A Review of Solid Phase Sorbents Over Time As Applied to Environmental Applications

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Abstract

- Sample preparation using solid phase extraction (SPE) has been in use for several decades. Over this time period the solid phases or sorbent materials used for extractions have been engineered into many different types and formats to solve specific or generic sample preparation problems in a wide variety of applications.
- This presentation will review the various silica and resin based sorbents used in environmental applications over time and use a selected development case for semi-volatile organics to provide an example on how analytical challenges can be met using multi-modal SPE.
- Additional discussion will look toward where SPE media may be headed in the future.

Definition of SPE

- Solid Phase Extraction (SPE) is a method of sample preparation that concentrates and purifies analytes from solution, by sorption onto a suitable sorbent material, followed by elution of the analyte(s), with a solvent that will remove the analytes of interest from the sorbent material.
- SPE can be used as a clean-up mechanism where the interferences are retained on the sorbent and the analytes pass through.
- The mechanisms of retention include reverse phase, normal phase, and ion exchange.
- SPE can be used to complement or replace Liquid-Liquid Extraction (LLE).

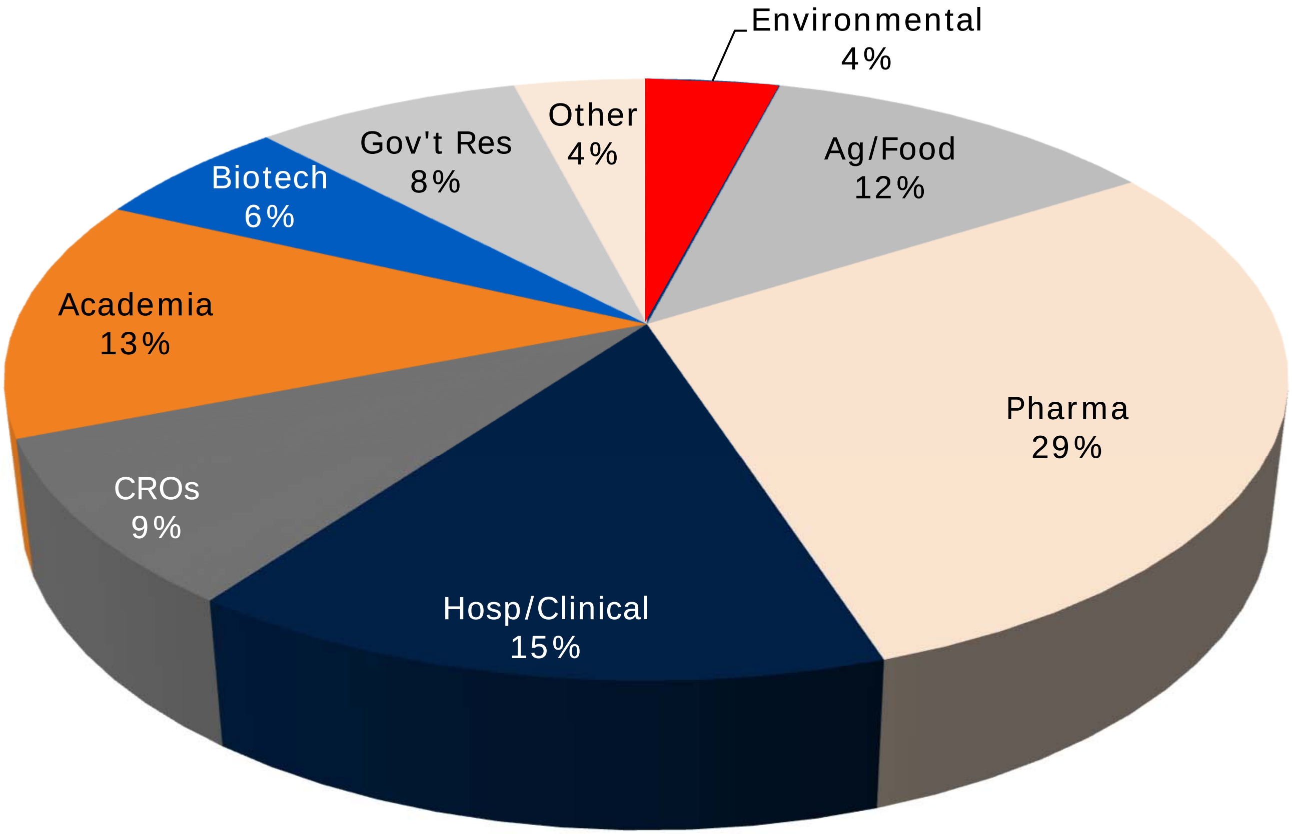
Why SPE is Used

- Traditionally, sample preparation consisted of dissolution, purification, and extraction, all carried out by LLE

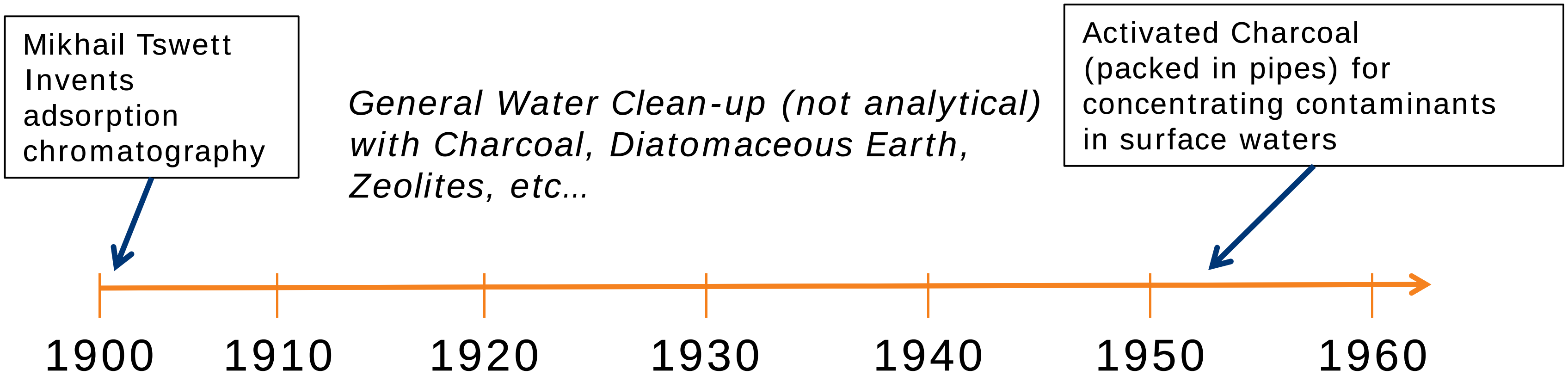
- LLE has many disadvantages
    - Uses large volumes of solvent
    - Cumbersome labware
    - Creates emulsions
    - Difficult to automate

