

# Automated Solid-Phase Extraction of Phthalates for Drinking Water Samples

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## Overview

**Purpose:** Demonstrate automated solid-phase extraction (SPE) of ppb level phthalate contaminants from drinking water.

**Methods:** Sample preparation used the Thermo Scientific™ Dionex™ AutoTrace™ 280 Solid-Phase Extraction instrument, and analysis was performed using a Gas Chromatograph (GC) with Electron-Capture Detector (ECD).

**Results:** Automated SPE using the Dionex AutoTrace 280 SPE Disk System extracts phthalates from large-volume drinking water samples with high efficiency, reproducibility and recovery rates.

## Introduction

Phthalates, or phthalate esters, are widely used in a large variety of consumer products to provide flexibility and durability to plastics such as polyvinyl chloride (PVC) including medical devices, children's toys, personal care products, and food packaging.

When used in PVC production, phthalates do not chemically bind to the PVC, but tend to evaporate into the air and leach into water and soil over time. Humans and other living organisms are exposed to these toxic phthalates through direct contact with contaminated food, water, and air. Therefore, in 2008 the U.S. Congress has permanently banned the following six types of phthalates as potential health risks:

- Dibutyl phthalate (DBP)
- Benzylbutylphthalate (BBP)
- Bis(2-ethylhexyl) phthalate (DEHP)
- Di-n-octyl phthalate (DNOP)
- Diisononyl phthalate (DINP)
- Diisodecyl phthalate (DIDP)

U.S. EPA has published Method 506 to determine phthalates in drinking water using liquid-liquid extraction (LLE) or solid-phase extraction and gas chromatography.

## Methods

### Sample Extraction Equipment

- Dionex AutoTrace 280 SPE instrument
  - Thermo Scientific™ Dionex™ SolEx™ SPE 6 mL C-18 cartridge system
  - 3M Empore 47 mm C-18 disk system
- Milli-Q DI Water System
- 40-mL sample collection vials

### Overview of Dionex AutoTrace 280 SPE Instrument

- Automates sample preparation for liquid samples using SPE
- Processes 1 to 6 samples
  - Sample volumes of 20 mL to 20 L
- Uses normal or reverse-phase cartridges and disks
- Accepts 1, 3 and 6 mL cartridges or 47 mm disks
- Saves time and reduces costs
- Automatically loads and elutes SPE cartridges/disks
  - Unattended operation
- Uses positive pressure to load and elute samples
  - Provides constant, reproducible flow of liquids
  - Independently controls flow for each channel
  - No hood is required—closed system with fan to vent solvent vapors

**FIGURE 1. Dionex AutoTrace 280 SPE instrument cartridge system (left) and disk system (right).**



### Sample Pretreatment

1. 80 mg sodium thiosulfate is added to 1 L of sample
2. Add phthalate standard

### Condition Rinse and Load Program:

1. Rinse column with 10 mL of dichloromethane (DCM) into solvent waste
2. Repeat 1
3. Rinse column with 10 mL of Methanol into solvent waste
4. Repeat 3
5. Condition column with 10 mL of DI water into aqueous waste
6. Load 1200 mL of sample onto column
7. Dry column with gas for 20 min

### Sample Elution Program for 47 mm Disks\*:

1. Collect 20 mL fraction into sample tube using acetonitrile (ACN)
2. Collect 20 mL fraction into sample tube using DCM
3. Repeat 1 and 2

### Sample Elution Program for 6 mL Cartridges\*:

1. Collect 20 mL fraction into sample tube using DCM
2. Collect 20 mL fraction into sample tube using DCM

\*Approved U.S. EPA methods requires DCM for elution from cartridges, and ACN/DCM for elution from disks

### Analysis of Extracts

GC-ECD were used to separate and identify phthalates.

