
# Advanced Automation of SPE Methods

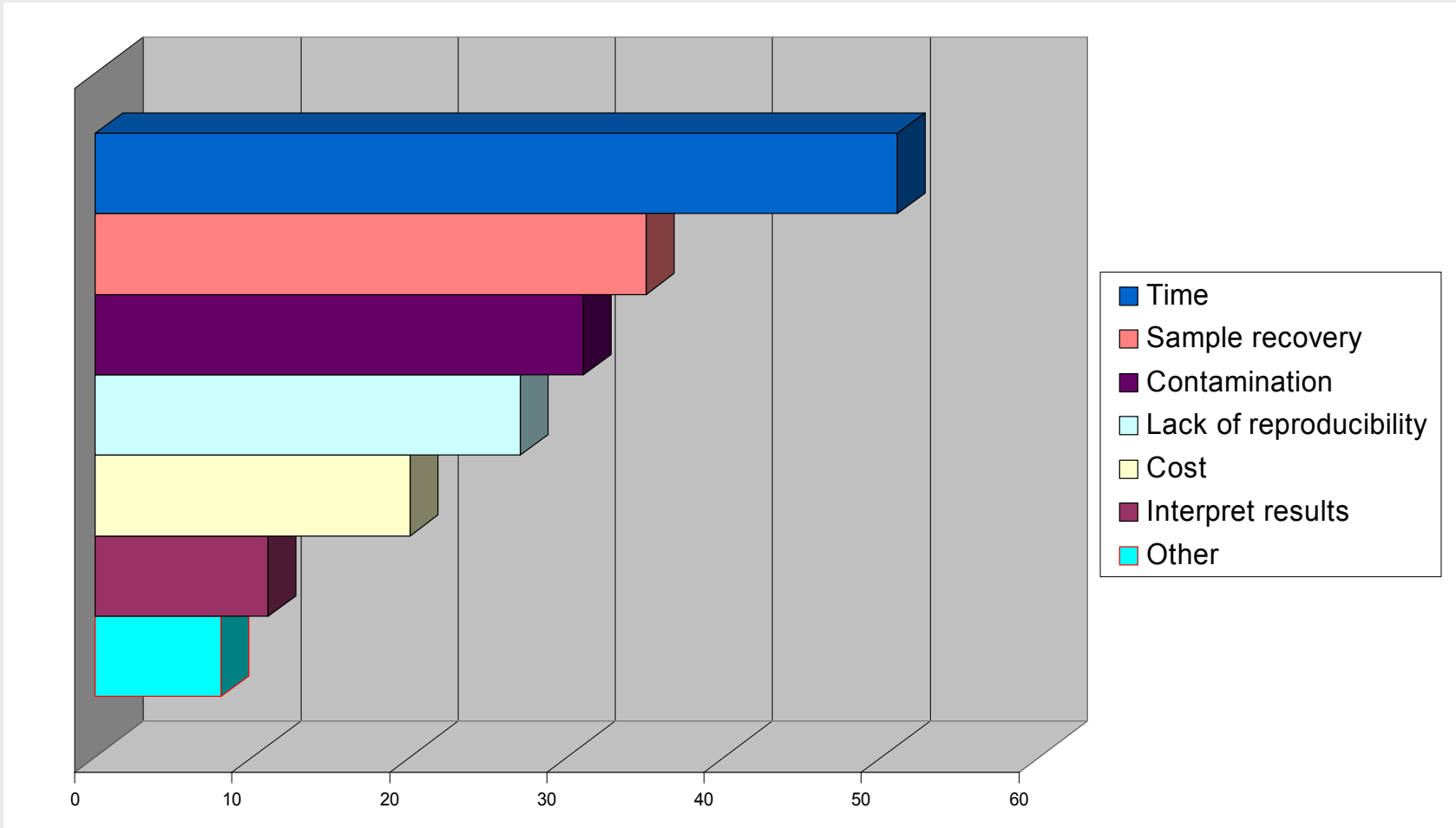
## Streamlining and Improving Sample Preparation Procedures for U.S. EPA Methods

Tom Hall

# Outline

- Does Your Lab Have a Problem?
- Brief Overview of SPE
- Comparison of LLE and SPE
- Evolution of SPE Technology
- Overview of SPE Automation - Benefits
- Optimization of SPE for new Analytical Procedures

# Sample Preparation Problems

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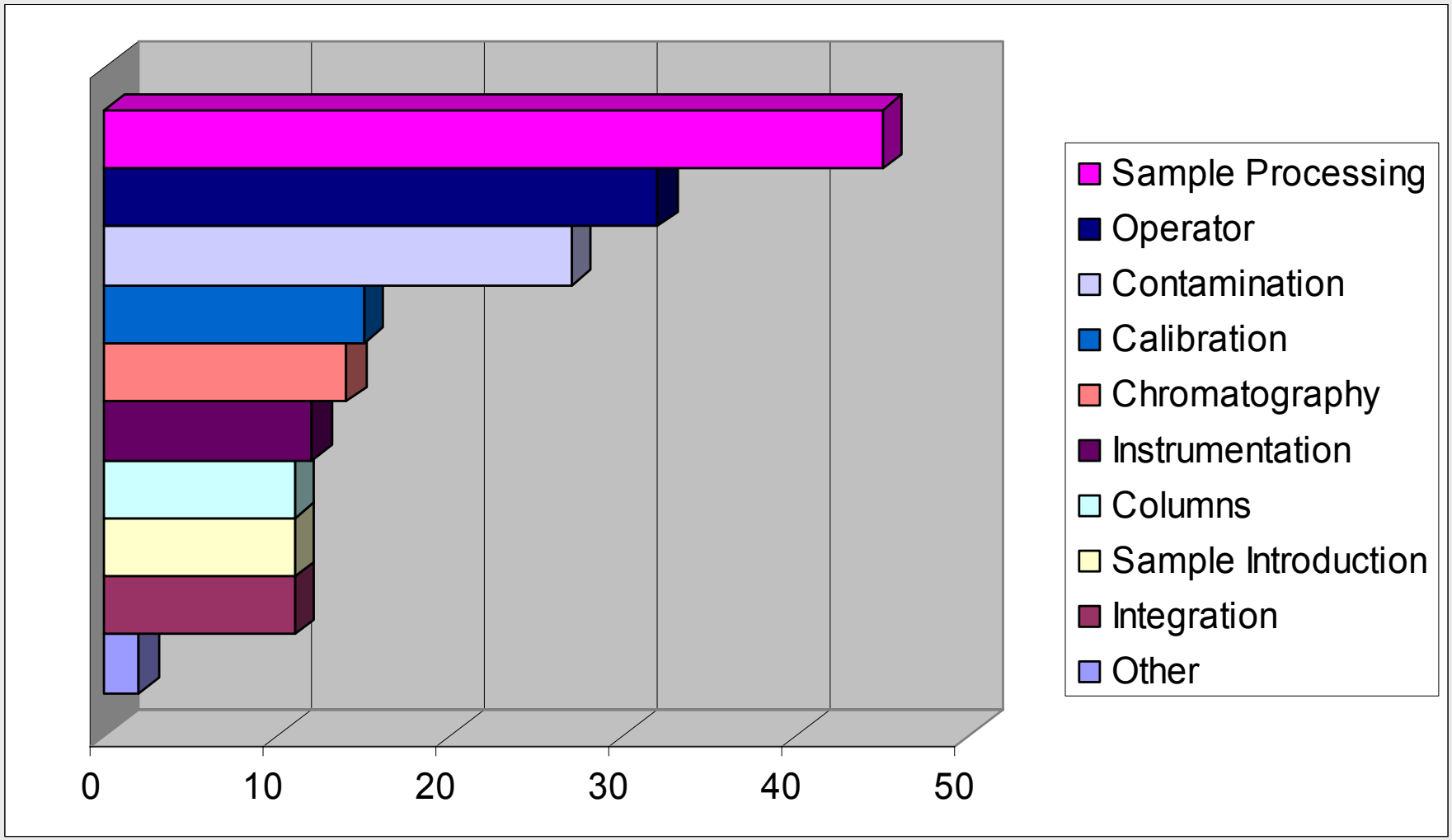
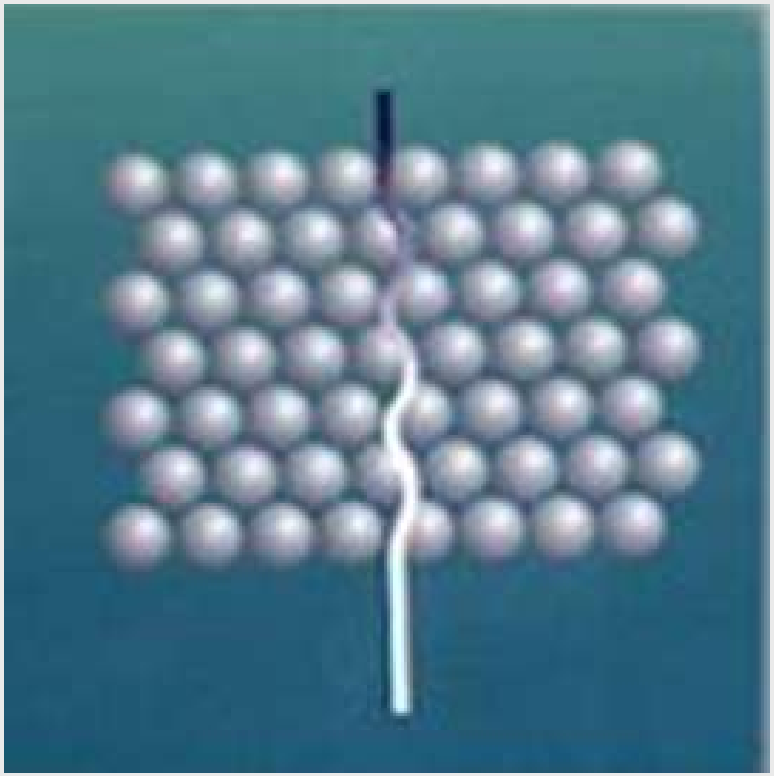
# Errors in Sample Preparation



