New Developments for "Greener" EPA Methods

Joseph Stefkovich
Xenosep Technologies
508 Main Street
Boonton, NJ 07005
P: 973.239.0247
joe.stefkovich@xenosep.com

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Abstract

Solid Phase Extraction (SPE) is a technology that has been around for several decades. The Green Chemistry benefits of reduced solvent usage, reduced solvent disposal cost and reduced solvent exposure to the analyst offered by SPE technology are more important today than ever before. However, many existing EPA methods still specify Liquid-Liquid Extraction (LLE) and the subsequent use of copious amounts of solvent, including dichloromethane, to perform the sample extraction. The author will review a variety of innovative developments that have been made in recent years to improve SPE technology so it can be more readily employed to help to make many existing EPA Methods "greener" in the future.

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Acknowledgement

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Twelve Principles of Green Chemistry

- Green chemistry, also known as sustainable chemistry, is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, and use.

- The 12 Principles of Green Chemistry, originally published by former EPA Assistant Administrator Paul Anastas, Ph.D. and John Warner, Ph.D. in ***Green Chemistry: Theory and Practice*** (Oxford University Press: New York, 1998), provide a road map for chemists to implement green chemistry.

http://www.epa.gov/sciencematters/june2011/principles.htm

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Twelve Principles of Green Chemistry

- **Prevention**
  It's better to prevent waste than to treat or clean up waste afterwards.

- **Atom Economy**
  Design synthetic methods to maximize the incorporation of all materials used in the process into the final product.

- **Less Hazardous Chemical Syntheses**
  Design synthetic methods to use and generate substances that minimize toxicity to human health and the environment.

http://www.epa.gov/sciencematters/june2011/principles.htm

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Twelve Principles of Green Chemistry

- **Designing Safer Chemicals**
  Design chemical products to affect their desired function while minimizing their toxicity.

- **Safer Solvents and Auxiliaries**
  Minimize the use of auxiliary substances wherever possible make them innocuous when used.

- **Design for Energy Efficiency**
  Minimize the energy requirements of chemical processes and conduct synthetic methods at ambient temperature and pressure if possible.

http://www.epa.gov/sciencematters/june2011/principles.htm

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Twelve Principles of Green Chemistry

- **Use of Renewable Feedstocks**
  Use renewable raw material or feedstock rather whenever practicable.

- **Reduce Derivatives**
  Minimize or avoid unnecessary derivatization if possible, which requires additional reagents and generate waste.

- **Catalysis**
  Catalytic reagents are superior to stoichiometric reagents.

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Twelve Principles of Green Chemistry

- **Design for Degradation**
  Design chemical products so they break down into innocuous products that do not persist in the environment.

- **Real-time Analysis for Pollution Prevention**
  Develop analytical methodologies needed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

- **Inherently Safer Chemistry for Accident Prevention** Choose substances and the form of a substance used in a chemical process to minimize the potential for chemical accidents, including releases, explosions, and fires.

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What makes a product "greener"?

- The answer to what makes a product "green" can be complicated.
- Generally, a product may be considered "greener" if scientific evidence demonstrates that human health or environmental impacts have been significantly reduced in comparison with other products that serve the same purpose.
- EPA works with manufacturers, environmental organizations, consumer groups and our federal and state partners to support the development of standards and criteria for greener products using EPA's scientific expertise.

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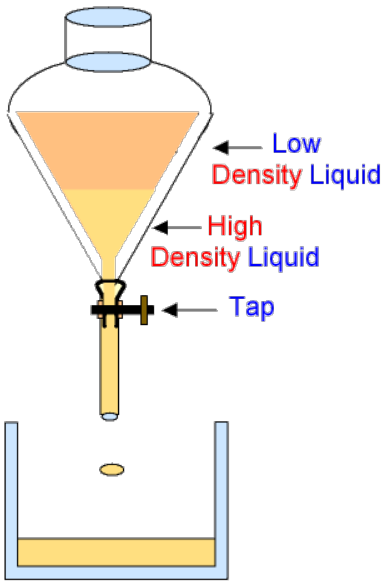
Sample Prep – a Necessary Evil

- The best sample prep is no sample prep
- Most instruments are not capable of handling complex samples directly and, as a result, a sample preparation step is unavoidable.
- The main goals of sample preparation
  - Clean up, isolate, and concentrate the analytes of interest
  - Render the final extract in a form that is compatible with the subsequent analytical system

