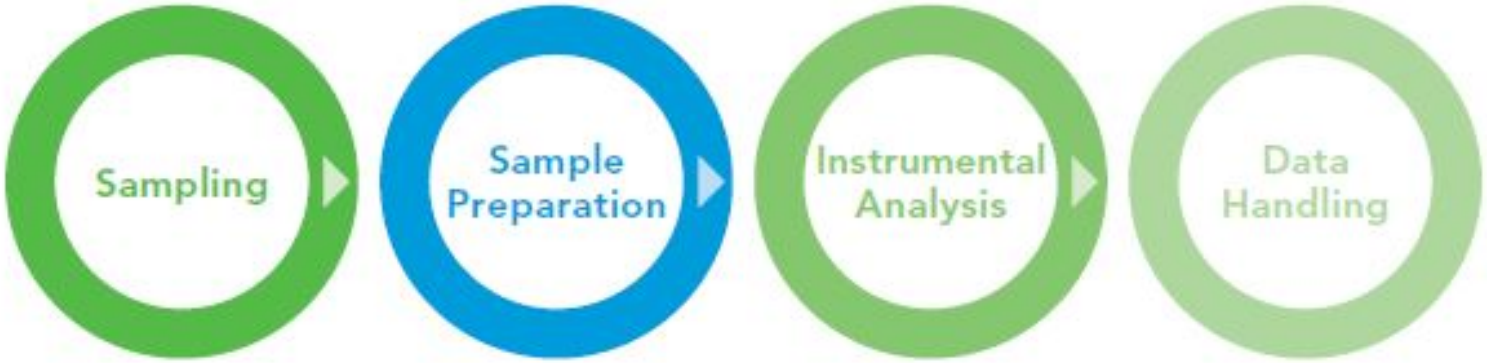
Solid Phase Extraction as another Tool in the Laboratory

William R. Jones, Zoe Grosser and Michael Ebitson
Horizon Technology, Inc., Salem, NH, USA

Analytical Process



Sample Preparation

Generally consists of several steps

- Extraction of the sample
- Clean up to remove interferences
- If water is present in the extract, drying is necessary
- Evaporation/concentration
  - Increase sensitivity
  - Best detection limit

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.

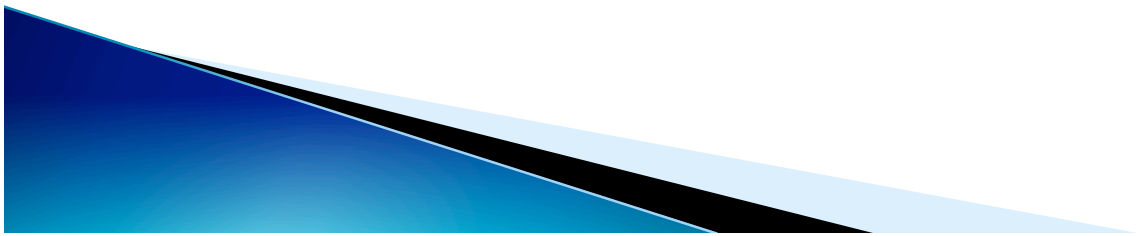
Sample Backlog

Time limits for SVOCs
14 days until extraction
7 days after extraction

Past time limit
Expensive resampling

Considerations for Technology Adoption

- Well-established
  - Reached a level of maturity
  - Generally accessible
- Compliant with required methodology
- Makes business sense



Sample Preparation Advances

- Improved Analytical Instrumentation for Less Sample preparation
  - Improved sensitivity
  - Direct sampling injection
  - Large volume injection
- Solid phase extraction
  - Greater Variety of SPE Media to Select From
  - Greater Variety of SPE formats
  - Improved quality of media – batch to batch
  - Larger Database of Methods
- Automation
  - More SPE formats
  - More specialized features to select from

Automation

- Requires some new thinking
- Requires an investment in sample preparation, a sometimes overlooked area of the lab
- Can provide more consistent analytical results and fewer re-runs
- Can reduce solvent usage, an increasing environmental concern in today's lab
- Improve technician safety and reduce exposure to solvents

