test for DMP.

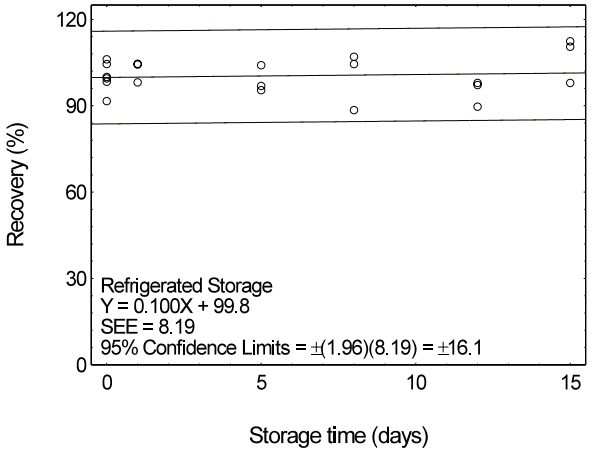


Figure 4.7.1.2. Refrigerated storage test for DMP.

Table 4.7.2
Storage Test for DEP

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	97.6	94.6	95.7	97.6	94.6	95.7
0	104.5	104.9	102.7	104.5	104.9	102.7
3	94.6	93.9	102.7	90.5	101.3	102.2
6	92.9	100.2	93.5	91.9	94.6	104.4
9	89.1	91.0	98.1	86.8	98.7	99.2
13	90.6	94.3	99.6	92.6	90.9	100.7
15	92.1	91.2	100.3	93.2	104.5	105.3

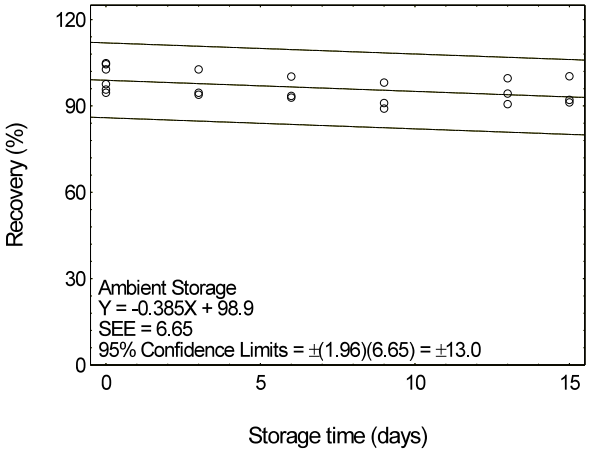


Figure 4.7.2.1. Ambient storage test for DEP.

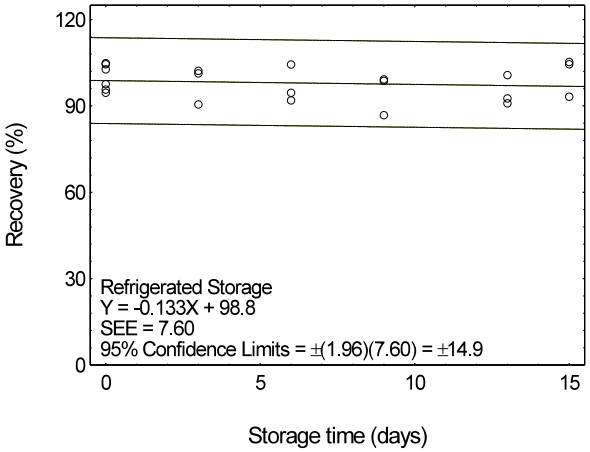


Figure 4.7.2.2. Refrigerated storage test for DEP.

Table 4.7.3
Storage Test for DBP

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	99.1	99.5	98.3	99.1	99.5	98.3
0	103.7	102.6	96.9	103.7	102.6	96.9
4	100.5	101.8	101.1	103.1	101.1	101.9
6	95.8	96.7	102.7	98.7	99.0	102.1
8	100.3	101.1	99.7	99.9	101.6	102.0
12	101.7	99.2	104.3	93.8	97.9	101.3
15	97.4	99.1	96.4	102.2	98.3	106.0