- Key Point - LLE is an ***equilibrium*** process

Where is SPE used Today?



SPE Development Timeline
1900 to the 1950s



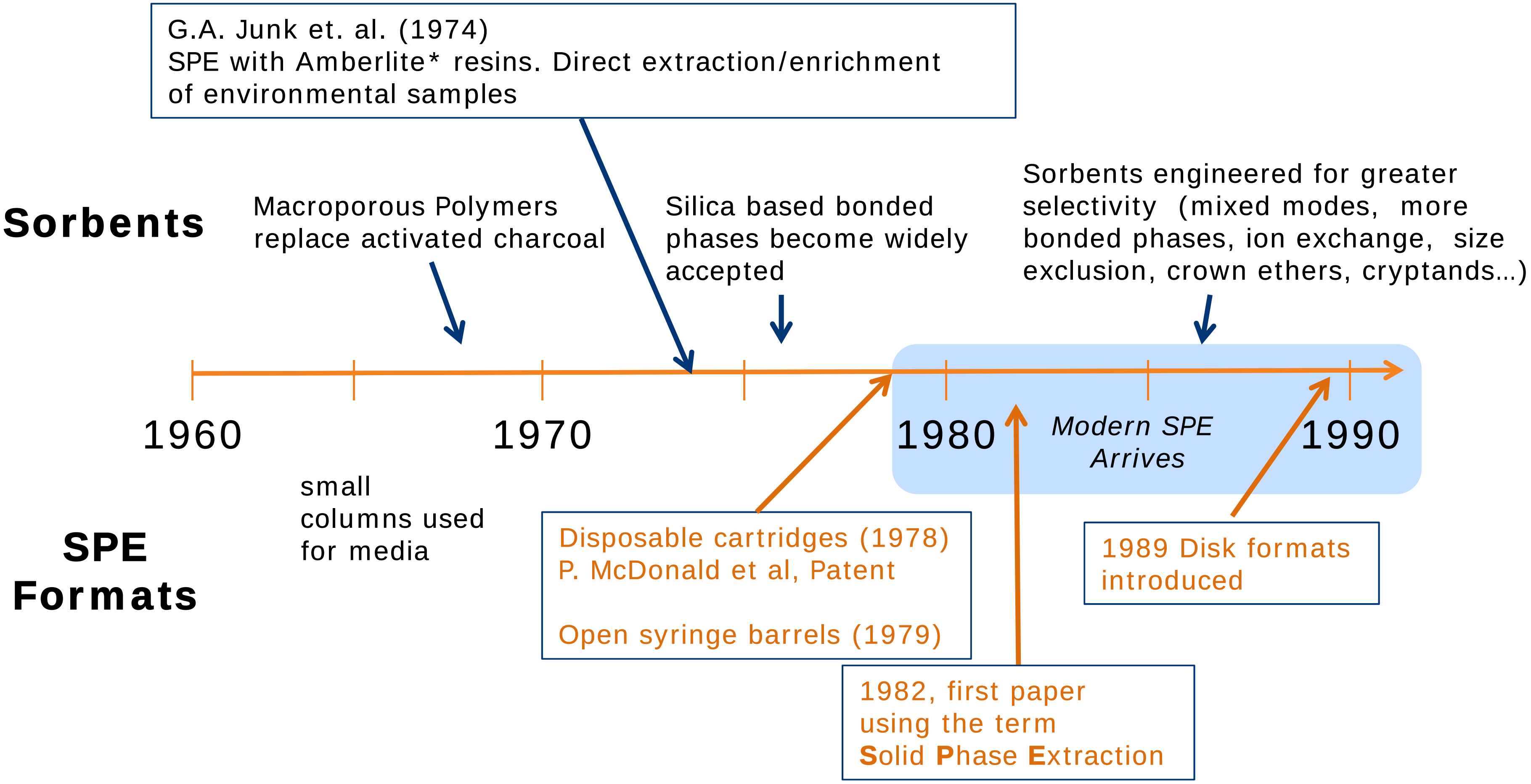
Mikhail Tswett Invents adsorption chromatography

General Water Clean-up (not analytical) with Charcoal, Diatomaceous Earth, Zeolites, etc…

Activated Charcoal (packed in pipes) for concentrating contaminants in surface waters

From the time that liquid chromatography is invented at the beginning of the 20th century it is more than 50 years later that a sorbent is used to isolate trace contaminants

SPE Development Timeline
1960s to the 1980s



G.A. Junk et. al. (1974)
SPE with Amberlite* resins. Direct extraction/enrichment of environmental samples

Sorbents

Macroporous Polymers replace activated charcoal

Silica based bonded phases become widely accepted

Sorbents engineered for greater selectivity (mixed modes, more bonded phases, ion exchange, size exclusion, crown ethers, cryptands…)

Modern SPE Arrives

SPE Formats

small columns used for media

Disposable cartridges (1978)
P. McDonald et al, Patent

Open syringe barrels (1979)