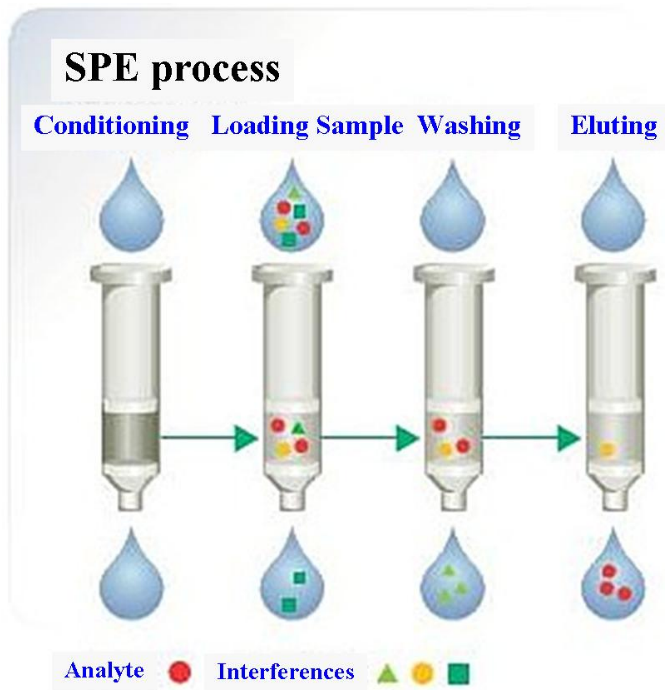
EPA Method 625 (proposed) Green Chemistry Comparison

LLE – DCM – 400mL



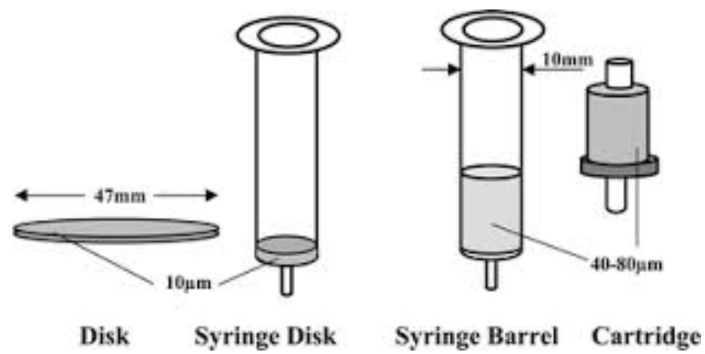
SPE – DCM – 90mL
ACE – 40mL

Solid Phase Extraction Process



Traditional SPE Products

- 1903 - Tswett extracts plant pigments
- 1970's - SPE Columns and Cartridges
- 1990's - SPE Filters
- 1990's - SPE Automation



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Google Scholar
“Text” and “Environmental”

Results	Acronym	Text
218,000	SPE	Solid Phase Extraction
58,200	LLE	Liquid Liquid Extraction
30,300	SPME	Solid Phase Micro Extraction
23,100	SFE	Supercritical Fluid Extraction
12,600	P&T	Purge and Trap
10,800	UE	Ultra Sonic Extraction
8,580	ASE	Accelerated Solvent Extraction
7,590	ME	Microwave Extraction
5,430	LPME	Liquid Phase Micro Extraction

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Google Scholar "Text" and "Environmental"

Results	Acronym	Text
5,020	CPE	Cloud Point Extraction
4,980	PLE	Pressurized Liquid Extraction
3,990	MSPD	Matrix Solid Phase Dispersion
3,870	SBSE	Stir Bar Sorptive Extraction
3,670	DLLME	Dispersive Liquid Liquid Micro Extraction
3,170	LVI	Large Volume Injection
2,660	DSPE	Dispersive Solid Phase Extraction
2,560	SDME	Single Drop Micro Extraction
1,060	MASE	Microwave Assisted Solvent Extraction

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Google Scholar
"Text" and "Environmental"

Results	Acronym	Text
727	SHS	Static Head Space
518	MSPE	Magnetic Solid Phase Extraction
355	DHS	Dynamic Head Space
256	MLLE	Micro Liquid Liquid Extraction
177	NDBE	Needle Device Based Extraction
142	MESI	Membrane Extraction Sorbent Interface
136	TFME	Thin Film Micro Extraction
101	ITEX	In Tube Extraction
14	SHWE	Super Heated Water Extraction

