Solid Phase Extraction: A Century of Chemical Development Combined with Recent Technological Advancements to Tackle Increasing Application Challenges

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Sample Preparation
Relevance

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"Good data out requires good data in"

- Basic analytical workflow:
  - sample collection
  - sample preparation
  - sample analysis
  - data reporting
- To ensure successful data generation, the sensitivity and accuracy requirements of the application must be met, while managing the challenges and pitfalls inherent to the workflow

Ensure that the stuff you are looking for can be found accurately and reliably

Sample Preparation
Challenges

- Sample preparation is often the most important step in the workflow, however…
  - Analysts without the proper skills are tasked with this step
  - Analysts are tasked with processing many samples
  - Analysts have different backgrounds and varying levels of experience

How do we produce accurate, reliable data from day to day, analyst to analyst?

The sample preparation step can contribute up to 20% in the total analysis variability

J. Lyn, M. Ramsey, R. Fussell, and R. Wood, Analyst, 2003, **128**, 1391-1398.

Sample Preparation

Evolution of the Technique

Liquid-Liquid Extraction → Solid Phase Extraction

Solid Phase Extraction

Benefits of Automation

Liquid-Liquid Extraction → Solid Phase Extraction

Laboratory Benefits:

- Use less solvent
- Generate less hazardous waste
- Produce fewer emulsions
- Use tailored, more selective chemistry
  - Improve analyte recoveries
- Reduce matrix interferences
  - Improve detection limits

Automation Benefits:

- Reduce transfer errors/losses
- Improve accuracy and reproducibility
- Flexibility to tackle challenging matrices

Solid Phase Extraction Media

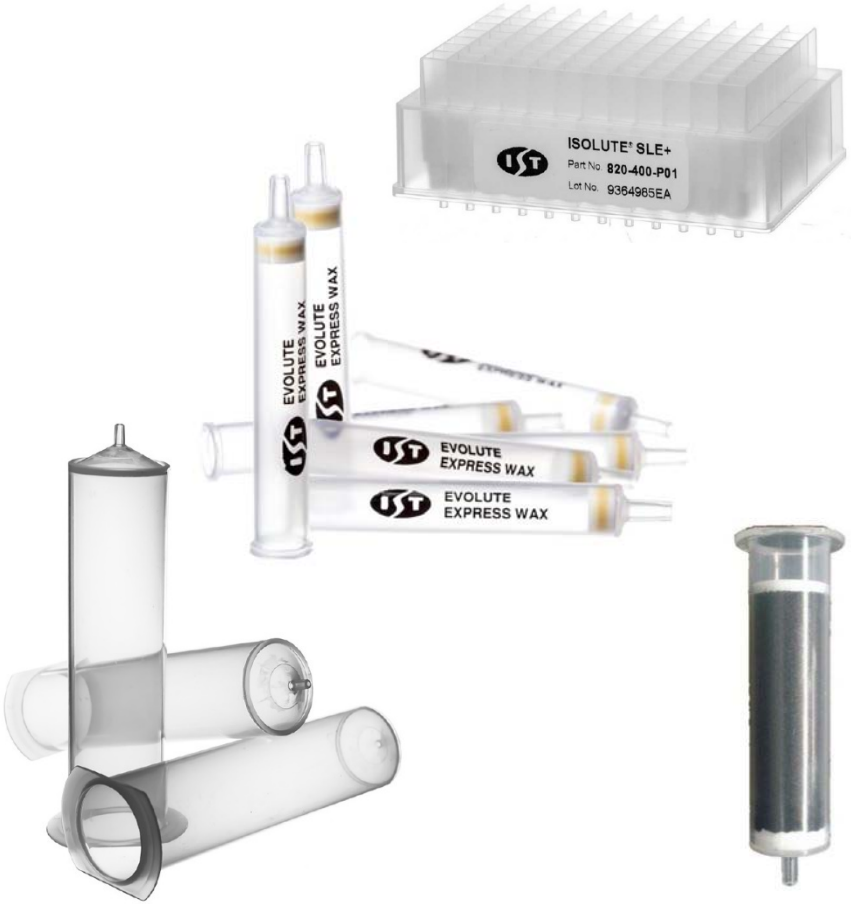
Examples and Characteristics

- C18 (octadecyl bonded silica) – EPA Method 525.2
  - Reversed phase media (hydrophobic interaction)
  - Effective for many compound classes, pH ranges 2-12
- DVB/SDVB (divinylbenzene/styrene divinylbenzene) – EPA Method 525.3
  - Reversed phase media
  - 3 to 5x more capacity over C18
- HLB (hydrophilic/lipophilic balanced) – EPA Method 608.3
  - A SDVB or DVB that is copolymerized with a hydrophilic moiety
  - Ideal for reversed phase and a range of polar compounds
  - 3 to 5x more capacity over C18
- C8 Silica – EPA Method 549.2
  - Less retentive than C18 for non-polar compounds
  - Method for paraquat /diquat analysis uses hexanesulfonic acid as an ion-pairing reagent for these two quaternary amine analytes
- Ion Exchange (SAX, SCX, WAX, WCX) – PFC expanded list
  - Resin based media with charged functional groups – amines, sulfonyl groups, etc
  - Ideal for capturing polar compounds (acidic and basic)