# What is Solid Phase Extraction?

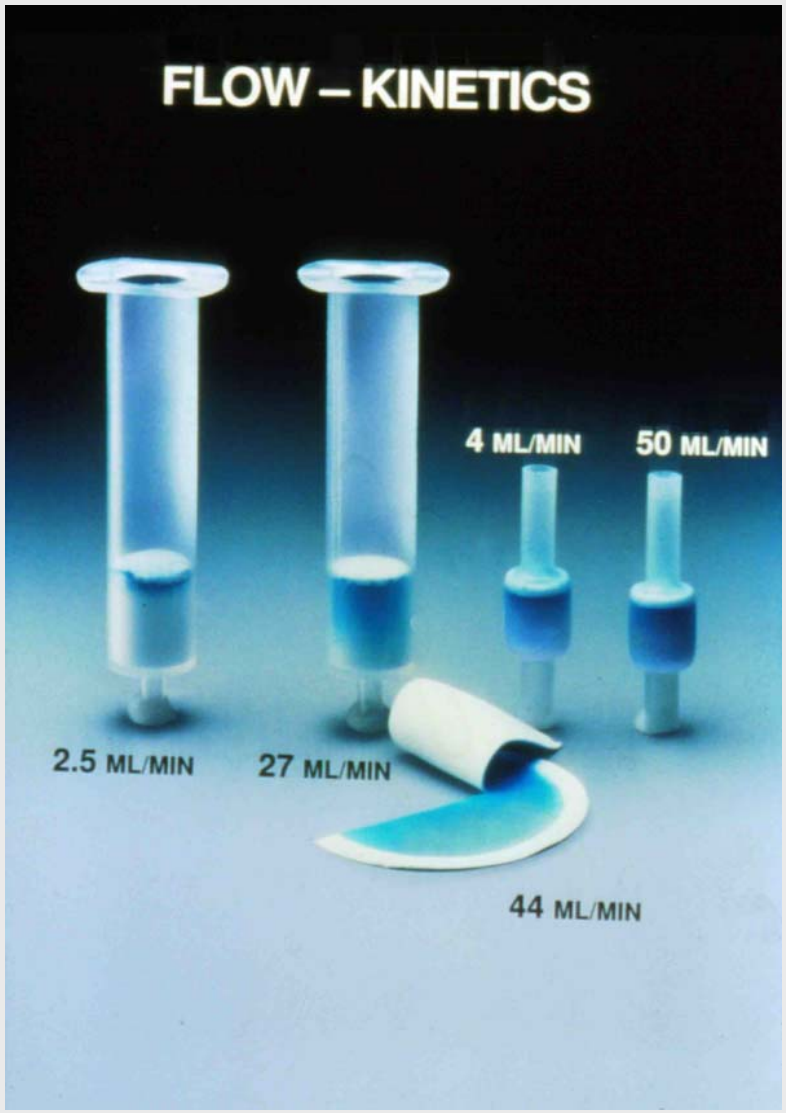
Solid Phase Extraction (SPE) is an extraction process whereby an aqueous sample is filtered through a bed of sorbent particles, the analytes of interest are removed from the aqueous sample, and adsorbed **(concentrated)** onto the sorbent. Once concentrated, the analytes are removed from the sorbent by a series of eluting solvent rinses.

# SPE Disk Mechanism



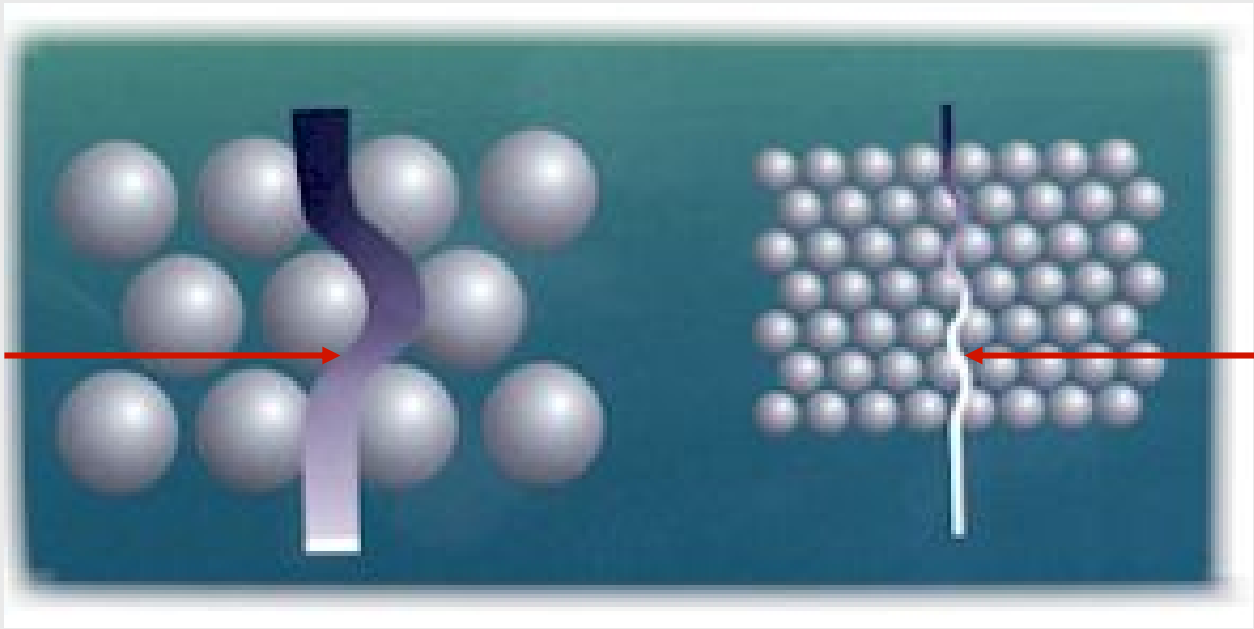
- SPE disk particles are typically 5 – 15 micron in size.
- As the water sample passes through the packing, the compounds of interest are retained by several mechanisms: reverse phase, anion exchange, and cation exchange interactions.
- The small particle sizes allow very fast flow rates; typically up to 85 - 125 ml/min, without breakthrough.

# SPE Cartridges




- Cartridges use 40 micron particles (size). This limits the flow rates to 1 – 10 ml / min. And typically reduces the sample size to 200 ml
- Low flow rates results in long sample prep times.
- Higher flow rates lead to breakthrough.
- Small surface area is not good for dirty samples; plugging will occur.

