

Automated SPE for Wastewater Analysis: EPA 600 Series Methods



David Knowles, Brian Dorich, Richard Carlson, Brett Murphy, Eric Francis, Jennifer Peterson, and Bruce Richter,
Dionex Corporation, Salt Lake City, UT, USA

INTRODUCTION

Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are both proven techniques that meet the requirements of many EPA methods for analysis of pollutants in water. Although the analyte list for these two methods is similar, LLE is time-consuming, labor intensive, and uses large amounts of solvent. Conversely, SPE is a good alternative to liquid-liquid extraction as SPE provides reliable, less labor-intensive solution to liquid extraction, and uses significantly less solvent. In addition, emulsion formation is eliminated by using SPE.

Many of the EPA Series 600 method samples—including wastewaters, plant effluents, and streams—often contain particulates. Particulates can adversely effect SPE analysis if proper consideration is not given to the type of SPE device (disk or cartridge) used. In the work shown here, comparison of cartridge and disk SPE methods are examined. Conclusions on what is the proper method for Series 600 samples is presented.

WHY USE SPE?

- Isolate and concentrate analyte(s) from liquid matrix
- Remove sample interferences
- Compatible with U.S. EPA approved clean water and groundwater methods
- Replace tedious liquid-liquid extraction
- Reduce solvent usage
- Reduce exposure to solvents
- Increase productivity
- Run unattended

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WHAT IS AUTOTRACE?

The AutoTrace® instrument automates sample preparation for liquid samples using SPE to process from one to six samples with volumes from 20 mL to 20 L. It uses normal or reversed-phase 1, 3, and 6 mL cartridges and 47 mm disks. The AutoTrace is the ideal instrument to save time and reduce costs.

AUTOTRACE 280 SPE INSTRUMENTS



Figure 1. AutoTrace 280 SPE instrument cartridge configuration (left) and disk configuration (right).

WHY USE THE AUTOTRACE INSTRUMENT FOR SPE?

The AutoTrace instrument:

- Automatically loads and elutes samples
 - Unattended operation
- Uses positive pressure to load and elute samples
 - Provides constant, reproducible flow of liquids
 - No hood required; uses fan to vent solvent vapors
- Works
 - Accurate, rugged, and reproducible

CHOOSING BETWEEN DISK OR CARTRIDGE SYSTEM

Either disks or cartridges will provide similar results for most samples. If throughput is the most important issue, disk methods are typically faster due to less backpressure allowing faster flow rates. Disk methods are typically used with samples containing >5% solids.

If cost per sample is the most important issue, cartridges provide lower cost, use less solvent (approximately 25% less). Cartridges are used with samples containing less than <2–5% solids.

AUTOTRACE INSTRUMENT BENEFITS

- SPE uses less solvent when compared to traditional extractions
- Positive pressure for SPE functions
 - Provides constant flow
 - Other systems use a vacuum
- Automates all four SPE steps
 - Condition, load, rinse, and elute
- Segregates aqueous and solvent waste using separate waste lines
- Processes ground, surface, and wastewater samples
- Easy-to-use, SPE-specific software
- Documented EPA methods for water testing

AUTOTRACE INSTRUMENT APPLICATIONS

- Selected AutoTrace instrument applications for wastewater methods
 - EPA Method 606 for phthalates
 - EPA Method 608 for organochlorine pesticides and polychlorinated biphenyls (PCBs)
 - EPA Method 610 for polycyclic aromatic hydrocarbons (PAHs)
 - EPA Method 625 for semivolatiles organics

SPE METHOD

EPA Method 625 Using the AutoTrace 280 Instrument

- Sample pretreatment
 - Add 2.5 mL methanol and 2 mL concentrated sulfuric acid to 500 mL of sample
- Condition, rinse, and load cartridge (SolEx™ C18, 6 mL)
 - Rinse cartridge with 2 mL methanol
 - Rinse cartridge with 5 mL of ethyl acetate and dichloromethane
 - Condition cartridge with 10 mL methanol and water
 - Load 550 mL of sample onto cartridge
 - Dry cartridge with gas for 10 min

- Sample elute program
 - Collect 5 mL fraction using ethyl acetate
 - Collect 2 mL fraction using dichloromethane

SPE Conditions for EPA Method 625

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

RESULTS

Table 1. 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 2. 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%

EPA METHOD 608

SPE Parameters

- Solvents
 - Solvent 1: Water (reagent grade) conditioning flow: 40 mL/min
 - Solvent 2: Methanol load flow: 3 mL/min
 - Solvent 3: Ethyl acetate rinse flow: 40 mL/min
 - Solvent 4: Dichloromethane elute flow 20 mL/min
 - Rinse air push 20 mL/min
- 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 final volume determination
 - Evaporation
 - Injection on GC or LC

CONCLUSIONS

The AutoTrace instrument can help reduce sample extraction cost by reducing solvent consumption and labor cost, 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 AutoTrace instrument provides improved analytical precision due to automated sample loading and elution using positive pressure.

Table 3. EPA Method 608

Compound	Mean	RSD%
Alpha-BHC	91.2	18.3
Gamma-BHC	72	18.6
Endosulfan I	69.7	13.7
Dieldrin	70.4	14.8
Endrin	61.1	12.4
Endosulfan Sulfate	81.5	15.8

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Dionex Corporation

1228 Titan Way
P.O. Box 3603
Sunnyvale, CA
94088-3603
(408) 737-0700

North America

U.S./Canada (847) 295-7500

South America

Brazil (55) 11 3731 5140

Europe

Austria (43) 1 616 51 25 Benelux (31) 20 683 9768; (32) 3 353 4294
Denmark (45) 36 36 90 90 France (33) 1 39 30 01 10 Germany (49) 6126 991 0
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Asia Pacific

Australia (61) 2 9420 5233 China (852) 2428 3282 India (91) 22 2764 2735
Japan (81) 6 6885 1213 Korea (82) 2 2653 2580 Singapore (65) 6289 1190
Taiwan (886) 2 8751 6655

www.dionex.com



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