Solid Phase Extraction Formats

Examples and Characteristics

Cartridges



» Disks

SPE Product Development

Disk Holders

Reusable disk holders

- Economical
  - Recurring cost just for the disks
  - Reduction in solid waste generation
- Accommodate any media type
- Adaptable to meet the demands of any application
  - Mesh screens
  - Pre-filters
  - Glass wool

WHY?

SPE Product Development

Disk Holders

Adaptable to meet the demands of any application

SPE Product Development
Disk Holders

Disposable disk holders

- The chemical capacity achievable with a reusable disk holder, the speed and convenience of a disposable disk holder
- Economical
  - Speed – accommodate the highest throughput demands
  - Convenience – no assembly, “dish washing” or training for new users
  - Built-in Pre-filter Capability

Example Applications

Extraction of pesticides and herbicides

Application

- Extraction of mixed-polarity analytes:
  - Polar: acid herbicides
  - Non-polar: chlorinated pesticides, PAHs, PCBs

Challenge

- Smaller, polar compounds, retained better on strongly retentive media
- Larger, non-polar compounds, retained better on weakly retentive media

Solution

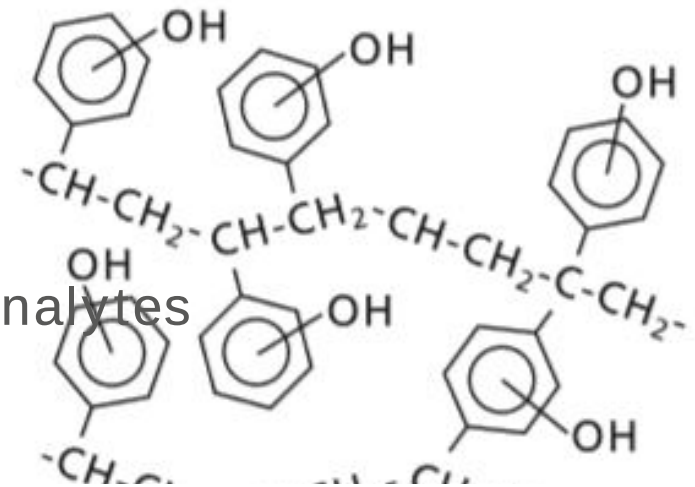
- Layered columns
- Tailor the chemistry to the target analytes

Example Applications

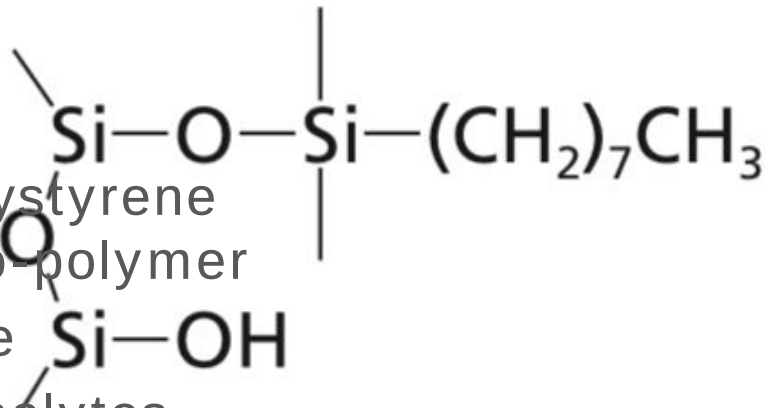
Extraction of pesticides and herbicides

Layered Column

- Top Layer
  - C_8 – silica based
  - Weakly retentive
  - Captures non-polar analytes



- Bottom Layer
  - Hydroxylated polystyrene divinylbenzene co-polymer
  - Strongly retentive
  - Captures polar analytes



Example Applications

Extraction of pesticides and herbicides

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Extraction

- Sample pre-treatment
  - Acidify sample to pH 2 with HCl
  - Add methanol (1%, v/v)
- Column Conditioning
  - Methanol
- Column Equilibration
  - Water
- Sample Load
  - Load sample up to 60 mL/min
- Column Drying
  - Air dry for 10 mins
- Sample Elution
  - 1:1 (v/v) acetone: ethyl acetate