# Particle Size of Cartridges vs. Disk SPE




-Larger particles in Cartridge allows sample breakthrough if flow rates are too fast

- SPE Disks prevent breakthrough even with fast flow rates

# SPE Disk Systems

## Single Sample Manifold

## Multiple Sample Manifold

## Automation System

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# Liquid-Liquid (LLE) Separatory Funnel Extraction

Adding solvent to Sep Funnel

Shaking Sep Funnel for 2 min

Solvent separation and collection

10 Technician hours for 20 samples

2 Technicians spend 5 continuous hours on task

1-Liter water samples extracted

# Comparison of Disk, Cartridge and LLE

| Disk | Cartridge | LLE |
|---|---|---|
| 15-25 ml solvent | 5-15 ml solvent | 200 - 500 ml solvent |
| Filtration | Filtration | Shaking |
| 85-125 ml/min | 5-10 ml/min | |
| No emulsions | No emulsions | Emulsions |
| Handles dirty samples | No dirt (clean) | Limited dirt |
| Up to 8 liter samples | 200-500 ml samples | 2 liter samples |
| 20 min / sample | 100 min / sample | 1-2 hours / sample |

# Advantages of Disk SPE

- Disk SPE Uses Less Solvent than a typical LLE Procedure
- Disk SPE is Faster; greater sample throughput
- Disk SPE can handle dirty samples; river water, waste water, etc
- Disk SPE has no emulsions
- Disk SPE can process large sample volumes (8 liters)
- Disk SPE Provides comparable / better recoveries than LLE
- New methods are constantly being developed for SPE

# Why Automate SPE Disks?

- Increases productivity by improving sample throughput
- Improves accuracy and precision by eliminating variations due to human operators
- Reduces laboratory costs by reducing operator time, glassware, and solvent usage
- Reduces worker exposure to solvents
- Consistent control over critical rinse and air dry steps

# Major SPE Disk Brands

- JT Baker Speedisks
- 3M Empore Disk
- Atlantic SPE Disks - *New*
  - Certified for Automation

# Atlantic Disk


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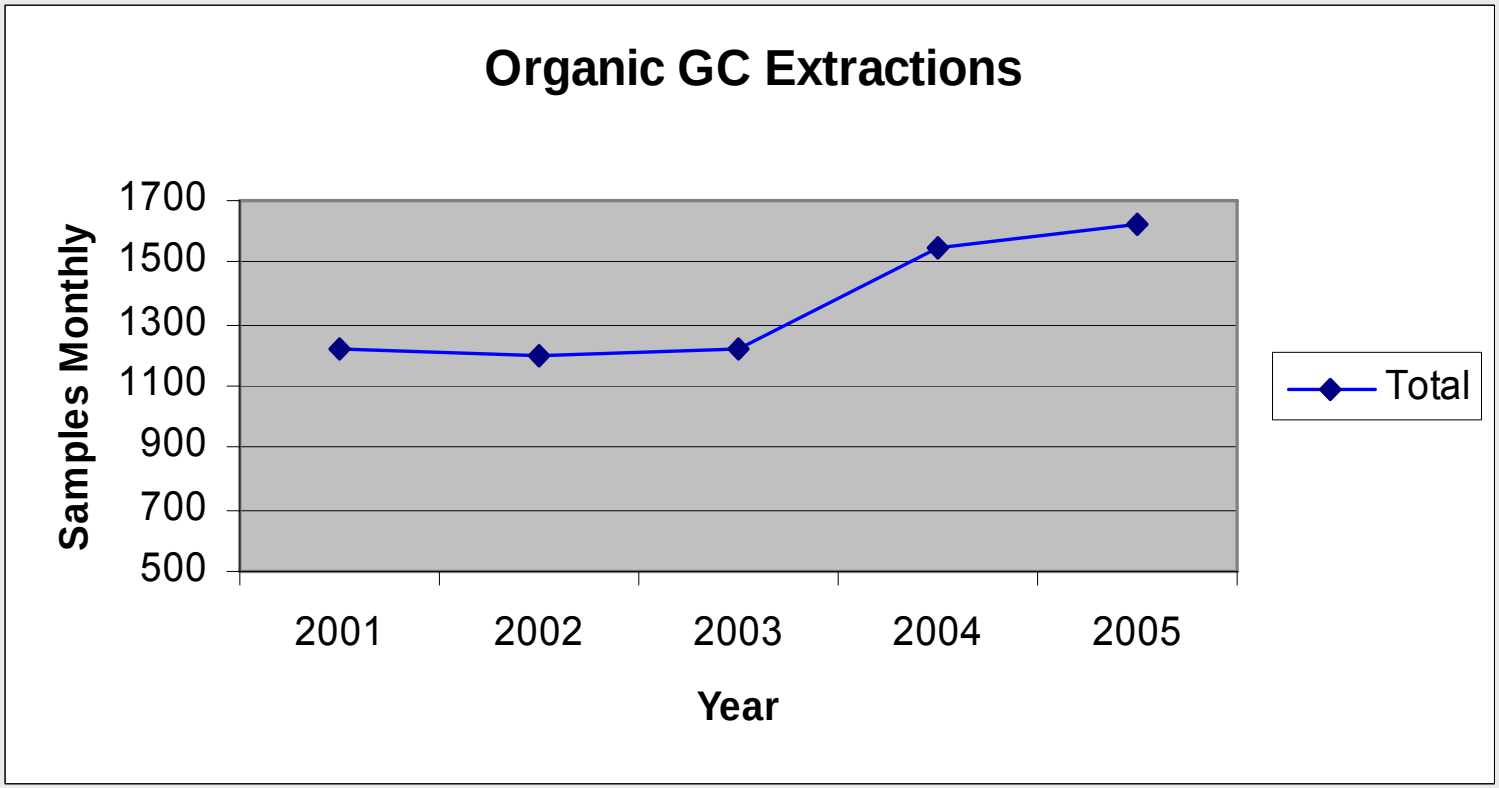
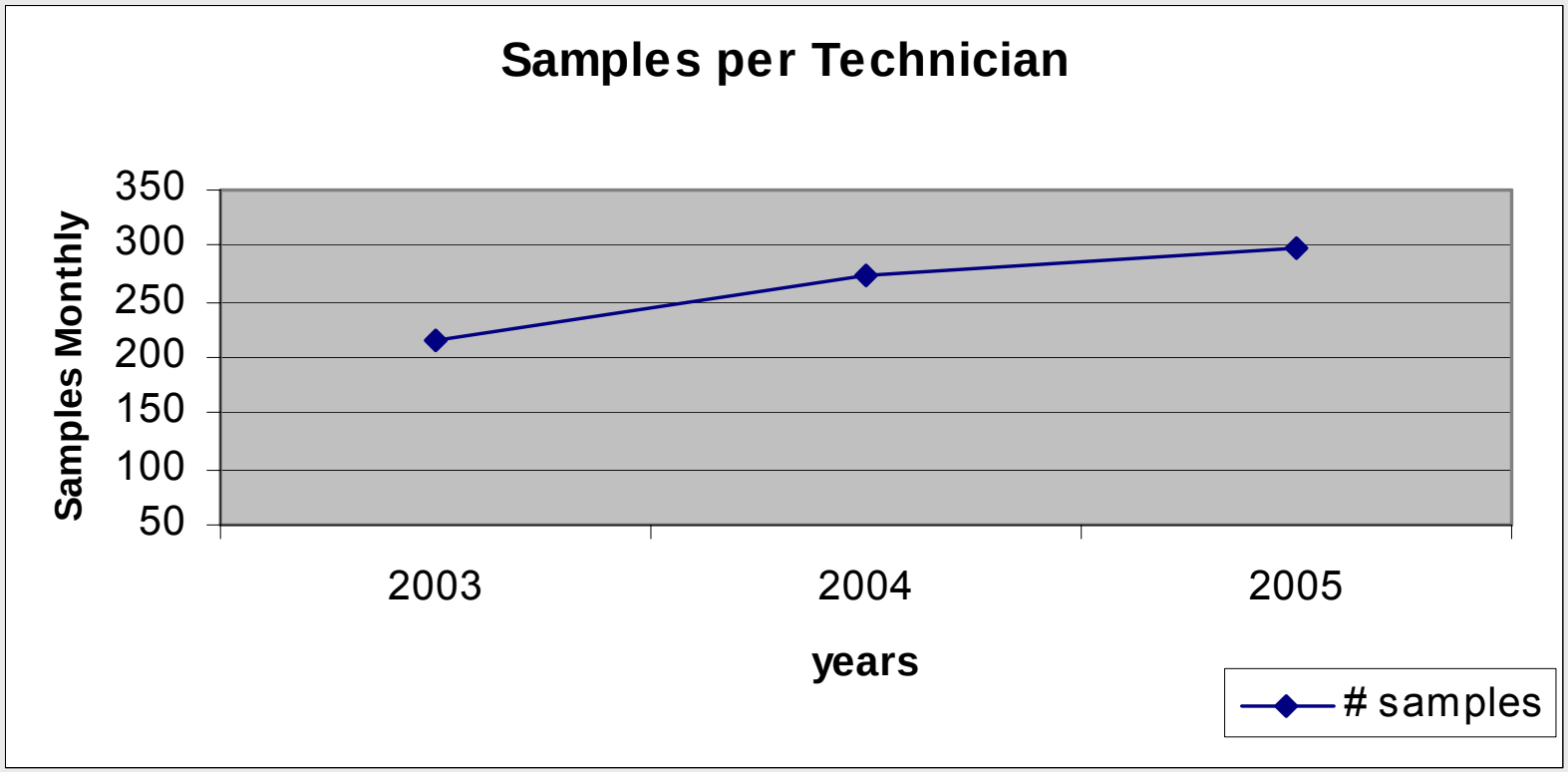
# Sample Workload




Pace Laboratory

# Increased Productivity

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# Justification - Cost Analysis

## SPE SAMPLE COST ANALYSIS WORKSHEET

This worksheet can be used to help calculate the cost per sample, and allows a cost comparison between a JT Baker Speedisk and a 90 mm CPI C-18 disk. The labor time to set up the extractor, with either disk, would be the same. The only time difference wi in the total time required to filter the sample. This is addressed in the Sample Throughput Worksheet. Clean samples would use th while dirty samples would use the 90 mm CPI disk. Follow the directions below to fill in the worksheet.