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New SPE Developments

- SPME Solid Phase Micro Extraction
- MSPD Matrix Solid Phase Dispersion
- SBSE Stir Bar Sorptive Extraction
- DSPE Dispersive Solid Phase Extraction
- MSPE Magnetic Solid Phase Extraction

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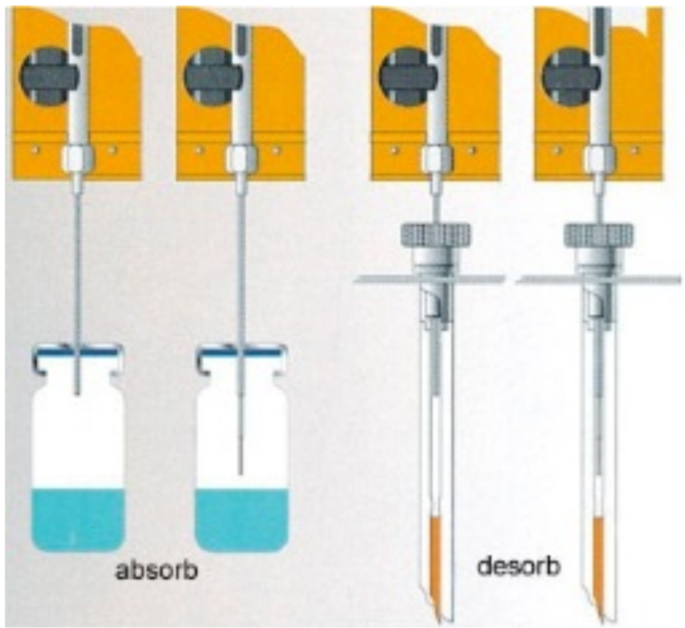
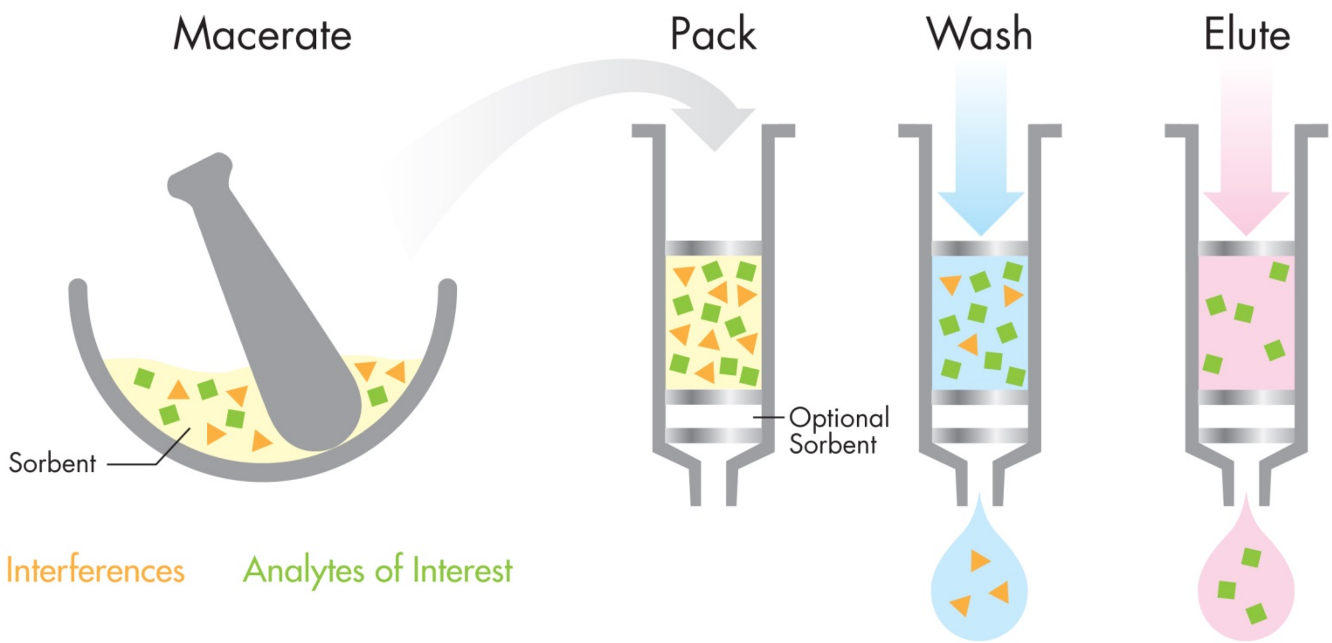
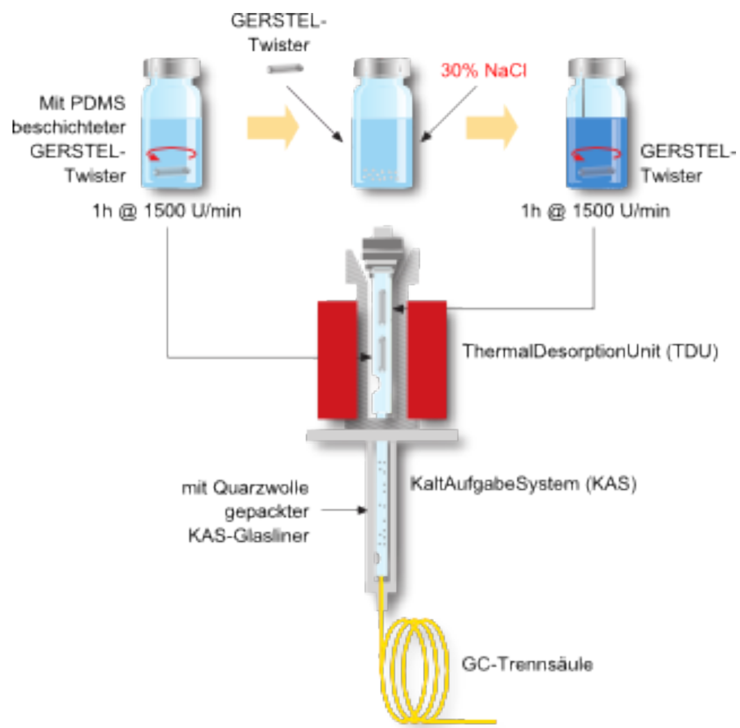
SPME
Solid Phase Micro Extraction



