

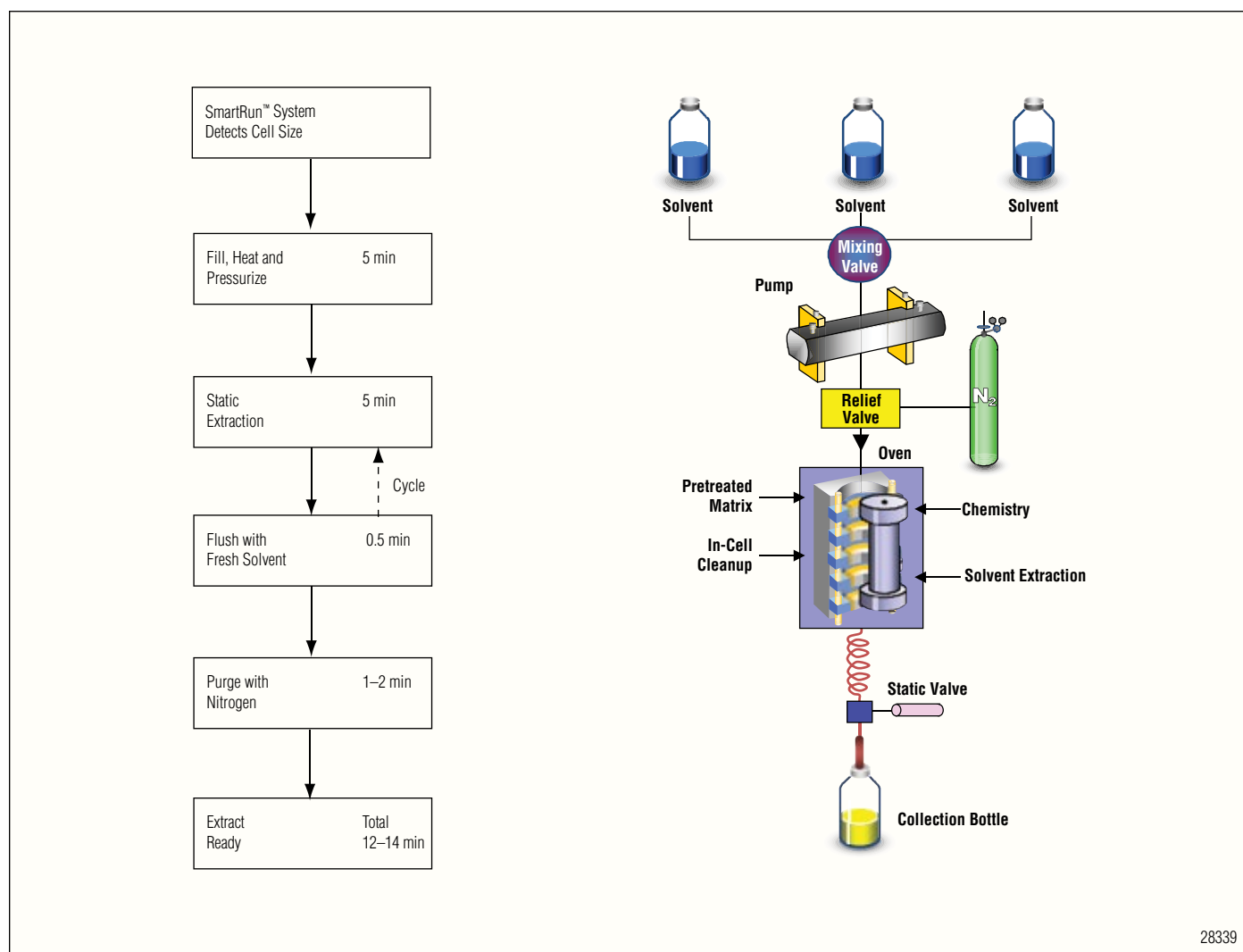
Extraction of Phthalates from Solid and Liquid Matrices

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INTRODUCTION

Phthalates are a group of chemicals used primarily in the consumer product industry. One of their main uses is as a softener in PVC plastic production for a wide range of products—everything from toys to footwear. They are also used in cosmetics, perfume and pharmaceutical 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. In this way, humans and other living organisms are exposed to these toxic phthalates through direct contact with contaminated food, water and air. Therefore, some phthalate compounds are classified as toxic to reproduction and can cause reduced fertility and/or potential harm to the unborn child.



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Figure 1. Automated solvent extraction schematic.