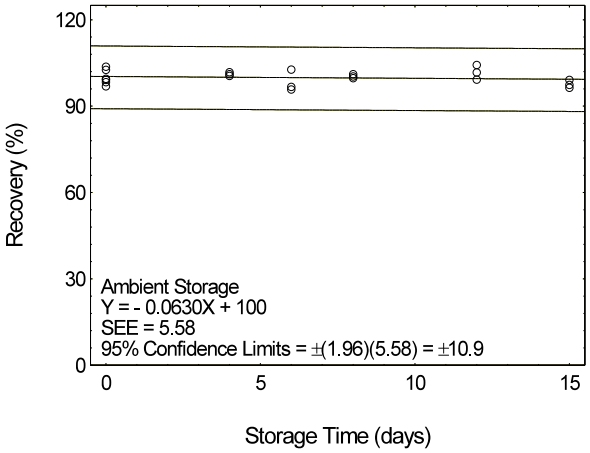


Figure 4.7.3.1. Ambient storage test for DBP.

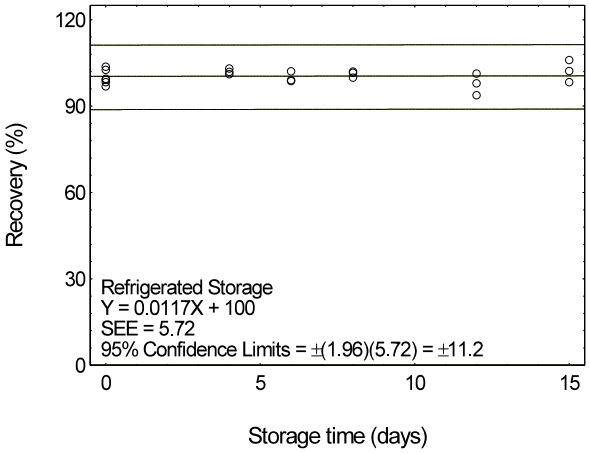


Figure 4.7.3.2. Refrigerated storage test for DBP.

Table 4.7.4
Storage Test for DEHP

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	99.5	99.8	98.7	99.5	99.8	98.7
0	102.2	102.0	97.8	102.2	102.0	197.8
4	100.6	102.9	102.8	104.8	99.8	102.0
6	95.7	97.4	101.0	97.8	98.3	102.0
8	100.0	101.5	98.6	99.8	100.5	101.5
12	98.1	101.9	104.2	105.9	100.8	102.4
15	101.6	101.4	104.5	96.5	98.1	94.5

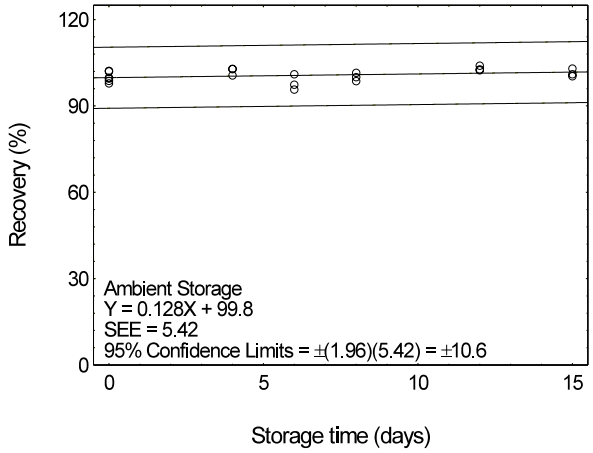


Figure 4.7.4.1. Ambient storage test for DEHP.

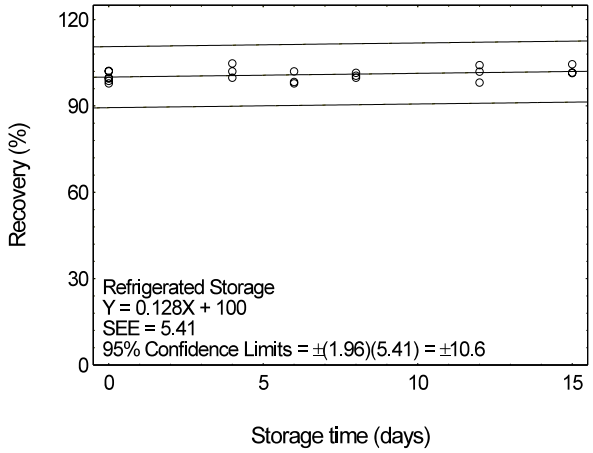


Figure 4.7.4.2. Refrigerated storage test for DEHP.