**Directions:**

1) Enter in the cost / ml for each of the reagents to be used.
2) If FilterAid400 is to be used, enter 4 under the ML column for the Baker table, and 16 under the ML column for the CPI t
3) If a Prefilter is to be used with the 90 mm disk, enter "1" in the PreFilter line in the 90 mm table.
4) Enter the above information in the "green" cells.

| Baker C-18 Speedisks | Cost | | |
|---|---|---|---|
| **REAGENTS** | **$** | **ML** | **TOTAL** |
| Methylene chloride | 0.05 | 20 | 1.00 |
| Acetone | 0.05 | 10 | 0.50 |
| Methanol | 0.05 | 5 | 0.25 |
| Reagent Water | 0.05 | 5 | 0.25 |
| | | | **$ 2.00** |
| **DISPOSABLES** | | | |
| Disk | 5.95 | 1 | 5.95 |
| FilterAid 400 (4 gms) | 0.184 | 0 | 0.00 |
| | | | **$ 5.95** |
| **LABOR COST** | | | |
| Operator time per sample (in minutes) | 5 | | **$ 1.25** |
| **TOTAL COST PER SAMPLE** | | | **$ 9.20** |

| CPI 90 mm Disks | Cost | | |
|---|---|---|---|
| **REAGENTS** | **$** | **ML** | **TOTAL** |
| Methylene chloride | 0.05 | 80 | 4.00 |
| Acetone | 0.05 | 40 | 2.00 |
| Methanol | 0.05 | 20 | 1.00 |
| Reagent Water | 0.05 | 20 | 1.00 |
| | | | **$ 8.00** |
| **DISPOSABLES** | | | |
| Disk | 14.79 | 1 | 14.79 |
| FilterAid 400 (16 gms) | 0.184 | 0 | 0.00 |
| PreFilter (GMF-150) | 1.75 | 0 | 0.00 |
| | | | **$ 14.79** |
| **LABOR COST** | | | |
| Operator time per sample (in minutes) | 5 | | **$ 1.25** |
| **TOTAL COST PER SAMPLE** | | | **$ 24.04** |

# Justification - Sample Throughput

## SPE SAMPLE THROUGHPUT and "BREAK-EVEN" WORKSHEET

This spreadsheet is used to calculate the run time per sample, the number of extractors needed for the expected work load, and the estimated break-even time period.
The SPE costs per run, calculated from the Cost Analysis Worksheet will automatically be entered into this Worksheet.

**Directions:**

1) Enter in the estimated time to filter a sample. This time will be a function of the sample size; 250 or 1,000 ml.
2) Enter in the necessary Air Dry Filtered Disk time, but do not exceed 10 minutes.
3) Enter in the total number of Extractors, and confirm the desired work load is achieved.
4) See the Purple line for the calculated Breakeven period (in days).
5) Enter in the "Expected" number of samples to be run per day.
6) Enter the above information in the "green" cells

| Time Per Sample Calculation | | | |
|---|---|---|---|
| **Prewet Steps** (time in sec's) | **Dispense** | **Soak** | **Dry** |
| Methylene chloride | 5 | 30 | 30 |
| Acetone | 5 | 30 | 30 |
| Methanol | 5 | 30 | 0 |
| Reagent Water | 5 | 30 | 0 |
| Time (in minutes) | 0.33 | 2.00 | 1.00 |
| **Total time for Prewet Steps** | | | **3.33** |
| | | | |
| **Filter Sample** | | | **10** |
| average estimated time | | | |
| | | | |
| **Air Dry Filtered Disk** | | | **2** |
| max air dry time not to exceed 10 min | | | |
| | | | |
| **Rinse Steps** (time in sec's) | | | |
| Acetone | 5 | 60 | 30 |
| Methylene Chloride | 5 | 60 | 30 |
| Methylene Chloride | 5 | 60 | 30 |
| Methylene Chloride | 5 | 60 | 60 |
| Time (in minutes) | 0.33 | 4 | 2.5 |
| **Total time for Prewet Steps** | | | **6.83** |
| | | | |
| **TOTAL TIME PER SAMPLE** | | | **22.17** |

| Samples Run / Shift / Day Calculation | | | | |
|---|---|---|---|---|
| 1) Enter in number of Horizon extractors | = | 2 | | |
| Calculated time per sample (in minutes) (equal "Total Time per Sample" plus 10 minutes prep) | | 32 | | |
| Max number of samples per hour | = | 4 | | |
| Max number of samples per 8 hr. shift | = | 30 | | |
| Max number of samples per 24 hr. day | = | 90 | | |
| Expected number of samples per day | = | 30 | | |
| Price, based on the number of Extractors | = | $25,400 | | |
| Current Cost to run Sample | = | $ 35.00 | | |
| | | **Baker Disk 50 mm** | | **CPI Disk 90 mm** |
| SPE Cost per Run | | **$ 9.20** | | **$ 24.04** |
| Savings per Sample with SPE | | **$ 25.80** | | **$ 10.96** |
| Number of Samples to run for Breakeven | | **984** | | **2318** |
| Max Number of Samples Run Per Day | | **90** | | **90** |
| **Number of Days to Breakeven (Max #)** | | **11.0** | | **25.9** |
| **Number of Days to Breakeven (Exp #)** | | **32.8** | | **77.3** |

# Commercial Lab Cost Justification

| BENEFIT | IMPACT | DESCRIPTION |
|---|---|---|
| Reduced solvent use | $9336 | Reduction in solvent use |
| Waste Disposal | $3960 | Less waste generated |
| Reduce Labor | $9408 | Reduction of O.T. |
| Reduce Solvent Contact | unknown | Safety |
| Reduce Labor | $7280 | Allow Analysts Flexibility |
| Reduce Glassware | $15,055 | Alleviate replacement costs |
| Method 525.2 | $116,780 | Maintain profit in-house |
| IDEM contract work | $150,000 | |
| ERO work | $10,000 | |
| Reduce ERO contamination | Unknown | Atmospheric Contamination reduced |
| Future markets | Unknown | Endocrine Disruptors, Personal Products, Pharmaceuticals |

TOTAL: $321,819

# Evolution of the Technology

- Since the introduction of disk SPE, there have been significant evolutionary growth

  - **Constant Improvements in the system hardware**
  - **New SPE Packings**
  - **More Analytical Methods for SPE disks**
  - **Improved ability to handle dirty samples**

# SPE-DEX 4790 Automated Extractor System

- Modular Design
- Run up to 8 Extractors
- Run independently
- Run individual methods
- Use 47, 50, and 90-mm SPE disks
- Designed for all SPE Chemistries
- Preprogrammed EPA methods
- Bench top operation
- Handle 4 liter samples – can be run multiple times for greater sample volume