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SAMPLE EXTRACTION ISSUES

- Sample handling is the primary source of errors
- Sample extraction causes 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-price chromatography and data systems do not improve the quality of data from poorly-prepared samples
- Dionex has developed the Accelerated Solvent Extractor (ASE®) and AutoTrace® 280 Solid-Phase Extraction Instrument to address these issues

OVERVIEW OF AUTOMATED SOLVENT EXTRACTION

The automated solvent extraction technique uses liquid solvents and solvent mixtures to extract solid or semisolid samples. This method uses elevated temperatures (40–200 °C) and pressure (1500–2000 psi) to accelerate the extraction process.

EXTRACTION OF PLASTIC SHOES USING THE ASE SYSTEM

Sample Preparation

Shoes were cut into pieces and put into 10 mL cells.

Extraction Conditions

Pressure:	1500 psi (6.89 MPa)
Oven Temperature:	120 °C
Heat Time:	5 min
Static Time:	2 × 15 min cycles
Flush Volume:	60% of cell volume
Purge Time:	60 s
Solvent:	Hexane



Figure 2. Dionex ASE 150 and ASE 350 instruments.

Table 1. Results for Plastic Shoes¹

Sample	Country of Purchase	Phthalate (Percent by Weight)					
		DBP	DEHP	BBP	DnOP	DiNP	DiDP
1	Philippines	—	6.90%	—	—	—	4.70%
2	Philippines	—	8.60%	—	—	—	—
3	Philippines	9.60%	0.90%	—	—	—	—
4	Indonesia	0.81%	12.70%	—	—	—	—
5	Indonesia	0.17%	6.70%	—	—	—	—
6	South Africa	-	23.2%	—	—	—	—
7	South Africa	0.24%	6.80%	—	—	—	—
8	South Africa	0.01%	7.20%	—	—	—	1.20%
9	Tanzania	0.02%	11.30%	—	3.60%	—	—
10	Tanzania	—	16.80%	—	19.40%	—	—
11	Tanzania	—	4.30%	—	—	3.20%	—
12	Sweden	8.40%	0.36%	—	—	—	—
13	Sweden	7.40%	5.00%	—	—	—	—
14	India	0.02%	18.60%	—	—	—	—
15	India	0.39%	18.10%	—	—	—	—
16	Uganda	7.90%	0.07%	—	—	—	—
17	Uganda	0.03%	15.80%	—	—	—	—

OVERVIEW OF AUTOTRACE 280 INSTRUMENT

- Automates sample preparation for liquid samples using solid-phase extraction (SPE)
- Processes one to six 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 reduce 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

EPA METHOD 625 USING AUTOTRACE 280 INSTRUMENT

Sample Pretreatment

- Add 2.5 mL of methanol and 2 mL of concentrated sulfuric acid to 500 mL of sample



Figure 3. AutoTrace 280 SPE instrument cartridge configuration (left) and disk configuration (right).

Table 2. River Water Sample #1			
Class (n = 3)	Number of Compounds	Range	RSD%
Surrogates	3	68%–104%	4.0%–8.4%
PAHs	16	46%–93%	5.0%–13.0%
Phthalate	4	85%–95%	3.0%–13.6%

Data all fall within acceptable limits for EPA Method 625

Table 3. River Water Sample #2

Class (n = 3)	Number of Compounds	Range	RSD%
Surrogates	3	60.6%–99.2%	4.7%–8.8%
PAHs	16	45.2%–79.0%	2.6%–14.3%
Phthalate	4	74.7%–81.9%	1.5%–6.9%

Tables 2 and 3. GC/MS results of two river water samples prepared with the AutoTrace 280 instrument.

Condition, Rinse, and Load Cartridge (SolEx® C18, 6 mL)

- Rinse cartridge with 2 mL of Methanol
- Rinse cartridge with 5 mL of EtOAc and DCM
- Condition cartridge with 10 mL of CH₃OH and water
- Load 550 mL of sample onto cartridge
- Dry cartridge with gas for 10 min

Sample Elute Program

- Collect 5 mL fraction using EtOAc
- Collect 2 mL fraction using DCM

SPE Parameters

Solvents

- Solvent 1: Water (reagent-grade)
- Solvent 2: Methanol
- Solvent 3: Ethyl acetate
- Solvent 4: Methylene chloride

Flow Rates

- Load flow: 3 mL/min
- Rinse flow: 40 mL/min
- Elute flow: 20 mL/min
- Rinse, air push: 20 mL/min

Sample Is Now Ready for Analysis

- Evaporation
- Analysis using gas chromatography/mass spectrometry (GC/MS)

CONCLUSIONS

Extraction of phthalates from liquid or solid samples can be made easier and faster by using automated sample preparation systems from Dionex. The data shows that the ASE system can automatically extract phthalates from solid samples quickly and effectively, using minimal amounts of solvent. Phthalates can also be extracted automatically from water samples using the AutoTrace 280 instrument. These two extraction systems offer laboratories powerful tools to decrease sample preparation bottlenecks and increase productivity, while cutting solvent costs.

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