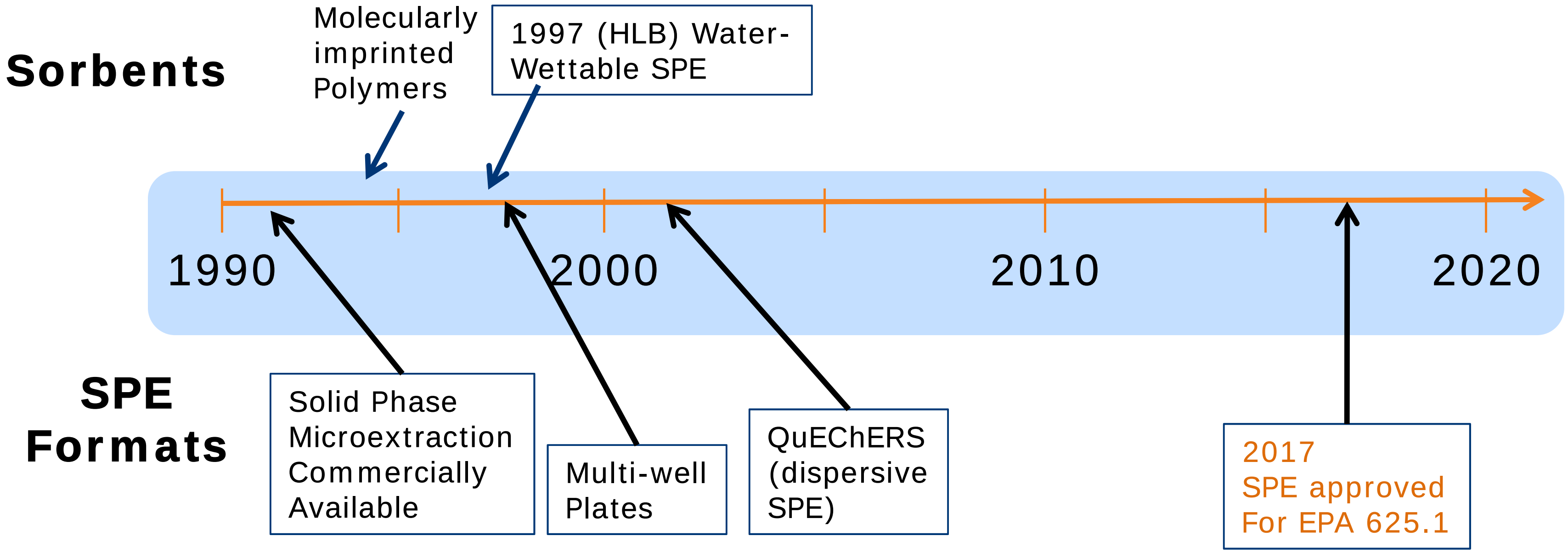
1982, first paper using the term **S**olid **P**hase **E**xtraction

1989 Disk formats introduced

*Amberlite® is a registered trademark of Rohm and Haas Co.

SPE Development Timeline
1990s to Now

EPA SPE methods published for environmental waters



Sorbents

Molecularly imprinted Polymers

1997 (HLB) Water-Wettable SPE

SPE Formats

Solid Phase Microextraction Commercially Available

Multi-well Plates

QuEChERS (dispersive SPE)

2017
SPE approved
For EPA 625.1

Automation for
SPE becomes available

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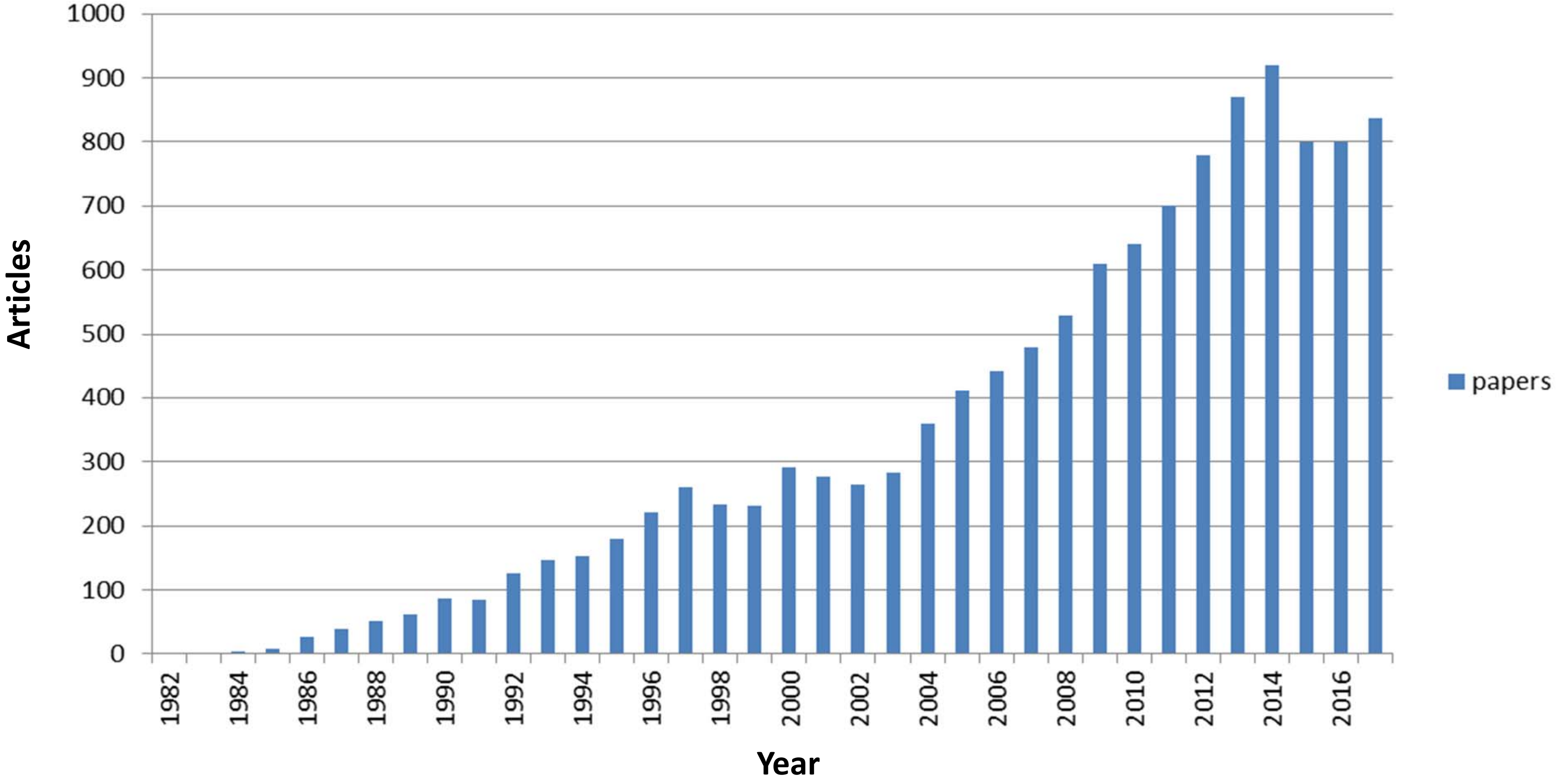
SPE Articles 1982-2017