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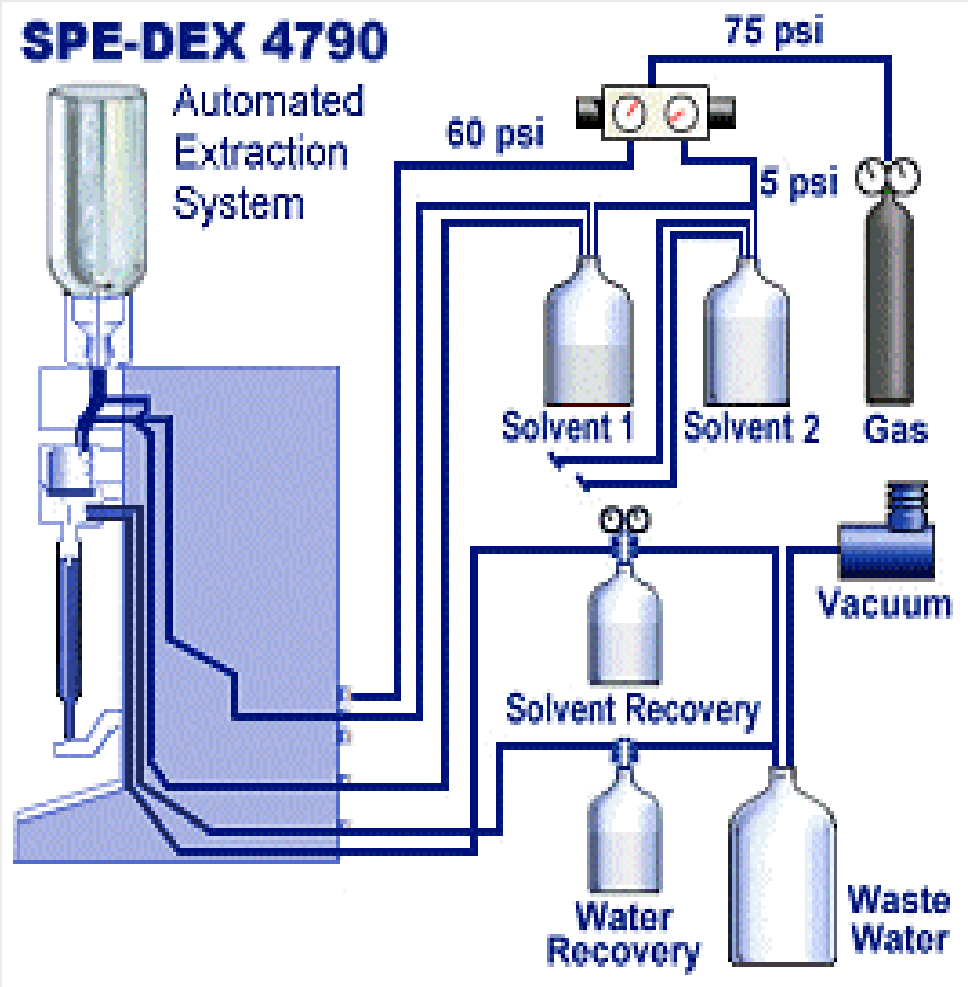
# SPE-DEX 4790 Automated Extractor System




- Gas to deliver solvents
- Vacuum to remove liquids
- All solvents are contained in separate bottles
- Separates waste solvent and waste water
- All sample and solvent pathways are PTFE, PEEK, and Kalrez
- Automatically rinses sample bottle
- Utilizes liquid sensors; keeps disk wet
- Modular design; handle up to 8 extractors.
- Handle up to 4 liter samples; better detection limits.

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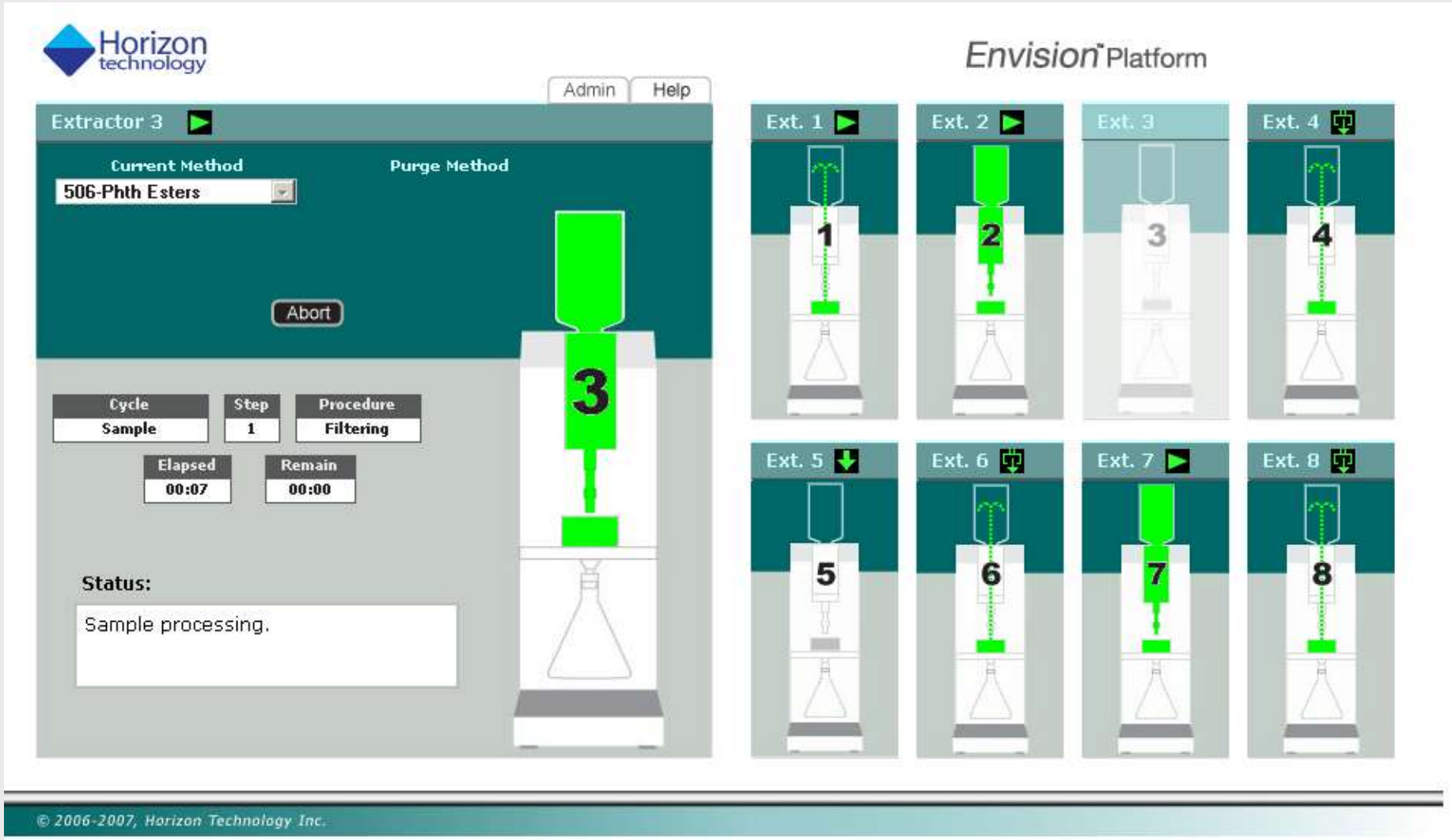
# Envision Controller

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# Optimizing the SPE Disk Chemistry

# Optimized SPE Cartridge for Automation


- Developed the Auto Barrel to house the DryDisk membrane
- Designed the Auto Barrel to also work on the 4790 extractors
- Use the Auto Barrel without the membrane
- Allows SPE packing material to be added for cartridge specific applications.
- Packing and frits optimized to provide maximum water sample flow rates, but with highest recoveries

# NDMA Carbon Cartridge


- Experimental Work:
- Used Auto Barrel to hold 5.0 gms of coconut charcoal
- Filter 1 liter of water in 40 to 50 minutes
- Used a glass fiber bottom layer to control the water sample flow rate
- No need to set and monitor the vacuum level – self optimizing
- Recovery values of 50 to 70%

# Sorbants / Packing Materials for SPE Disks

SPE Disks come in similar packing materials as SPE Cartridges for a wide range of applications:

- C8 - Octyl
- C-18 - Octadecyl
- SDB - Styrene Divinyl Benzene
- DVB - Hydrophobic
- DVB - Hydrophilic
- Oil & Grease
- Anion Exchange
- Chelating
- Activated Carbon
- Mixed Phases – with functional groups