Table 4.7.5
Storage Test for DNOP

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	101.7	101.7	101.6	101.7	101.7	101.6
0	98.7	99.7	96.6	98.7	99.7	96.6
3	101.7	103.7	100.1	104.4	99.0	98.9
6	99.7	94.8	-	98.8	99.2	96.3
9	99.9	99.9	95.5	98.9	98.4	98.5
13	102.1	100.0	98.7	103.5	102.2	99.9
15	100.5	101.9	98.3	100.0	96.3	98.8

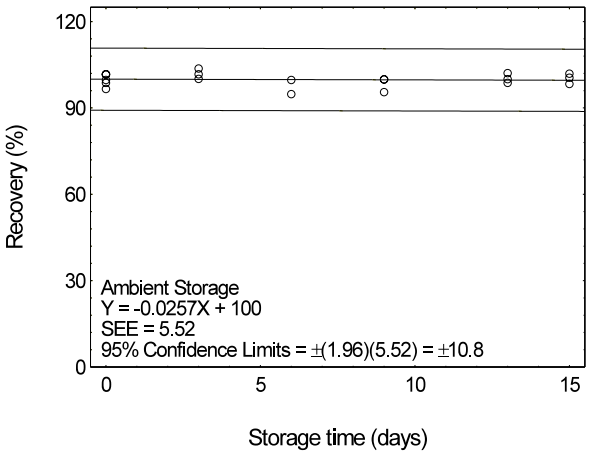


Figure 4.7.5.1. Ambient storage test for DNOP.

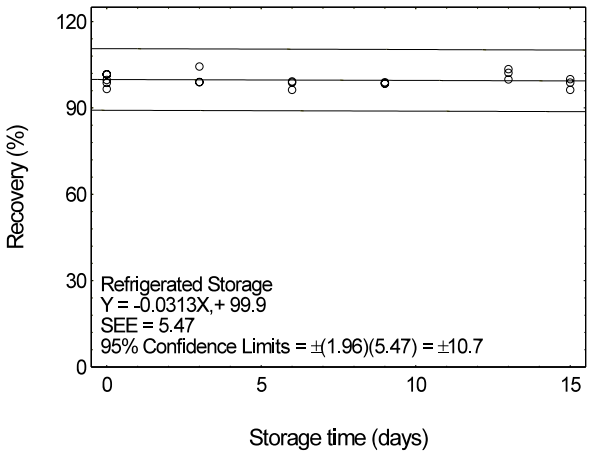


Figure 4.7.5.2. Refrigerated storage test for DNOP.

4.8 Reproducibility

Reproducibility samples were prepared from controlled test atmospheres of mixed phthalates. They were prepared in two batches: DMP/DEP and DBP/DEHP/DNOP. The samples were submitted to an SLTC service branch for analysis. The samples were analyzed after being stored for 13 days at ambient temperature. No sample result had a deviation greater than the precisions of the overall procedure determined in Section 4.7, which are ±13.4%, ±13.0%, ±10.9%, ±10.6%, and ±10.8% for DMP, DEP, DBP, DEHP, and DNOP, respectively.

Table 4.8.1
Reproducibility Data for DMP

µg expected	µg found	percent found	percent deviation
787	756	96.1	-3.9
788	775	98.4	-1.6
785	757	96.4	-3.6
780	774	99.2	-0.8
804	819	101.9	+1.9
782	770	98.5	-1.5

Table 4.8.2
Reproducibility Data for DEP

µg expected	µg found	percent found	percent deviation
695	655	94.2	-5.8
696	676	97.1	-2.9
693	650	93.8	-6.2
688	680	98.8	-1.2
710	713	100.4	+0.4
690	668	96.8	-3.2

Table 4.8.3
Reproducibility Data for DBP

µg expected	µg found	percent found	percent deviation
1323	1412	106.7	+6.7
1328	1425	107.3	+7.3
1329	1408	105.9	+5.9
1307	1380	105.6	+5.6
1375	1446	105.2	+5.2
1334	1412	105.8	+5.8

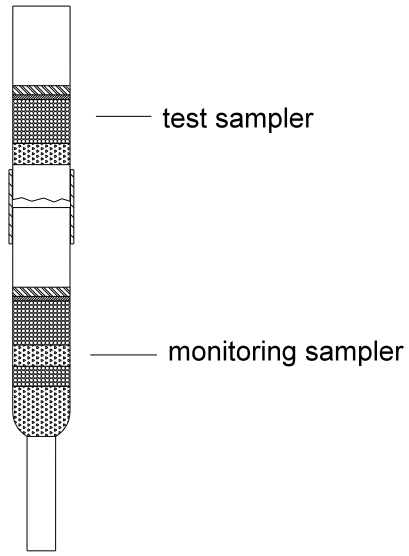
Table 4.8.4
Reproducibility Data for DEHP