- Google Scholar Search term “solid phase extraction” in the title
- Omitted citations and patents



EPA SPE Methods 500/600 Series (1990s)

C18, SDVB, SAX, & C8

Year	EPA Method	Sample Matrix	Media	Format	Compound Classes	Analytes	Analytical Technique
1990	550.1	Drinking water	C18	Cartridge/Disk	Polycyclic Aromatic Hydrocarbons (PAH)	16	HPLC-UV-FL
1992	553	Water, waste water	C18; SDVB	Cartridge	Benzidines and N-containing pesticides	14	HPLC-MS
1992	554	Drinking water	C18	Cartridge	Carbonyl Compounds by DNPH derivatization	12	HPLC UV
1992	555	Finished drinking water	C18	online conc. column	Chlorinated acids	17	HPLC-DAD
1992	548.1	Drinking water	Biorex 5 anion exchange resin	Cartridge	Endothal	1	GC/MS or FID
1994	1613	Water, soil, sludge & tissue	C18	Disk	Tetra to Octa-chlorinated Dioxins and Furans	17	isotope dil. HRGC/HRMS
1995	506	Drinking water	C18	Cartridge	phthalate and adipate esters	7	GC-PID
1995	508.1	Drinking water	C18	Cartridge/Disk	Chlorinated pesticides, herbicides and organohalides	45	GC-ECD
1995	515.2	Ground water, finished drinking water	SDVB	Cartridge/Disk	Chlorinated acids	14	GC-ECD
1995	525.2	Drinking water	C18	Cartridge/Disk	Semi-volatile organics (SVOs)	118	GC/MS
1995	608 ATP	Waste water	C18	Disk	Organochlorine Pesticides and PCBs	26	GC-ECD
1997	549.2	Drinking water	C8	Cartridge/Disk	Paraquat, Diquat	2	HPLC UV

*Biorex®5 is a registered trademark name from Bio-Rad Laboratories (classified as an intermediate strength anion exchange resin)

EPA SPE Methods 500/600 & Selected 1600 Series
(21st Century) C18, SDVB, Carbon, HLB & DVB

Year	EPA Method	Sample Matrix	Media	Format	Compound Classes	Analytes	Analytical Technique
2000	526	Drinking water	SDVB	Cartridge/Disk	Selected SVOs	11	GC/MS
2000	528	Drinking water	SDVB	Cartridge	Phenols	12	GC/MS
2000	532	Drinking water	C18	Cartridge/Disk	Phenylurea Compounds	8	HPLC UV
2002	529	Drinking water	DVB/VPD (HLB) cartridge; sulfonated SDVB disk	Cartridge/Disk	Explosives and Related Compounds	14	GC/MS
2004	521	Drinking water	Coconut charcoal;	Cartridge	Nitrosamines	7	GC-NCI-MS/MS
2005	535	Drinking water	nonporous graphitized carbon	Cartridge	Chloroacetanilide and degradates	12	LC/MS/MS
2005	527	Drinking water	SDVB	Disk	Selected pesticides and flame retardants	25	GC/MS
2007	1614	water, soil, sludge & tissue	C18	Disk	Brominated Diphenyl Ethers	209	HRGC/HRMS
2007	1694	water, soil, sludge & tissue	HLB	Cartridge	P & PCPs	74	LC/MS/MS
2008	522	Drinking water	Coconut charcoal; activated carbon	Cartridge	1,4-Dioxane	1	GC MS w/SIM
2008	1668B	water, soil, sludge & tissue	C18	Disk	Chlorinated biphenyl congeners	209	HRGC/HRMS
2009	537	Drinking water	SDVB	Cartridge	Perfluorinated alkyl acids	14	LC/MS/MS
2010	539	Drinking water	C18	Disk	Hormones	7	LC-ESI-MS/MS
2011	523	Drinking water	Carbon	Cartridge	Triazine Pesticides and degradates	13	GC/MS
2012	525.3	Drinking water, finished drinking water	SDVB (disk); DVB (disk); DVB/N-VPD (HLB), Cartridge; DVB (cartridge); C18 (NO EC) cartridge	Cartridge/Disk	Semi-volatile organics (SVOs)	+200	GC/MS
2016	625.1	waste water	OnePass CC	Disk/Cartridge	Base/Neutrals and Acids	+300	GC-MS

EPA Method Media Count

1990s

21st Century

Year	C18	SDVB	Carbon	HLB	DVB	C8	SAX	SCX
1990	1							
1992	2						1	
1994								
1995	4	1						
1997						1		
2000	1	2						
2002				1				1
2004			1					
2005		1	1					
2007	1			1				
2008	1		1					
2009		1						
2010	1							
2011			1					
2012	1	1		1	1			
sum	12	6	4	3	1	1	1	1