## Alpha Labs, Westborough, MA

# SPE-DEX Automated Extractor System

| Analyte | Set 1 Ext 1- 5 (ng) | Set 2 Ext 1- 5 (ng) | Set 3 Ext 1- 5 (ng) | Ave All Runs (ng) | Ave %Rec | SD | %RSD |
|---|---|---|---|---|---|---|---|
| **26DANT** | 22.99 | 23.08 | 23.12 | 23.06 | **92** | 0.832 | 3.607 |
| **24DANT** | 22.94 | 23.28 | 23.62 | 23.28 | **93** | 0.864 | 3.711 |
| **HMX** | 23.21 | 23.43 | 22.00 | 22.88 | **92** | 1.146 | 5.010 |
| **RDX** | 24.49 | 24.39 | 23.42 | 24.10 | **96** | 1.129 | 4.686 |
| **PICRIC** | 24.57 | 24.92 | 25.40 | 24.96 | **100** | 1.034 | 4.143 |
| **1,3,5-TNB** | 18.64 | 18.83 | 18.16 | 18.54 | **74** | 0.920 | 4.963 |
| **1,2-DNB (Surrogate)** | 23.42 | 23.54 | 23.59 | 23.52 | **94** | 0.853 | 3.626 |
| **1,3-DNB** | 24.46 | 24.56 | 23.37 | 24.13 | **97** | 1.289 | 5.342 |
| **NB** | 22.91 | 23.04 | 22.16 | 22.70 | **91** | 1.383 | 6.092 |
| **Tetryl** | 36.28 | 35.38 | 35.13 | 35.59 | **142** | 1.476 | 4.147 |

# Recovery of List 1 Pesticides

## MN Dept. Agriculture Laboratory
## St. Paul, MN

**SPE-DEX Automated Extractor System**

| Compound | % Rec. | RSD | MDL |
|---|---|---|---|
| EPTC | 70 | 13.65 | 0.14 |
| Propachlor | 96 | 7.39 | 0.11 |
| Ethafluralin | 85 | 6.97 | 0.09 |
| Trifluralin | 85 | 4.70 | 0.06 |
| Phorate | 87 | 8.48 | 0.11 |
| Dimethoate | 108 | 4.26 | 0.07 |
| Simazine | 94 | 2.19 | 0.03 |
| Propazine | 95 | 1.59 | 0.02 |
| Terbufos | 91 | 6.34 | 0.09 |
| Fonofos | 88 | 5.30 | 0.07 |
| Diazinon | 98 | 3.45 | 0.05 |
| Triallate | 86 | 4.65 | 0.06 |
| Methyl Parathion | 108 | 3.50 | 0.06 |
| Malathion | 111 | 1.34 | 0.02 |
| Chlorpyrifos | 99 | 2.60 | 0.04 |
| Pendimethalin | 96 | 2.60 | 0.04 |

# River Water Sample from Taiwan

**1 Liter River Water Sample**

**JT Baker Speedisk**


SPE-DEX Automated Extractor System

Extracting Chlorinated Pesticides from 1 Liter River Water Sample

Start Time = 0 min

Note the time clock

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# River Water Sample from Taiwan


Automated SPE Disk Extraction of Chlorinated Pesticides

1 Liter Sample

Start Time = 0 min

← Note the time clock

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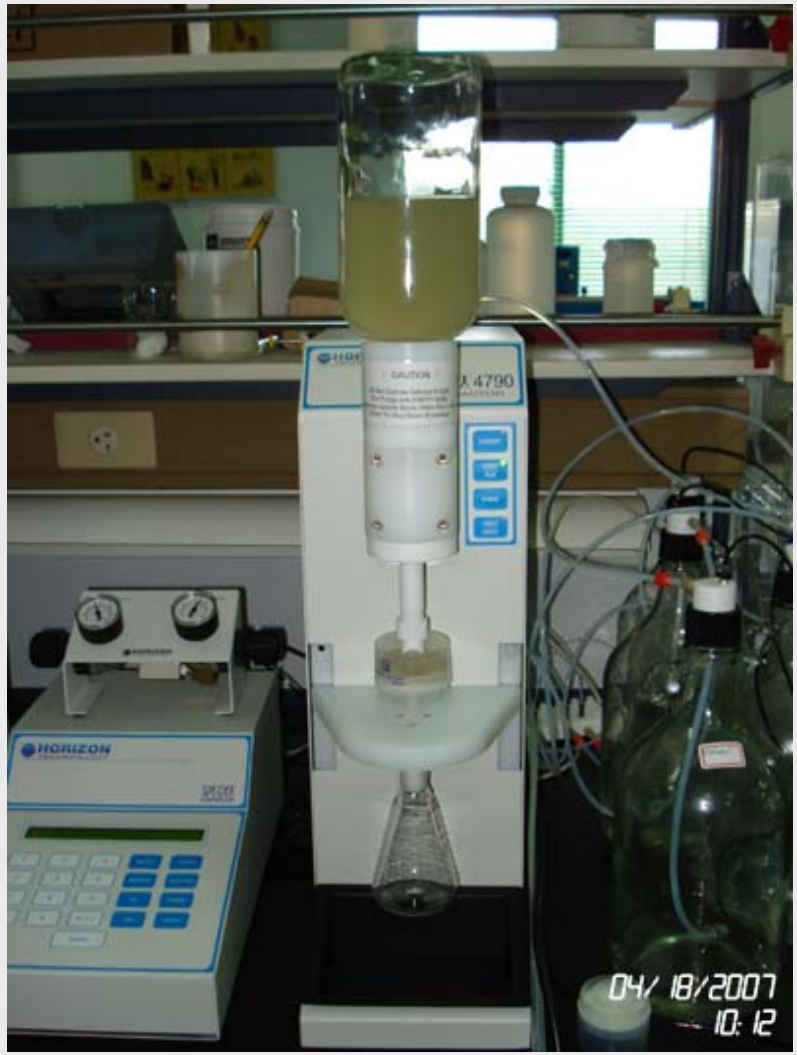
# River Water Sample from Taiwan




Automated SPE Disk Extraction of Chlorinated Pesticides

500 mL Extracted

Elapsed Time = 6 min

← Note the time clock

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# River Water Sample from Taiwan


Automated SPE Disk Extraction of Chlorinated Pesticides

Elapsed Time = 13 min

Note the time clock

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# River Water Sample from Taiwan


SPE-DEX Automated Disk Extraction Completed

1Liter River Sample Extracted in 14 Minutes

Unattended operation

Total Time = 14 min

← Note the time clock

# River Water Sample from Taiwan


Automated Extraction and SPE Disks Extract Sediment & Particulate Samples

- Fast
- Precise
- No Emulsions

Total Time = 14 min

**Note the time clock**

# Common Applications/Methods Using SPE Disk

- Drinking Water (EPA - 500 Series)
- Waste Water (EPA - 600 Series)
- Oil and Grease (EPA - 1664A)
- SW-846 (EPA - 3535A - 8000 Series)
- Endocrine Disruptors
- Hormones
- Food and Beverages
- Crops / Soils

# U.S. EPA SPE Solid Waste Methods

- 8061 Phthalate esters
- 8081 TCLP Organochlorine pesticides
- 8082 PCB's
- 8095 Explosives
- 8141 Organophosphorus pesticides
- 8270 TCLP Semi-volatiles
- 8321 TCLP Phenoxyacid herbicides
- 8330 Nitroaromatics / Nitramines

# Typical 8270 SPE Method

Prewet:

| Solvent | Soak Time (min:sec) | Dry Time (min:sec) |
|---|---|---|
| • DCM | 1:00 | 0:30 |
| • Acetone | 1:00 | 0:30 |
| • Water | 1:00 | 0:05 |
| • Water | 1:00 | 0:05 |

Extract Sample: Typically 5 – 10 min depending on % solids.

- Air dry disk: 0:05

Rinse

| Solvent | Soak Time (min:sec) | Dry Time (min:sec) |
|---|---|---|
| • Acetone | 3:00 | 0:30 |
| • DCM | 1:00 | 0:30 |
| • DCM | 1:00 | 0:30 |
| • DCM | 1:00 | 1:00 |

# Recovery of Phenols – EPA Method 8270

## SPE-DEX Automated Extractor System

Spike Level 5 ppb

| Compound | SPE Run 1 | 2 | 3 | Ave | SD | RSD |
|---|---|---|---|---|---|---|
| Phenol* | 93 | 90 | 87 | **90** | 3.12 | 3.45 |
| 2-chloro | 90 | 84 | 88 | **87** | 2.65 | 3.03 |
| 2-methyl | 103 | 92 | 100 | **98** | 5.54 | 5.64 |
| 4-methyl | 87 | 77 | 80 | **81** | 5.43 | 6.69 |
| 2,4-dimethyl | 56 | 49 | 52 | **52** | 3.60 | 6.87 |
| 2,4-dichloro | 91 | 81 | 83 | **85** | 5.54 | 6.53 |
| 2,6-dichloro | 94 | 85 | 87 | **89** | 4.79 | 5.40 |
| 4-chloro-3-methyl | 105 | 104 | 92 | **100** | 6.96 | 6.94 |
| 2,4,6-trichloro | 94 | 84 | 81 | **86** | 6.68 | 7.74 |
| 2,4,5-trichloro | 90 | 81 | 83 | **85** | 4.63 | 5.45 |
| 2,3,4,6-tetrachloro | 145 | 108 | 89 | **114** | 28.5 | 25.06 |