µg expected	µg found	percent found	percent deviation
1367	1428	104.5	+4.5
1372	1436	104.7	+4.7
1373	1418	103.3	+3.3
1351	1392	103.0	+3.0
1421	1462	102.9	+2.9
1379	1422	103.1	+3.1

Table 4.8.5
Reproducibility Data for DNOP

µg expected	µg found	percent found	percent deviation
1374	1495	108.8	+8.8
1379	1448	105.0	+5.0
1381	1427	103.3	+3.3
1358	1396	102.8	+2.8
1429	1472	103.0	+3.0
1386	1395	100.6	+0.6

4.9 Sampler capacity



The sampler capacity was assessed by sampling from a dynamically generated test atmosphere of phthalate at 2 times the target concentration and at 25°C and 80% RH. The test atmosphere of phthalate was generated by pumping a 2-propanol solution of phthalate at a rate of approximately 6 mg/min (12 mg/mL × 0.5 mL/min) through a TSI Model 3076 atomizer where it was dispersed with an air stream of 3.5 L/min. The aerosol passed through an electrostatic charge neutralizer and was diluted with an air stream of 47 L/min. The diluted aerosol was fed to a test chamber fitted with 18 sampling ports. The test atmosphere was drawn through the test sampler and a monitoring sampler at 1.0 L/min. The test sampler was prepared by cutting off the lower half of the tube and removing the rear foam and the 70-mg section of the resins (see figure at right). At 60-min intervals, the flow was stopped and the monitoring samplers were replaced with new ones. This was repeated six times. At the end of the experiment, all the monitoring samplers as well as the test sampler were analyzed. The downstream air concentration was obtained by dividing the amount found on the back sampler by the air volume. The upstream concentration was obtained by dividing the sum of amounts found on the front as well as all the back sampler by the total air volume. The actual upstream concentrations obtained were 13.55, 14.23, 8.78, 15.38, 17.76 mg/m^3 for DMP, DEP, DBP, DEHP, and DNOP, respectively. The breakthrough is defined as the downstream concentration divided by the upstream concentration. The average breakthroughs for each sampling period versus the air volume[1] were plotted in Figures 4.9.1 and 4.9.2.

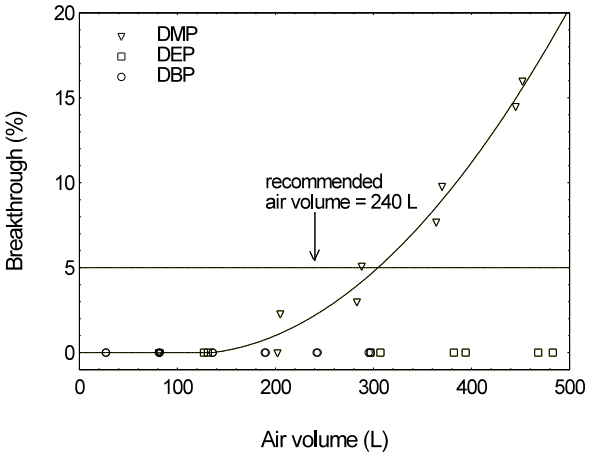


Figure 4.9.1. Breakthrough curves for DMP, DEP, and DBP.

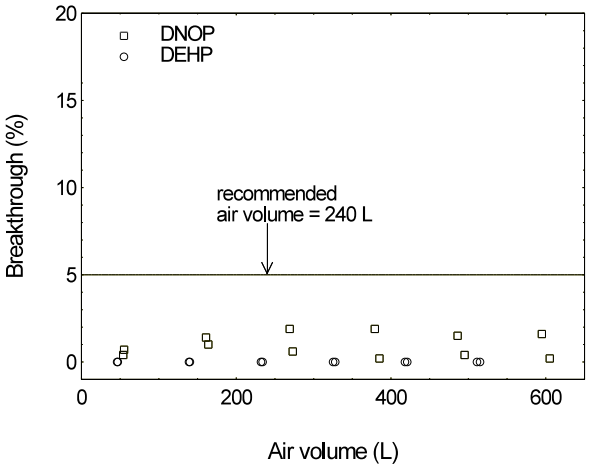


Figure 4.9.2. Breakthrough curves for DEHP and DNOP.