C18	41%
SDVB	21%
Carbon	14%
HLB	10%
Others	3-4%

Carbon, HLB, DVB and SCX are now being used in the 21st Century

Characteristics of the Media (1 of 3)

C18 (Octadecyl bonded silica)

- Reversed phase media (hydrophobic interaction)
- Sample pH ranges (2 – 8)*.
- Effective for many compound classes
- Cost effective.
- Requires activation with MeOH , ACN, or equiv.
- Can deactivate if media dries
- Often requires endcapping of silanols to minimize unwanted retention of organic bases

**Actual useful pH range can be extended as the media is used once, unlike analytical columns that will have severe degradation.*

DVB (Divinylbenzene)

- Reversed phase media
- 3 to 5x more capacity over C18
- No sample pH limitations
- No solvent required for activation

Characteristics of the Media (2 of 3)

SDVB (Styrene Divinylbenzene)

- Reversed phase media
- 3 to 5x more capacity over C18
- No sample pH limitations
- No solvent required for activation
- Similar to DVB but EPA methods may specify one over the other or a format (disk vs cartridge)

HLB (Hydrophilic/Lipophilic balanced).

- 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
- No sample pH limitations
- No solvent required for activation
- Polar groups make resin water wettable

Characteristics of the Media (3 of 3)

Activated Carbon

- Selected for applications when analytes are highly to infinitely soluble in water
- Generally not used for non-polar compounds as large solvent elution volumes may be required, and or loss of analyte to media.
- Porous material, can be sourced from coconut shells
- Not the same as non-porous graphitic carbon as specified in EPA 535

C8 Silica

- Less retentive than C18 for non-polar compounds
- Method 549.2 for paraquat /diquat analysis uses hexanesulfonic acid as an ion-pairing reagent for these two quaternary amine analytes.

SCX (Strong Cation Exchange)

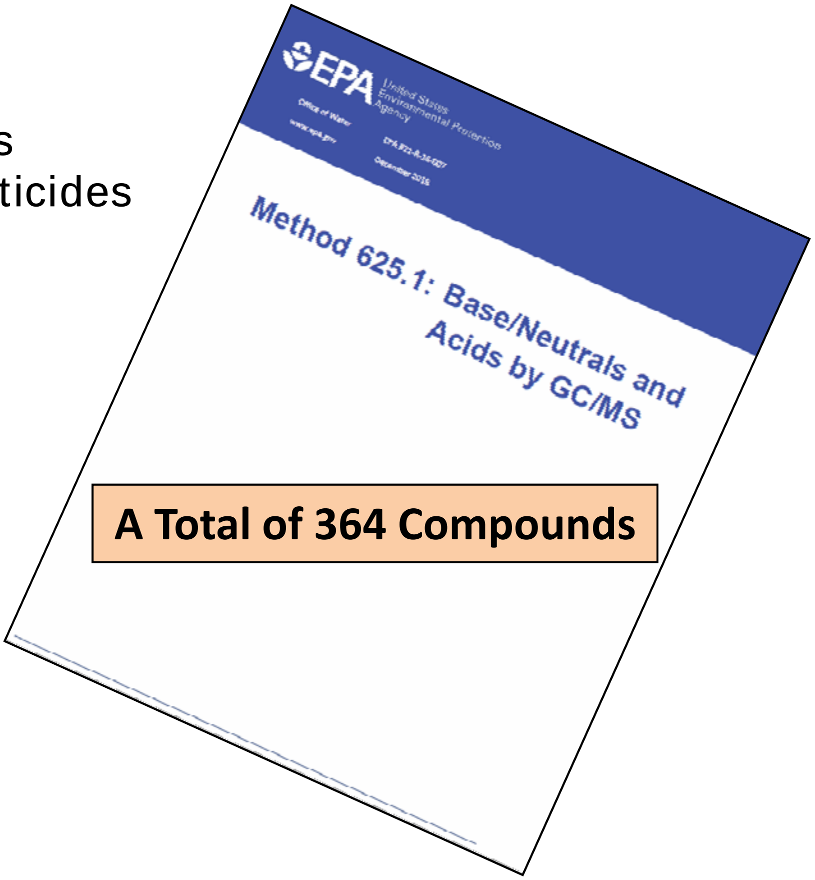
- It is a resin based media with negatively charged sulfonyl groups for capture of organic bases (cations).
- Charge of sulfonyl groups are pH independent.

EPA Method 625.1

Used to determine acidic, basic, and neutral semi-volatile organic compounds in municipal and industrial wastewater using GC-MS.

Such compounds include:

- Polynuclear aromatic hydrocarbons
- Chlorinated hydrocarbons and pesticides
- Phthalate esters
- Organophosphate esters
- Nitrosamines
- Haloethers
- Aldehydes
- Ethers
- Ketones
- Anilines
- Pyridines
- Quinolines
- Aromatic nitro compounds
- Phenols (including nitrophenols)