# Recovery of Poly Aromatic Hydrocarbons (PAH's)

## SPE-DEX Automated Extractor System

| Compound | RT | Ave Rcvry (n=3) | RSD (n=3) |
|---|---|---|---|
| naphthalene | 10.18 | **87.56** | 6.02 |
| 2-methyl naphthalene | 11.87 | **89.02** | 7.22 |
| 1-methyl naphthalene | 12.10 | **90.48** | 7.72 |
| acenaphthylene | 13.97 | **87.45** | 2.80 |
| acenaphthene | 14.41 | **78.41** | 3.63 |
| fluorene | 15.63 | **89.04** | 4.03 |
| phenanthrene | 17.86 | **89.50** | 5.40 |
| anthracene | 17.97 | **85.75** | 9.56 |
| fluoranthene | 20.65 | **91.65** | 8.34 |
| pyrene | 21.15 | **88.23** | 2.59 |
| benz(a)anthracene | 24.02 | **102.46** | 6.86 |
| chrysene | 24.10 | **109.31** | 1.93 |
| benzo(b)fluoranthene | 26.39 | **102.54** | 5.59 |
| benzo(k)fluoranthene | 26.44 | **108.54** | 2.90 |
| Benzo(a)pyrene | 27.02 | **105.38** | 10.66 |
| indeno(1,2,3-c,d-) perylene | 29.09 | **96.08** | 13.74 |
| Benz(a,h)anthracene | 29.17 | **99.92** | 3.06 |
| benzo(g,h,I)perylene | 29.51 | **92.46** | 9.28 |

# Persistent Organic Pollutants

Data Generated by the US EPA using the SPE-DEX 4790 Automated Extractor System

Compounds Listed in Red are POP's

| ng/L | Average | Recovery | % STDEV | MDL |
|---|---|---|---|---|
| TCMX | 35.6 | 71% | 8.5% | 8.5 |
| alpha-BHC | 42.4 | 85% | 4.3% | 4.3 |
| Lindane | 43.6 | 87% | 4.0% | 4.0 |
| beta-BHC | 49.0 | 98% | 4.1% | 4.1 |
| Heptachlor | 42.1 | 84% | 5.6% | 5.6 |
| delta-BHC | 41.2 | 82% | 5.0% | 5.0 |
| Aldrin | 38.6 | 77% | 5.2% | 5.2 |
| Hept Epoxide | 43.5 | 87% | 4.5% | 4.5 |
| gamma-Chlordane | 41.3 | 83% | 7.4% | 7.4 |
| alpha-Chlordane | 42.1 | 84% | 6.7% | 6.7 |
| Endosulfan I | 41.6 | 83% | 3.8% | 3.8 |
| p,p'-DDE | 35.2 | 70% | 9.5% | 9.5 |
| Dieldrin | 40.3 | 81% | 5.4% | 5.4 |
| Endrin | 40.8 | 82% | 7.1% | 7.1 |
| p,p'-DDD | 37.9 | 76% | 10.3% | 10.3 |
| Endosulfan II | 41.9 | 84% | 5.1% | 5.1 |
| p,p'-DDT | 44.8 | 90% | 11.2% | 11.2 |
| Endrin Aldehyde | 56.2 | 112% | 10.2% | 10.2 |
| Endosulfan Sulfate | 43.7 | 87% | 5.5% | 5.5 |
| Methoxychlor | 51.0 | 102% | 9.2% | 9.2 |
| Endrin ketone | 41.6 | 83% | 7.5% | 7.5 |
| Decachlorobiphenyl | 42.6 | 85% | 7.9% | 7.9 |

# Trace Level PCBs in Water (1 ppt)

Northeast Analytical, Inc.
2190 Technology Dr., Schenectady, NY

- Rugged, Fast and Cost effective
- Achieves MDLs (1 PPT (ng/L) for 8-liter samples and 9 PPT (ng/L) for 1-liter samples)
- Reproducible results
- Capable of extracting 1 to 8 liter sample volume
- Minimal solvent usage  (30ml/sample)
- No glassware to replace or clean
- Unattended operation
- Limited technician time
- Easy to use

# MDL for PCB Congeners

## 1-Liter Analysis - 1.25 ng/L per Congener Spiked

| Congener IUPAC# | Conc ng/L | Rcvry (%) | SD (ng/L) | RSD (%) | MDL (2) (ng/L) |
|---|---|---|---|---|---|
| 22 | 1.24 | **98.92** | 0.06 | 5.11 | 0.20 |
| 23 | 1.25 | **100.01** | 0.04 | 3.46 | 0.14 |
| 24 | 1.24 | **98.86** | 0.04 | 3.00 | 0.12 |
| 25 | 1.20 | **96.21** | 0.02 | 1.26 | 0.05 |
| 26 | 1.32 | **105.38** | 0.04 | 2.93 | 0.12 |
| 27 | 1.24 | **98.86** | 0.04 | 3.00 | 0.12 |
| 28 | 1.14 | **91.46** | 0.06 | 4.86 | 0.17 |
| 29 | 1.29 | **103.00** | 0.06 | 4.55 | 0.18 |
| 30 | 1.16 | **92.69** | 0.04 | 3.51 | 0.13 |
| 31 | 1.20 | **96.40** | 0.05 | 4.00 | 0.15 |
| 32 | 1.21 | **96.91** | 0.06 | 5.21 | 0.20 |
| 33 | 1.32 | **105.62** | 0.04 | 2.73 | 0.11 |
| 34 | 1.25 | **100.20** | 0.04 | 3.06 | 0.12 |

**Data From Northeast Analytical Lab using SPE-DEX 4790 Automated Extractor System**

# Emerging SPE Methods

- Endocrine Disruptors
  - Nonyl Phenol and Bisphenol A
  - Estrogens
- Microcystins
- Tri-Butyl Tin
- TPH – Total Petroleum Hydrocarbons
- GRO's and DRO's (Gas and Diesel Range Organics)
- SPE – IR for Off-Shore Oil Platforms

# Nonyl Phenol

- Endocrine Disruptors – Nonyl Phenol
  - SPE Work done in Japan by Horizon distributor
  - 3M SDB-XD 47mm disk
  - 0.1 ppm spiked with 1 liter sample
  - Prewet 1 = 50% Methanol / 50% Acetone
  - Prewet 2 = Methanol
  - Prewet 3 = Reagent Water
  - Wash 1 = Reagent Water
  - Rinse 1 = 50% Methanol / 50% Acetone
  - HPLC = ODS-3 4.6mm ID, 150mm length
  - Mobile phase = 60% acetonitrile and 40% water, pH 2.6
  - Flow rate = 1.0 ml.min
  - UV at 270 nm

| Recovery Values |
| --- |
| Run 1 = 89.7% |
| Run 2 = 86.8% |
| Run 3 = 90.8% |
| Run 4 = 92.4% |
| Run 5 = 90.8% |
| Run 6 = 90.4% |
| Run 7 = 91.9% |
| Run 8 = 92.9% |
| Ave = 90.7% |
| RSD = 2.1% |

# Bisphenol A

- Endocrine Disruptors – Bisphenol A
  - SPE Work done in Japan by distributor
  - 3M SDB-XD 47mm disk
  - 0.1 ppm spiked with 1 liter sample
  - Prewet 1 = 50% Methanol / 50% Acetone
  - Prewet 2 = Methanol
  - Prewet 3 = Reagent Water
  - Wash 1 = Reagent Water
  - Rinse 1 = 50% Methanol / 50% Acetone
  - HPLC = ODS-3 4.6mm ID, 150mm length
  - Mobile phase = 40% acetonitrile and 60% buffer solution, pH 2.7
  - Flow rate = 1.0 ml.min
  - UV at 270 nm

| Recovery Values |
| --- |
| Run 1 = 93.8% |
| Run 2 = 92.1% |
| Run 3 = 98.2% |
| Run 4 = 96.1% |
| Run 5 = 94.8% |
| Run 6 = 93.4% |
| Run 7 = 92.6% |
| Ave = 94.4% |
| RSD = 2.3% |

# Estrogens

17-α estradiol, 17-β estradiol, estrone, 17a-ethinylestradiol

BAKERBOND™ *Speedisk* Extraction Disk C18 XF

The pH of the 2L water samples was adjusted to 7 using HCl or NaOH (1 M).