[1]The air volume for each sampling period was adjusted to 2 times the target concentrations. The air volume of the mid-point of the sampling period is multiplied by 10 mg/m^3 and divided by the actual upstream concentration (13.55 mg/m^3 for DMP, for example).

4.10 Desorption efficiency and stability of desorbed samples

4.10.1 Desorption efficiency

The desorption efficiencies (DE) of phthalates were determined by liquid-spiking the front section of the OVS-Tenax with phthalates at 0.05 to 2 times the target concentrations. These samples were stored overnight at ambient temperature and then extracted and analyzed. The average extraction efficiencies over the working range of 0.5 to 2 times the target concentration were 98.4%, 99.3%, 99.8%, 99.5%, and 98.6%, respectively, for DMP, DEP, DBP, DEHP, and DNOP.

Table 4.10.1.1
Desorption Efficiency for DMP

× target conc (µg)	0.05× 61.5	0.1× 123.0	0.2× 246.0	0.5× 615	1.0× 1230	2.0× 2460
DE (%)	90.1	90.8	94.3	97.4	98.0	98.5
	90.3	91.4	94.1	98.9	99.5	98.5
	97.7	91.5	94.0	100.1	98.6	98.6
	89.2	95.1	98.8	96.5	98.6	99.0
	89.9	89.7	94.5	97.6	98.5	98.4
	90.5	89.9	95.1	97.9	97.9	98.9
$\bar{x}$	91.3	91.4	95.1	98.1	98.5	98.6

Table 4.10.1.2
Desorption Efficiency for DEP

× target conc (µg)	0.05× 62.0	0.1× 93.0	0.2× 247.9	0.5× 619.8	1.0× 1239.5	2.0× 2479
DE (%)	100.0	98.2	102.7	101.1	98.5	98.6
	101.8	98.2	98.8	99.5	100.1	98.6
	96.2	98.2	98.1	101.9	99.0	98.4
	97.5	100.9	99.8	98.1	98.5	99.0
	103.2	101.5	101.9	99.8	99.4	98.1
	100.9	96.0	99.9	101.2	98.3	98.7
$\bar{x}$	99.9	98.8	100.2	100.3	99.0	98.6

Table 4.10.1.3
Desorption Efficiency for DBP

× target conc (µg)	0.05× 61.8	0.1× 123.6	0.2× 247.1	0.5× 617.8	1.0× 1235.5	2.0× 2471
DE (%)	115.8	97.8	98.9	101.7	98.8	99.1
	98.1	97.4	101.9	100.0	99.5	99.2
	98.1	96.1	98.2	102.5	99.2	99.0
	104.9	96.1	101.4	100.7	98.9	99.7
	97.5	101.8	102.1	100.3	99.3	99.0
	93.9	96.3	98.1	101.2	99.2	99.4
$\bar{x}$	101.4	97.6	100.1	101.1	99.2	99.2

Table 4.10.1.4
Desorption Efficiency for DEHP

× target conc (µg)	0.05× 62.3	0.1× 124.7	0.2× 249.3	0.5× 623.3	1.0× 1246.5	2.0× 2493
DE (%)	108.5	95.2	100.4	98.7	98.8	100.5
	95.7	96.0	101.0	99.4	98.7	100.4
	95.4	95.3	100.3	101.7	98.9	99.8
	95.9	94.7	99.3	97.9	100.4	99.5
	97.6	94.9	98.9	97.4	100.5	99.7
	96.6	96.9	98.8	98.3	99.5	100.5
$\bar{x}$	98.3	95.5	99.8	98.9	99.5	100.1

Table 4.10.1.5
Desorption Efficiency for DNOP

× target conc (µg)	0.05× 63.1	0.1× 126.3	0.2× 252.5	0.5× 631.3	1.0× 1262.5	2.0× 2525
DE (%)	109.4	92.0	95.7	95.5	97.4	102.1
	100.1	91.5	95.3	96.5	97.5	101.9
	96.6	92.5	95.2	99.3	97.9	100.5
	96.4	93.1	94.9	95.1	100.2	100.2
	97.4	91.6	94.3	94.5	100.4	100.5
	96.8	92.7	94.2	95.2	98.6	101.8
$\bar{x}$	99.4	92.2	94.9	96.0	98.7	101.2

4.10.2 Stability of desorbed samples

The stability of the desorbed samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed three vials were recapped with new septa while the remaining three retained their punctured septa. The samples were reanalyzed with fresh standards.