EPA United States Environmental Protection Agency

Office of Water

www.epa.gov

EPA 821-R-16-007

December 2016

Method 625.1: Base/Neutrals and Acids by GC/MS

A Total of 364 Compounds

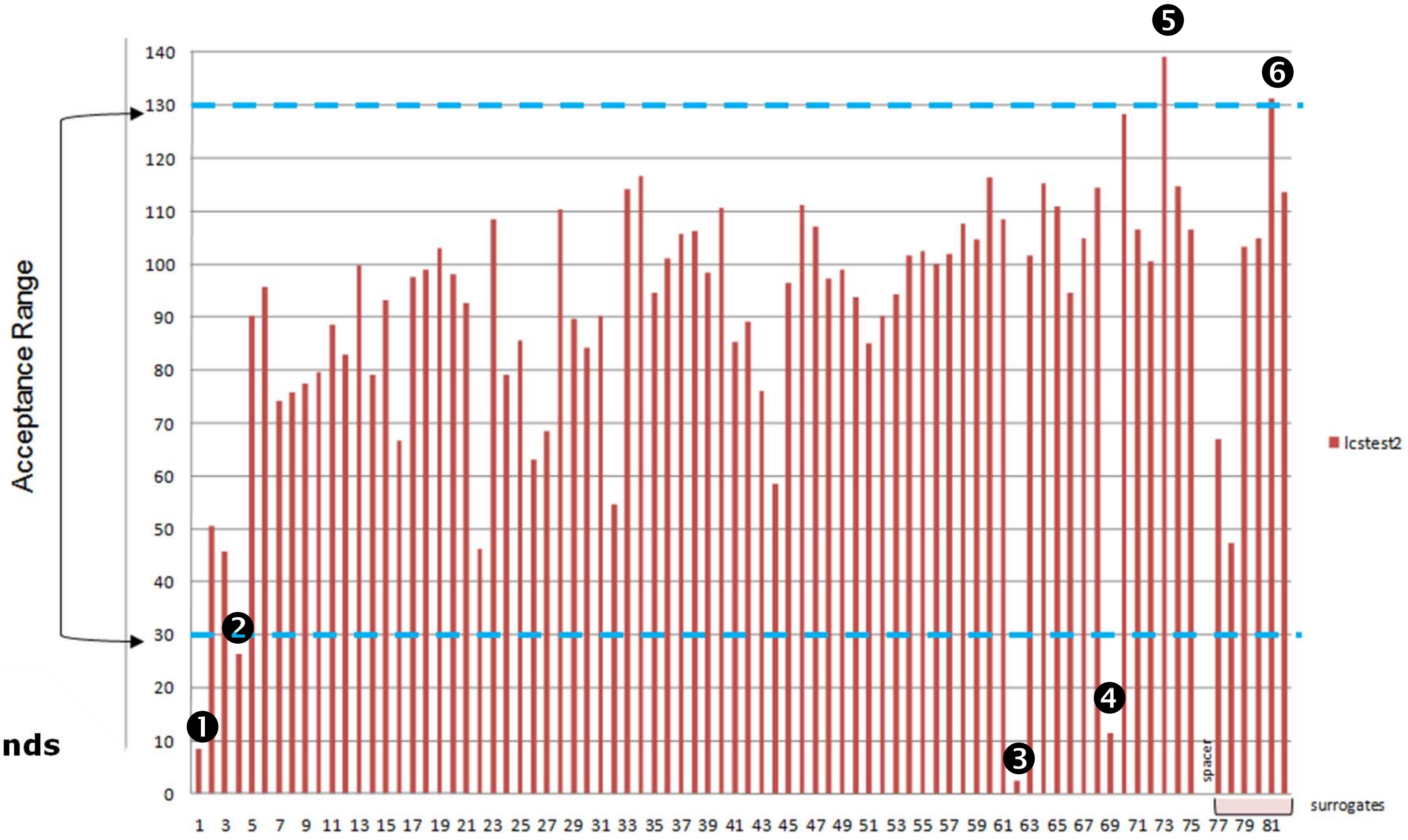
625 Liquid-Liquid Extraction

1. Basify 1 Liter sample to **pH 12,** place in separatory funnel.
2. Add 60 mL methylene chloride, shake for 2 minutes.
3. Let stand for 10 minutes, collect solvent.
4. Repeat 2 more times.
5. Acidify sample to **pH 2.**
6. Add 60 mL methylene chloride, shake for 2 minutes.
7. Let stand for 10 minutes, collect solvent.
8. Repeat 2 more times.
9. A min. of 360 mL of solvent is collected and dried over Na_2SO_4 (min 20g).
10. Amount of Na_2SO_4 is adjusted based on water in sample.
11. Concentrate to ~15 mL using KD or other large volume evaporator.
12. Transfer to NEvap to bring volume down to 1 mL .
13. Add internal standard, transfer to GC vial for analysis.

- Technique is prone to emulsions
- Large solvent consumption (360 mL)
- ~3 hr 45 min from start to finish

Semi-Volatile Analyte Recoveries

LLE Results Based on Laboratory Control Spike



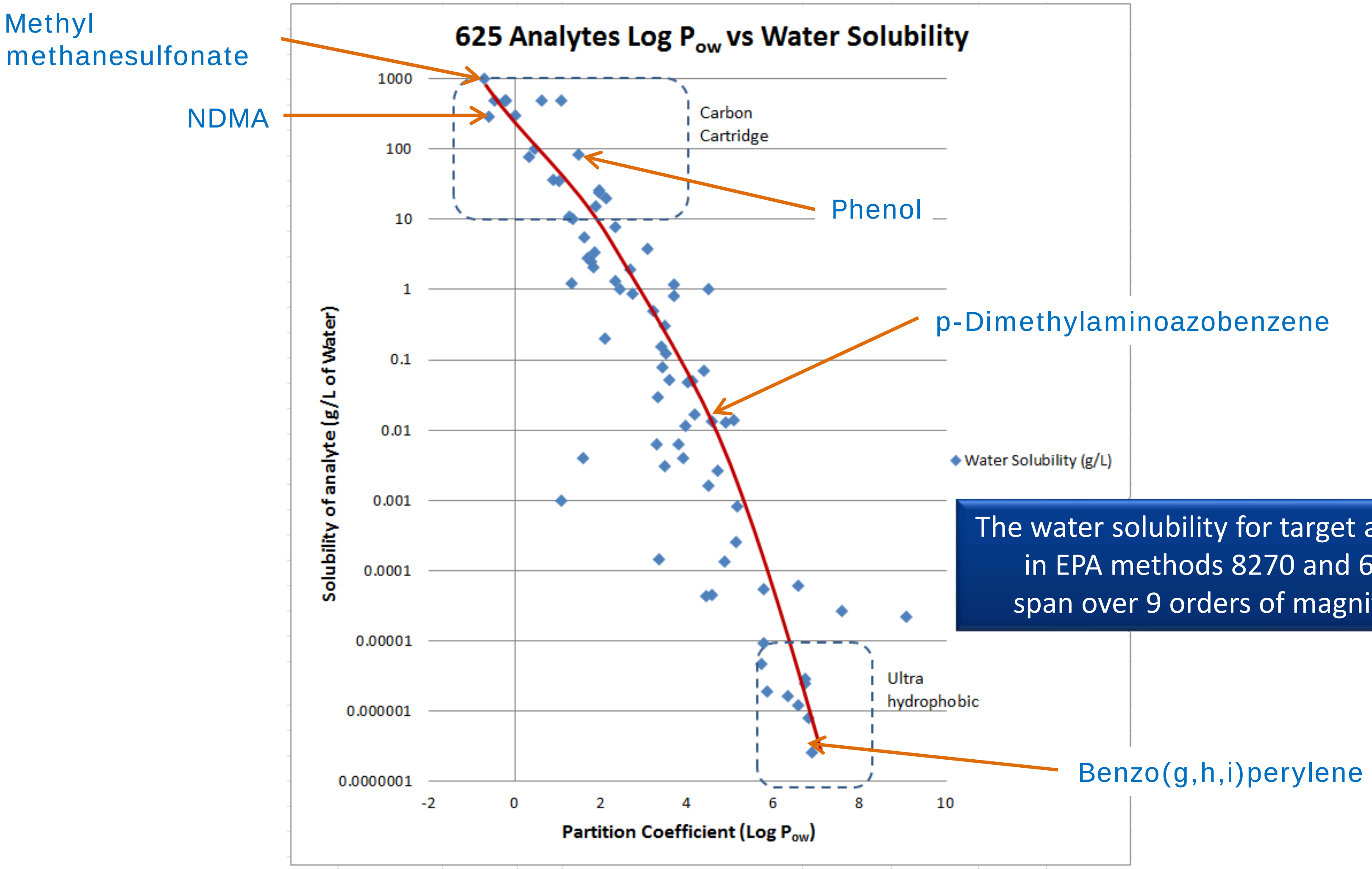
Dried with Na_2SO_4,
Concentrated with KD & NEvap