Example Applications

Extraction of pesticides and herbicides

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Example Data

Analyte	% Recovery	Analyte	% Recovery
BASE NEUTRAL HERBICIDES		**PHENOLS**	
Metribuzin	90	Phenol	84
Atrazine	92	2-chlorophenol	90
Desethyl atrazine	89	2-nitrophenol	87
Ametrine	90	4-chloro-3-methylphenol	86
Terbutaline	95	**PAHs**	
Metolachlor	95	Naphthalene	87
ACID HERBICIDES		Acenaphthalene	90
MCPA	95	Fluorene	92
MCPB	94	Pyrene	96
MCPP	92	Benzo(a)anthracene	96
Bentazone	88	Benzo(a)pyrene	95

Example Applications

Wastewater Analysis

Example Applications
Wastewater Analysis

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Extraction Protocol

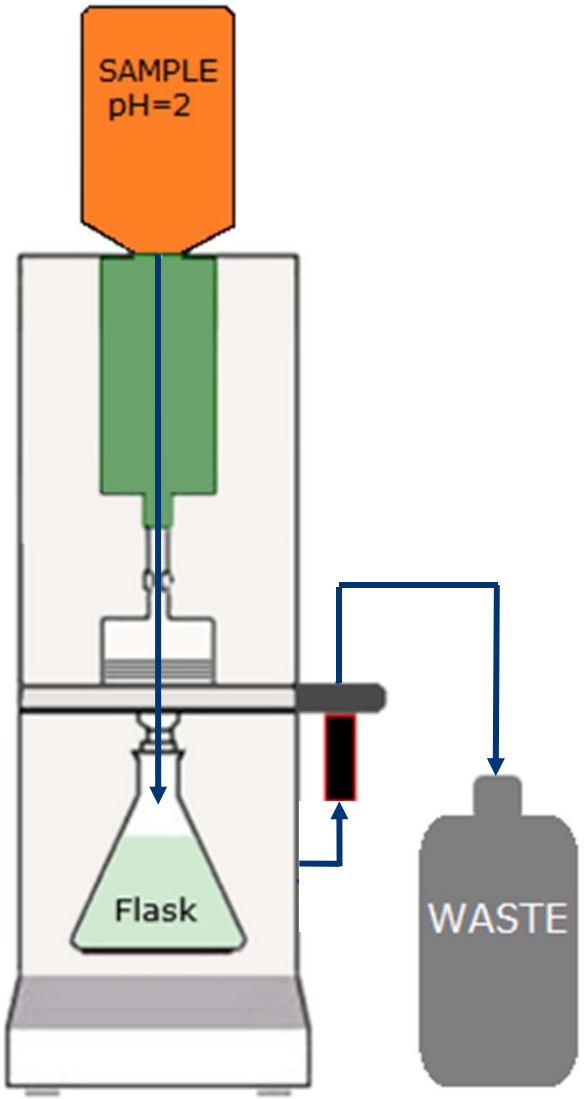
- Fast Flow Disk Holder
  - Accommodates high capacity filter materials to remove coarse and fine particulates before reaching the SPE disk
- Atlantic® 8270 One Pass Disk (47 mm)
  - SPE disk with HLB and ion exchange media for multi-mode functionality
  - Extracts bases, neutrals and acids at pH 2
  - Eliminates basification step and eliminates metal hydroxide precipitation
- One Pass Carbon Cartridge
  - Recovers light-end organics from post-disk sample effluent (hydrophilic compounds)
  - Ex. NDMA, benzyl alcohol, & methyl methanesulfonate

Example Applications

Results – Recovery Data for MS and MSD

Analyte	Avg. MS, MSD Recovery (%)	Acceptance Range (%)	RPD (%)	RPD Limit (%)
Fluorene	85.1	59-121	5.18	38
Hexachlorobutadiene	48.8	24-120	5.56	62
Aniline*	84.0		7.85	
Benzidine*	105.5		9.38	
Naphthalene	71.4	21-133	4.06	65
Pentachlorophenol	93.5	14-176	3.03	86
Phenol	62.2	5-120	5.59	64
Phenanthrene	88.8	54-120	6.07	39
2,4-dichlorophenol	89.0	39-135	0.47	50
Isophorone	85.0	21-196	0.36	93
Dibenzofuran*	82.7		6.37	

*Table 3 compound – no method-defined acceptance criteria



Summary

- Sample preparation accounts for a significant portion of the success of an analytical workflow
- Automating sample preparation (and moving from LLE to SPE) improves accuracy and reproducibility:
  - Sample to sample
  - Day to day
  - Technician to technician
- Improved data quality increases the ease with which a laboratory maintains EPA compliance
- General benefits to SPE advancements:
  - Improved lab efficiency, regardless of sample load, sample volumes, sample matrices
  - Reduce operating costs – improve lab profits
  - Improve SOP ruggedness – turnover, sample throughput