Table 4.10.2.1
Stability of desorbed samples for DMP

punctured septa replaced			punctured septa retained		
initial DE (%)	DE after one day (%)	difference	initial DE (%)	DE after one day (%)	difference
98.0	99.0	+1.0	98.6	99.0	+0.4
99.5	99.5	0.0	98.5	99.4	+0.9
98.6	99.0	+0.4	97.9	99.0	+1.1
	(averages)			(averages)	
98.7	99.2	+0.5	98.3	99.1	+0.8

Table 4.10.2.2
Stability of extracted samples for DEP

punctured septa replaced			punctured septa retained		
initial DE (%)	DE after one day (%)	difference	initial DE (%)	DE after one day (%)	difference
98.5	99.8	+1.3	98.5	99.5	+1.0
100.1	99.9	-0.2	99.4	99.6	+0.2
99.0	99.7	+0.7	98.3	99.4	+1.1
	(averages)			(averages)	
99.2	99.8	+0.6	98.7	99.5	+0.8

Table 4.10.2.3
Stability of extracted samples for DBP

punctured septa replaced			punctured septa retained		
initial DE (%)	DE after one day (%)	difference	initial DE (%)	DE after one day (%)	difference
98.8	98.2	-0.6	98.9	98.2	-0.7
99.5	99.0	-0.5	99.3	98.8	-0.5
99.2	98.8	-0.4	99.2	98.2	-1.0
	(averages)			(averages)	
99.2	98.7	-0.5	99.1	98.4	-0.7

Table 4.10.2.4
Stability of extracted samples for DEHP

punctured septa replaced			punctured septa retained		
initial DE (%)	DE after one day (%)	difference	initial DE (%)	DE after one day (%)	difference
98.8	96.8	-2.0	100.4	96.9	-3.5
98.7	97.7	-1.0	100.5	97.6	-2.9
98.9	98.0	-0.9	99.5	97.2	-2.3
	(averages)			(averages)	
98.8	97.5	-1.3	100.1	97.2	-2.9

Table 4.10.2.5
Stability of extracted samples for DNOP

punctured septa replaced			punctured septa retained		
initial DE (%)	DE after one day (%)	difference	initial DE (%)	DE after one day (%)	difference
97.4	95.7	-1.7	100.2	96.1	-4.1
97.5	96.4	-1.1	100.4	96.3	-4.1
97.9	97.7	-0.2	98.6	95.9	-2.7
	(averages)			(averages)	
97.6	96.6	-1.0	99.7	96.1	-3.6

4.11 Qualitative analysis

The GC/MS of phthalates can be obtained by using GC conditions similar to those given in Section 3.5. A Perkin-Elmer Ion Trap Detector interfaced to a Hewlett-Packard Series II GC was used to obtain the mass spectra shown below.

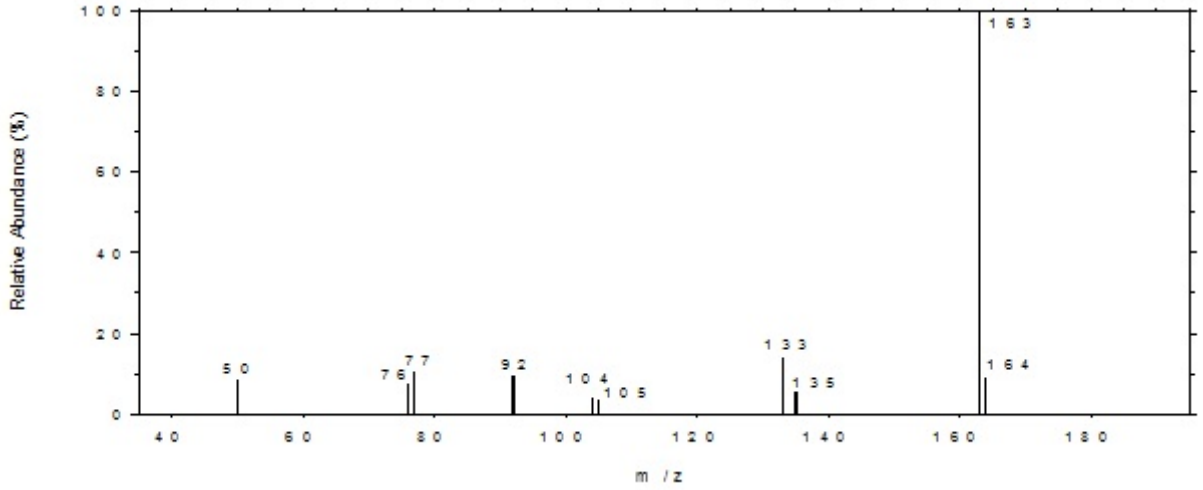


Figure 4.11.1. Mass spectrum of DMP.