Problem compounds

1. Pyridine 8%
2. Aniline 26%
3. Benzidine 3%
4. Di-n-octyl phthalate 12%
5. Indeno (1,2,3,-cd)pyrene 140%
6. 2,4,6,Tribromophenol (surr) 135%

EPA 625.1 Analytes

Extreme Range of Analyte Water Solubility



The water solubility for target analytes in EPA methods 8270 and 625.1 span over 9 orders of magnitude!

SPE Method for 625.1

Using a Multimodal Disk and Carbon Cartridge

SPE Materials

- 8270 OnePass Disk, 47mm (HLB & SCX)
- 8270 Carbon Max Detect Cartridge

Procedure

- Acidify wastewater to pH 2 (only)
  - *No pH 12 adjustment means the sample is passed through disk once*
  - *No pH 12 adjustment means no metal hydroxide flocculants to plug disk*
- Pass sample once through disk and carbon cartridge to waste.

Elution Process

- 1st Disk Elution with (Acetone/DCM) for neutrals and acids (collect extract in flask 1)
- 2nd Disk Elution with (dil. NH_4OH, Acetone, DCM) (collect extract in 2nd flask)
- Elution of Carbon cartridge for hydrophilics with acetone and DCM (collect extract in 1st flask).

Recombine Elution fractions in the drying step (DryDisk® membrane)

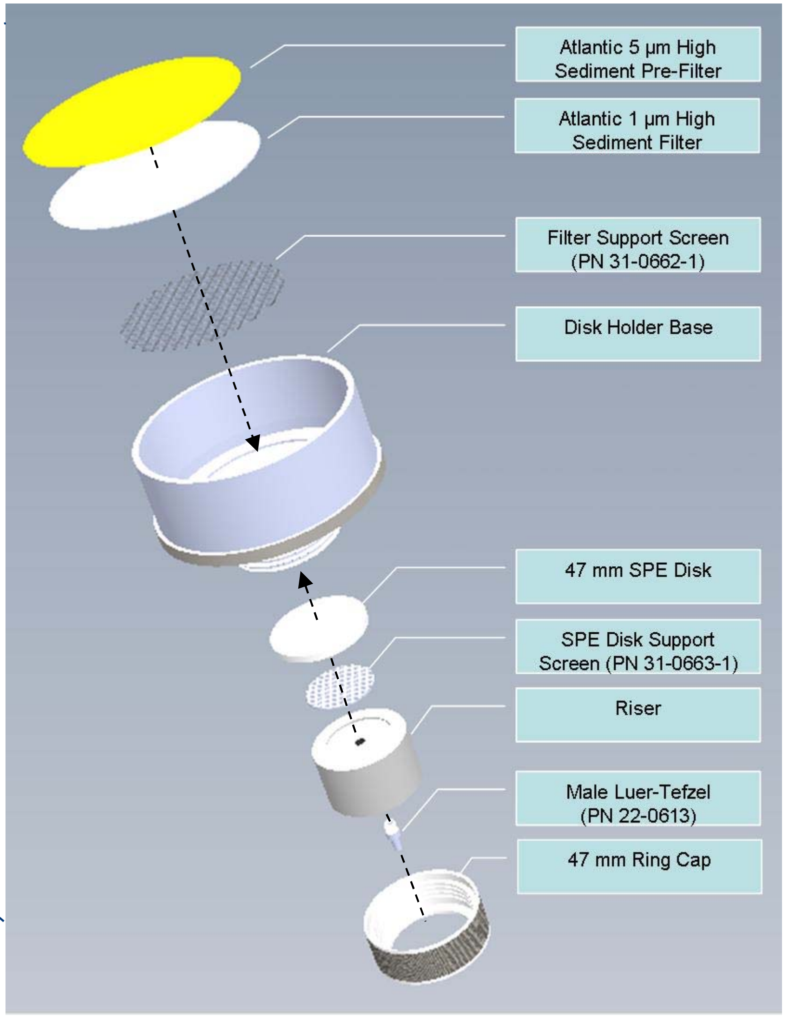
- Dry fractions 1 and 3 through membrane, discard water.
- Dry fraction 2 (base) through membrane again, combining all 3 fractions.
- Concentrate to final volume and analyze with GC/MS.