### GC/MS Mass Spectrometry

GC-ECD Conditions	
Column:	Thermo Scientific TraceGOLD TG-1MS GC column
Injection Port Temperature:	250 °C
Injection Mode:	Splitless
Makeup Gas:	Nitrogen
Column Flow Rate:	1.5 (mL/min) constant flow
Oven Temperature:	100 °C (hold for 1 min) to 200 °C at 30 °C/min to 320 °C at 2 °C/min (hold for 2 min)

## Results

### Sample Extraction Issues

- Sample handling is the primary source of errors
- Sample extraction is the biggest bottleneck for most analysis methods
- Costs are increasing for solvent purchase and disposal
- The data is only as good as the sample preparation:
  - High-priced chromatography data systems do not improve the quality of data from poorly-prepared samples
- The Dionex AutoTrace 280 Automated SPE instrument was developed to address these issues

### Why Use Automated SPE?

- Compatible with U.S. EPA approved clean water and groundwater methods
- Replaces tedious LLE
- Automate all 4 steps of SPE
- Runs unattended
- Removes sample interferences
- Isolates and concentrates analytes from liquid matrix
- Reduces solvent consumption
- Reduces exposure to solvents
- Increases productivity
  - Chemists or technicians can load 6 samples using only 15 min of their time
  - 6 samples completed and ready for injection onto GC or LC in just 2-3 hours

### Comparison of Cartridge and Disk Systems

As shown in Tables 1, the Dionex AutoTrace 280 SPE Disk System extracts all six phthalates with the percent recoveries and RSD within acceptable U.S. EPA recovery limits.

**TABLE 1. Extraction Using the Dionex AutoTrace 280 SPE Disk System.**

Phthalates	Disks (with ACN/DCM)		
	SD	%RSD	%Recovery
DBP	0.47	10.43	89.52
BBP	0.73	16.57	88.20
DEHP	0.94	17.34	108.20
DNOP	0.51	9.69	105.04
DINP	0.60	11.34	105.56
DIDP	0.39	6.87	112.88

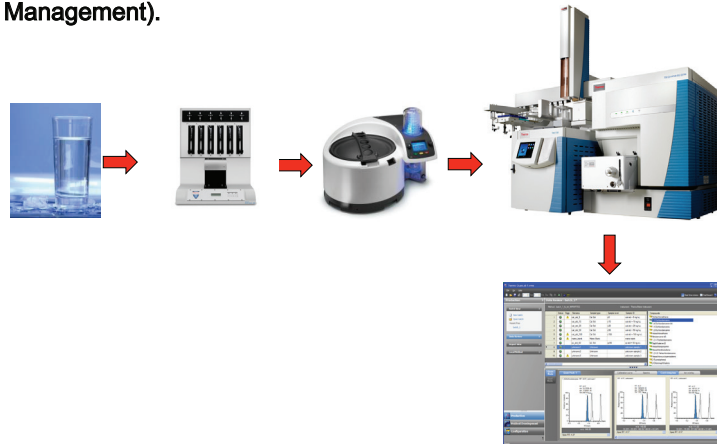
While the results from Dionex AutoTrace 280 SPE Cartridge System (Table 2) were very good for other phthalates, diisononyl phthalate (DINP) has poor reproducibility and low recovery.

**TABLE 2. Extraction Using the Dionex AutoTrace 280 SPE Cartridge System.**

Phthalates	Cartridges (with DCM)		
	SD	%RSD	%Recovery
DBP	0.07	1.84	71.28
BBP	0.07	2.14	67.52
DEHP	0.08	2.03	82.72
DNOP	0.06	1.77	62.56
DINP	0.97	39.39	49.32
DIDP	0.27	9.91	55.24

From the data shown above, the Dionex AutoTrace 280 SPE Disk System using 47 mm disks is recommended for using U.S. EPA methods to extract phthalates in drinking water samples. The Dionex AutoTrace 280 SPE instrument is the sample preparation component of the complete Thermo Scientific workflow solutions.

**FIGURE 2. The Thermo Scientific Total Workflow Solutions (Sample Preparation, Evaporation, Analysis, and Data Management).**



## Conclusion

Extraction of phthalates from drinking water samples can be made easier and faster by using the Dionex AutoTrace 280 SPE instrument. The data shows that the Dionex AutoTrace 280 SPE instrument can automatically extract phthalates among other contaminants from water samples with high efficiency and recovery.

The Dionex AutoTrace 280 SPE instrument can help reduce sample extraction costs by reducing solvent consumption, labor costs, as well as minimizing exposure to hazardous solvents. With this improved productivity, chemists can load six samples, which are then extracted automatically. The samples are completed and ready. The Dionex AutoTrace 280 SPE instrument provides improved analytical precision due to automated sample loading and elution using positive pressure.

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