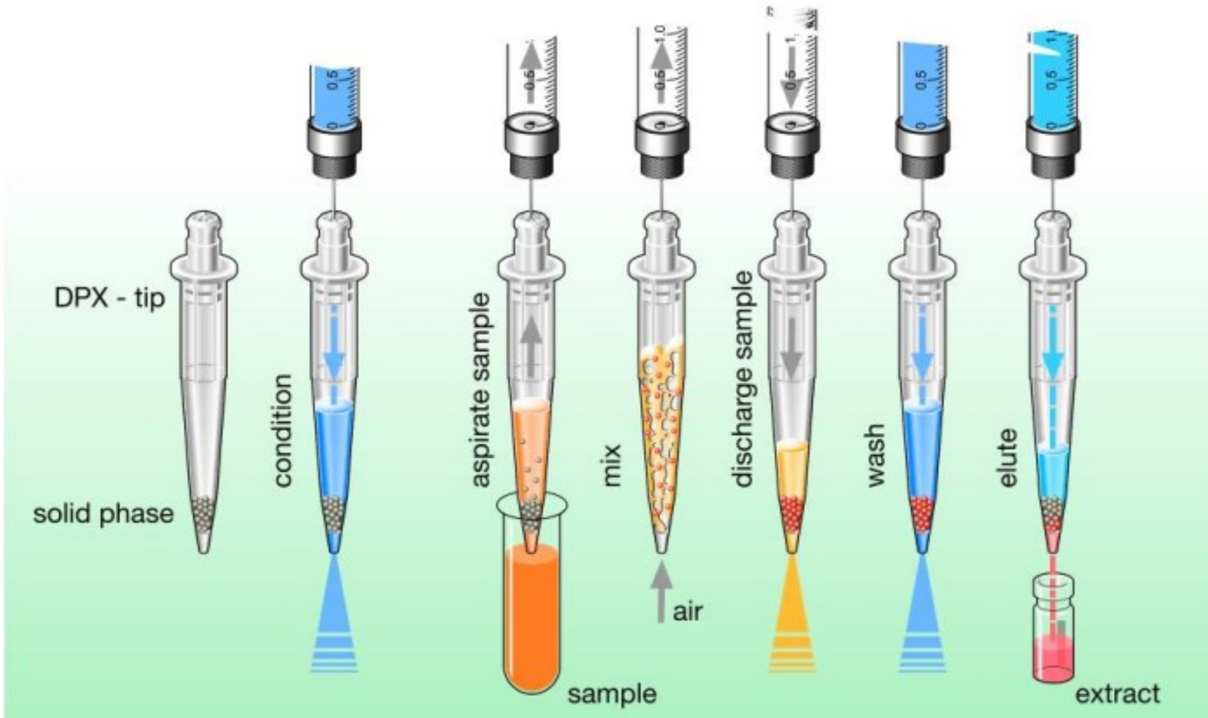
MSPD
Matrix Solid Phase Dispersion



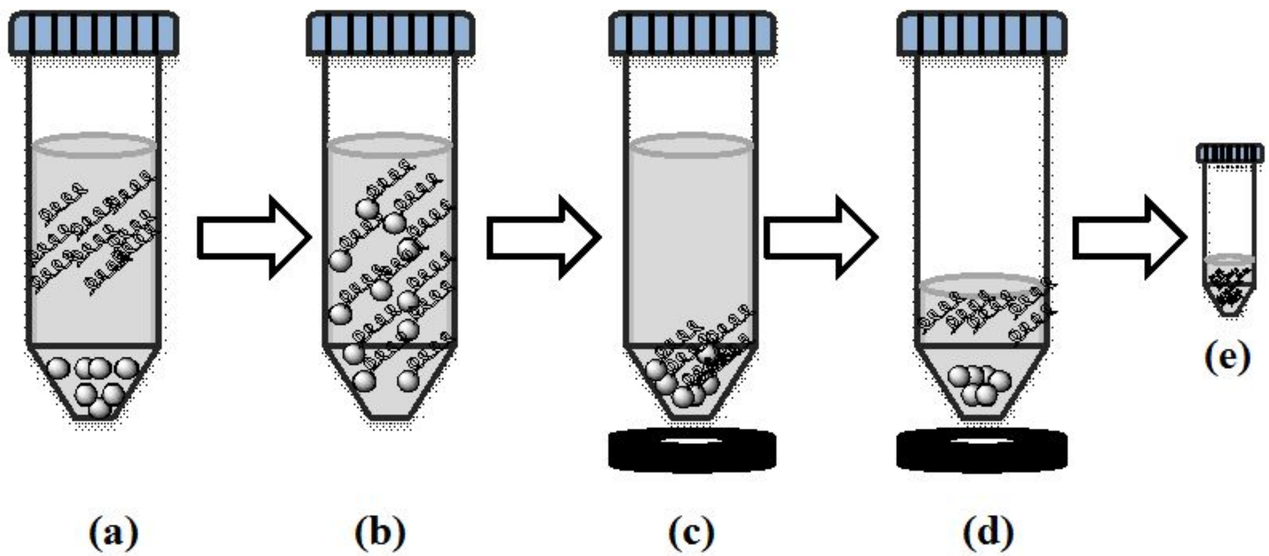
SBSE
Stir Bar Sorptive Extraction



DSPE
Dispersive Solid Phase Extraction



MSPE
Magnetic Solid Phase Extraction



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New SPE Success

- Appropriate for the Application
- High Recovery and Reproducibility
- Handle Matrix and Interferences
- Faster – less tedious and time consuming
- Less Expensive
- Easy to Automate

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European PAHs at 10ng/L Green Method Comparison

Method	LLE	SPE	SBSE
Sample (mL)	500	100	5
Solvent (mL)	75 DCM	5 ACE	-
Hexane	1mL/2µL	0.2mL/2µL	-
On column	2pg	10pg	50pg

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Conclusions – Dr. Pat Sandra

- Many different SPE methods reduce or eliminate solvent consumption
- Implementation is not always straightforward
  - Regulatory requirements
  - (Re)validation studies
  - Obtaining accreditation
- Implementing these new developments, especially those that can be automated, into routine laboratories is an important step in greening analytical chemistry.

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Questions? More information?

Joseph Stefkovich
Xenosep Technologies
508 Main Street
Boonton, NJ 07005
Tel: 973.239.0247
Joe.stefkovich@xenosep.com

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