**CONDITIONING STEP**
20 ml Acetone
20 ml Methanol
2 x 10 ml Water

**SAMPLE LOADING STEP**

**WASHING STEP**
No washing
Disk dried under vacuum for at least 30 min

**ELUTION STEP**
(max 1 ml/min)
5 ml Acetone
15 ml Methanol

| Compounds | Recovery (%)±SD* | Recovery (%)±SD** |
|---|---|---|
| 17-α estradiol | 105 ± 20 | 107 ± 22 |
| 17-β estradiol | 104 ± 25 | 103 ± 27 |
| Estrone | 108 ± 21 | 107 ± 18 |
| 17a-ethinylestradiol | 102 ± 21 | 103 ± 27 |

JT Baker Application Note

## Effect of SPE Dry Time on Recoveries

| | Microcystins | Dry Time (min) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0 | 5 | 10 | 20 | 40 | 80 |
| C18 SD | RR | 100 | 103 | 85 | 86 | 78 | 39 |
| | YR | 101 | 95 | 83 | 82 | 64 | 22 |
| | LR | 99 | 103 | 89 | 89 | 70 | 30 |
| SDB-XD | RR | 95 | | 84 | | | 71 |
| | YR | 100 | | 95 | | | 70 |
| | LR | 102 | | 99 | | | 83 |

# Hormones / Antibiotics

Estrone, 17β-estradiol, estriol, 16α-hydroxyestrone, 17α-ethinylestradiol, mestranol, bestradiol, 17-acetate, β-estradiol 3-sulfate, estone 3-sulfate, roxithromycin, clarithromycin, erythromycin

## BAKERBOND *Speedisk* Hydrophobic DVB Extraction Disk

**CONDITIONING STEP**

15 ml Methanol
15 ml Water

**SAMPLE LOADING STEP**
(10 ml/min)

**WASHING STEP**

15 ml water
Air dried for 5 min

**ELUTION STEP** (max 1 ml/min)

15ml *terc*-butyl methyl ether
15 ml methanol

| Analytes | Recovery (%) | RSD (%)* |
|---|---|---|
| mestranol | 105±12 | 11 |
| 16α-hydroxyestrone | 74±15 | 21 |
| 17β-estradiol | 98±9 | 9 |
| Estrone | 105±16 | 15 |
| 17α-ethinylestradiol | 83±6 | 7 |
| 17β-estradiol acetate | 109±15 | 14 |
| β-estradiol 3-sulfate | 92±8 | 9 |
| estone 3-sulfate | 95±12 | 13 |
| estriol | 58±14 | 24 |
| clarithromycin | 82±6 | 7 |
| erythromycin | 100±15 | 15 |
| roxithromycin | 79±8 | 11 |

## JT Baker Application Note

# Paracetamol, Caffeine, *N,N*-diethyl-3-toluamide, Carbamazepine, Oxazepam, Fluoxetine, Metoprolol, Propranolol, Estrone, 17ß-Estradiol, Clofibric acid, Bezafibrate, Ibuprofen, Diclofenac

## BAKERBOND™ SDB-1

**CONDITIONING STEP**

5 ml hexane
5 ml ethylacetate
10 ml methanol
10 ml water

**SAMPLE LOADING STEP**
(15 ml/min)

Sample (1 L)

**WASHING STEP** (5 ml/min)

5 ml water
Dried under nytrogen

**ELUTION STEP**

30 ml methanol

| Compound | Recovery (%) |
|---|---|
| Paracetamol | **60** |
| Caffeine | **99** |
| *N,N*-diethyl-3-toluamide | **96** |
| Carbamazepine | **100** |
| Oxazepam | **65** |
| Fluoxetine | **69** |
| Metoprolol | **81** |
| Propranolol | **68** |
| Estrone | **92** |
| 17ß-Estradiol | **96** |
| Clofibric acid | **54** |
| Bezafibrate | **55** |
| Ibuprofen | **46** |
| Diclofenac | **42** |

## JT Baker Application Note

# Tri-butyl Tin (Marine Sediments)

- Adjust 100 ml sample, containing 1-2% methanol to pH 4.5
- Use C18 disk
- Prewet 1 = Ethyl Acetate
- Prewet 2 = Methanol
- Prewet 3 = Reagent Water pH 7.0
- Prewet 4 = Reagent Water pH 4.5
- Filter sample through disk
- Dry SPE Disk in desiccator overnight
- Elute with Ethyl Acetate (acidified with HCL)
- Refrigerate extract overnight – for stability

**Otis Evans, Betty Jacobs, and Arnold Cohen - US EPA, Cincinnati, OH**

**Analyst, January 1991, Vol; 116**

# Application Note Downloads

**http://www.horizontechinc.com**

| Automated Solid Phase Extraction Notes | |
|---|---|
| EPA Method 506 | Phthalate and Adipate Esters |
| EPA Method 508.1 | Chlorinated Pesticides, Herbicides and Organohalides |
| EPA Method 515.2 - Note 1<br>EPA Method 515.2 - Note 2 | Chlorinated Acids |
| EPA Method 525.2 - Note 1<br>EPA Method 525.2 - Note 2 | Semivolatile Organic Compounds |
| EPA Method 526 | Semivolatile Organic Compounds |
| EPA Method 548.1 - Note 1<br>EPA Method 548.1 - Note 2 | Endothall |
| EPA Method 549.1 | Diquat and Paraquat |
| EPA Method 550.1<br>PAH Note | Polycyclic Aromatic Hydrocarbons (PAHs) |
| EPA Method 552.1 - Note 1<br>EPA Method 552.1 - Note 2 | Haloacetic Acids and Dalapon |
| EPA Method 608 - Note<br>EPA Method 608 - Note 2 | Chlorinated pesticides and PCB's |
| EPA Method 625 | Bases, Neutrals and Acids |
| EPA Method 1664A - Note 1<br>EPA Method 1664A - Note 2 | N-Hexane Extractable Material; Oil and Grease |
| EPA Method 1668A | Chlorinated biophenyl congeners by HRGC/HRMS |
| EPA Method 8015 - Note 1<br>EPA Method 8015 - Note 2 | Total Petroleum Hydrocarbons (TPH) |
| EPA Method 8061A | Phthalate Esters |
| EPA Method 8081A | Automated Solid Phase Extractions of Organochlorine Pesticides from Water Using Certified for Automation Atlantic SPE Disks |
| EPA Method 8081B | Organochlorine Pesticides |
| EPA Method 8082A - Note 1 | Polychlorinated Biphenyls (PCBs) |
| EPA Method 8082A - Note 2 | NEW Application of Automated Solid Phase Extraction for Determination of Polychlorinated Biphenyls (PCB) in Water |
| EPA Method 8141B - Note 1<br>EPA Method 8141B - Note 2 | Organophosphorus Compounds |
| EPA Method 8270D - Note 1<br>EPA Method 8270D - Note 2<br>EPA Method 8270D - Dual pH | Semivolatile Organic Compounds |
| EPA Method 8321B | Solvent-Extractable Nonvolatile Compounds |
| EPA Method 8330A | Nitroaromatics & Nitramines |

**Unique Studies**

High Throughput Multi-Residue Screening of Drinking Water using the SPE-DEX and Pegasus GC-TOF MS

Analysis of Bentazone in River Water

**DryVap Notes**

Fast Solvent Exchange DryVap® System Procedure for Pesticides and PCBs

Impact of Excessive Solvent Washing on Recovery Values

Neutral and List 1 Pesticides with Horizon Technology DryVap® Concentrator System.

Optimizing the DryVap® System for use with High Boiling Solvent Mixtures

Recoveries of Organochorine Pesticides Using MeCl with the DryVap™ System

Solvent Exchange with DryVap® System for Organochorine Pesticides with GC-ECD

Using the Learn Mode to Optimize Recoveries With the DryVap™ System

Concentrating PCB Congeners 10 Thousand Fold with Horizon DryVap™ Automated Concentrator System

**Dry Disk Notes**

Study of DryDisk Background Contamination

An Improved Solvent Drying Technique for Enhanced Recovery of Organic Compounds

**GC Racer Notes**

Fast Separation of TRPH and Diesel Fuel with GC Racer

5 Minute Analysis of Organochlorine Pesticides with GC Racer

# Summary

- SPE Disks are a proven technique
- Automation is a cost effective solution to laboratory sample throughput problems
- There are significant advances to automating sample preparation for trace analysis
- Wide Range of Applications developed for SPE disks
- New SPE disk packing materials are being developed for enhanced analyte recoveries


Questions?