Method 1: 1 Liter Sample Volume

1 µL is injected (10/90 split mode) into the GC-MS.

Fast Flow Disk Holder

- 6x more filtering surface area
- Uses 90 mm pre-filters (1 and 5 µm)
- 200 mL extract volume
- 3 hr to extract, dry and concentrate.



Method 2: 100 mL Sample Volume


100 mL
Sample


47 mm
Disk Holder

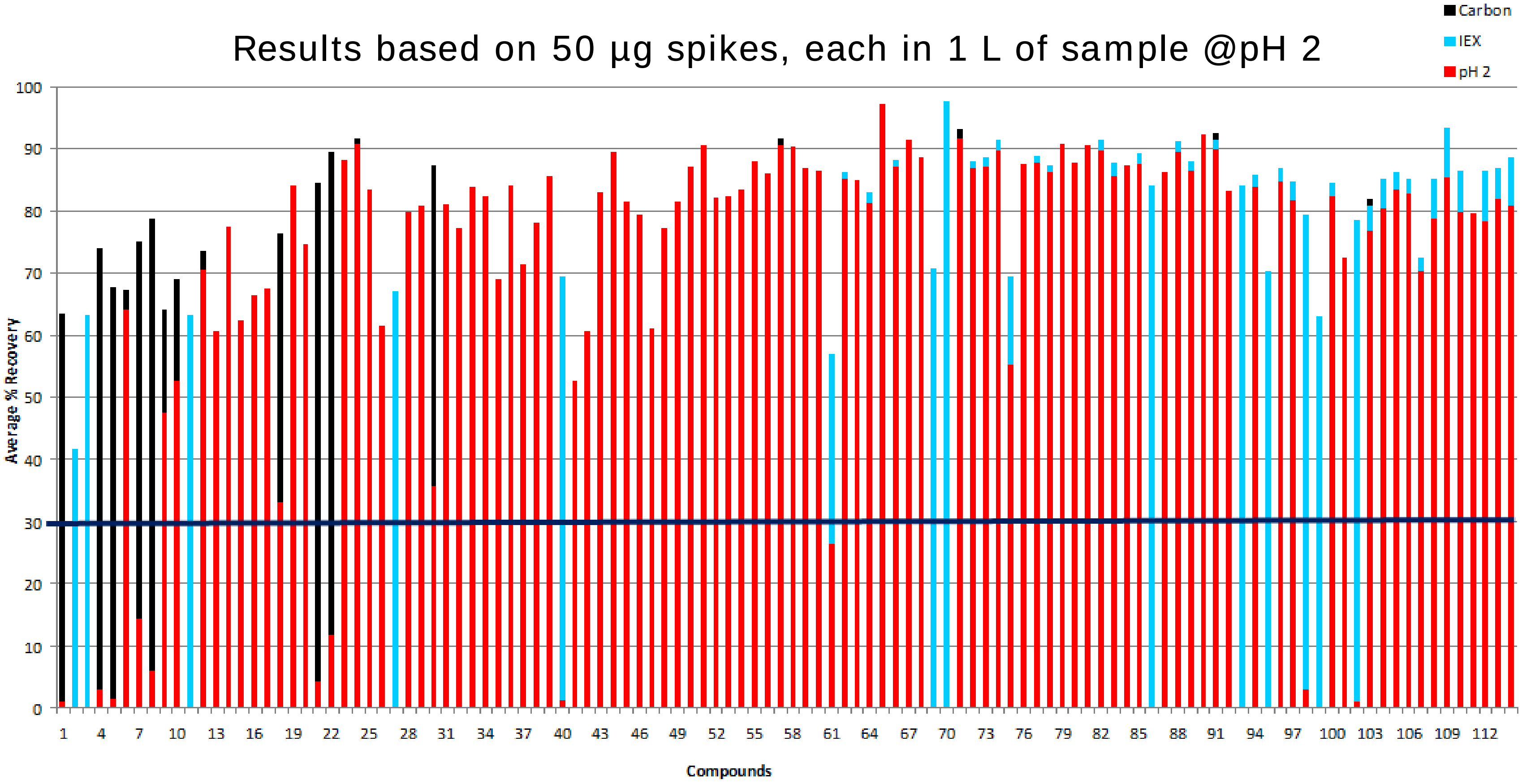
1 µL is injected into the GC-MS.

This maintains the same mass loading as the 1 liter sample method.

- 80 mL extract volume
- 1 hr 30 min to extract, dry and concentrate

EPA Method 625 – Semi-Volatile Analytes

Results based on 50 µg spikes, each in 1 L of sample @pH 2



To illustrate what media contributed to recovery,
Red is the first elution (HLB) for acids and neutrals
Blue is the second elution (SCX) for organic bases
Black is the third elution (Carbon) for the hydrophilic compounds

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Conclusion

- A time perspective of SPE development and milestones has been shown.
- SPE as applied to environmental water applications started with C18, SDVB, SAX, & C8 in the 90s and continued with HLB, SCX, DVB and Carbon.
- Applying 3 of the above media types HLB, SCX and carbon the process to do the recent 2017 method update 625.1 for SVOCs in wastewater was illustrated.

The Future of Solid Phase Extraction

- It is always challenging to predict directions where SPE is headed for environmental applications
- The concern over the rapid proliferation of PFCs (perfluorinated compounds and their intermediates) push the limit of the current SDVB methods that are ideal for hydrophobic compounds. As the carbon chain decreases with these anionic compounds, we will be probably see more development with WAX (weak anion exchangers)
- Field collection of samples on disks may become more prevalent as methods are refined. Resin based (HLB) disk with pore sizes <90 Å provide substantial surface area available for analyte capture while excluding bacteria from access (potentially a more stable means of preserving samples and easier transport over transporting water samples)

Selected References

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