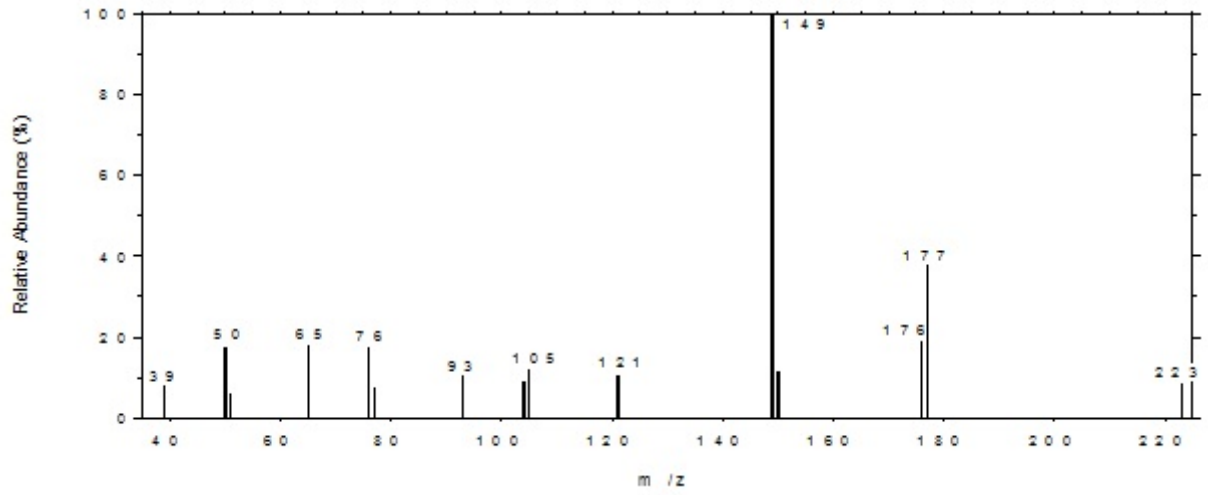


Figure 4.11.2. Mass spectrum of DEP.

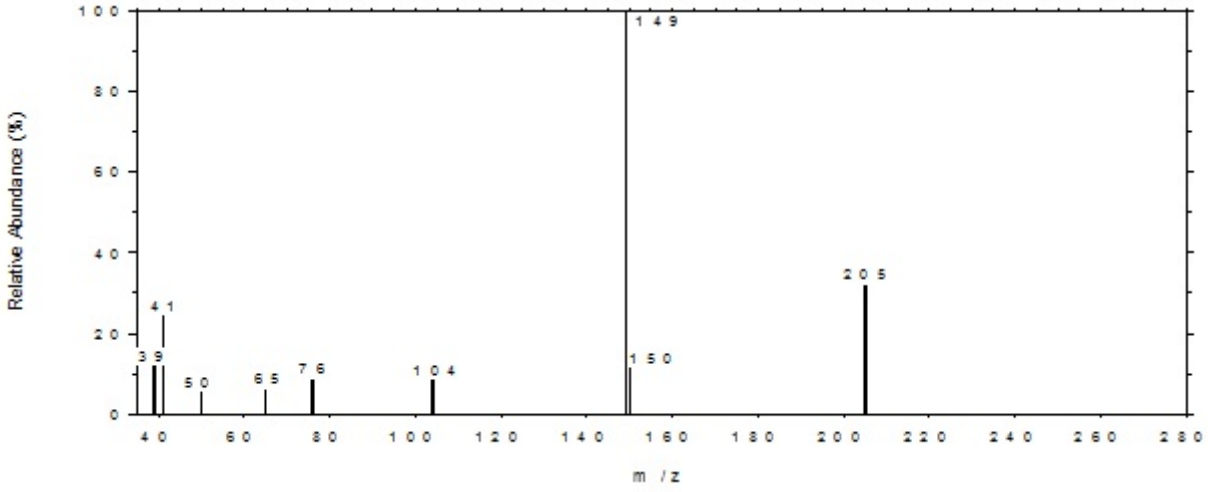


Figure 4.11.3. Mass spectrum of DBP.

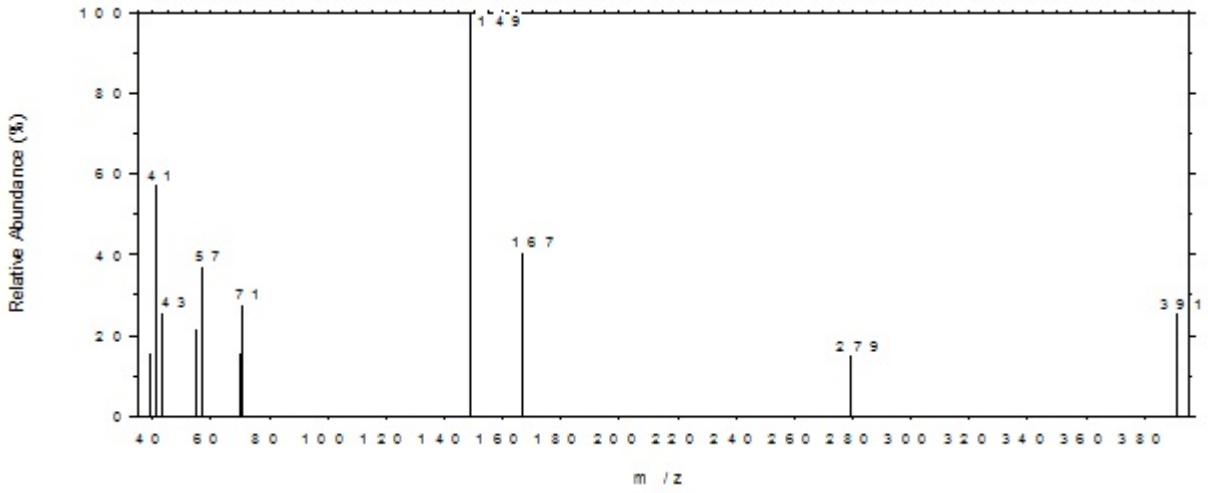


Figure 4.11.4. Mass spectrum of DEHP.

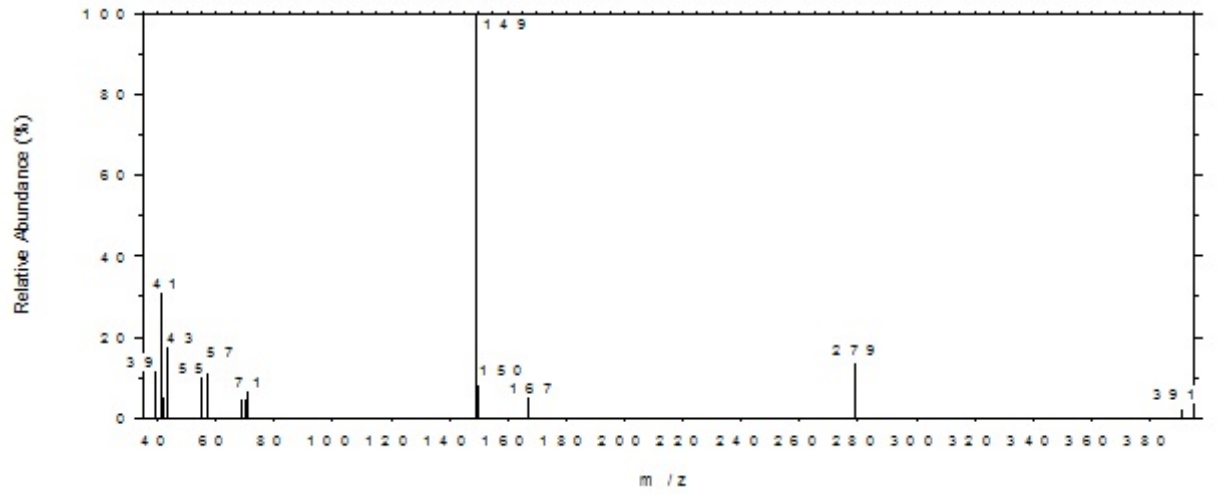


Figure 4.11.5. Mass spectrum of DNOP.

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