Solid Phase Extraction

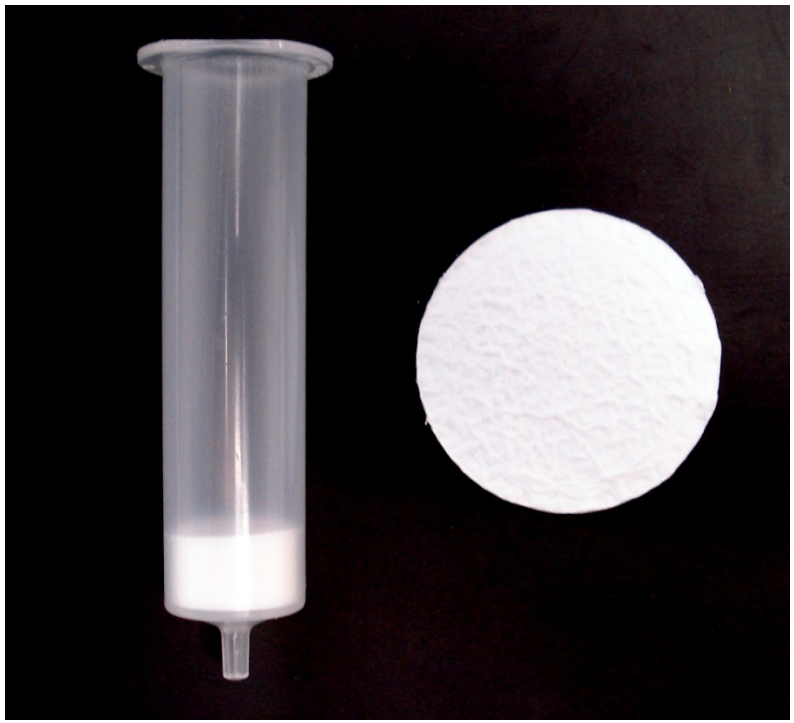
- Used to concentrate the analyte by retaining on the SPE media and eluting the analyte off the media with solvent into a smaller volume
  - Many media materials to select from, Silica, C18, SDVD, DVB, HLB, WAX, SCX, mixed mode, MIP…….
- May also be used as clean-up, where the matrix/interferences are retained on the material
  - Alumina, Florisil®……

Solid-Phase Extraction

- Established in many markets, such as food and pharmaceutical
- Established in some parts of the world, such as Europe
- Can be used in disk or cartridge format

SPE-DEX 4790

SmartPrep



History of SPE

- Some scholars claim that the first literature reference is found in the Bible (Exodus, Chapter 15, verse 24 and 25)
- SPE has been in use for thousands of years
- Considerable disagreement on “who” performed the first SPE, or produced the first SPE cartridge
- The term Solid Phase Extraction was only used several years after the technique became available

Developments in SPE Continue

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[CITATION] Analysis of the chiral antineoplastic drug ifosfamide in environmental samples by **solid-phase extraction** and liquid chromatography-tandem mass …
M Camacho-Munoz… - 'Emerging contaminants in …, 2015 - opus.bath.ac.uk
Camacho-Munoz, M. and Kasprzyk-Hordern, B., 2015. Analysis of the chiral antineoplastic drug ifosfamide in environmental samples by **solid-phase extraction** and liquid chromatography-tandem mass spectrometry. In: 'Emerging contaminants in waters and soils, practical **...**
Cite Save More

Magnetic silica nanomaterials for **solid-phase extraction** combined with dispersive liquid-liquid microextraction of ultra-trace quantities of plasticizers
Y Yamini, M Faraji, M Adeli - Microchimica Acta, 2015 - Springer
Abstract We are presenting surface modified magnetic silica nanoparticles (m-Si-NPs) for use in **solid-phase extraction** combined with dispersive liquid-liquid microextraction (DLLME). The m-Si-NPs were surface-functionalized with octadecyl groups to give a **...**
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Speciation of As (III) and As (V) in water samples by graphite furnace atomic absorption spectrometry after **solid phase extraction** combined with dispersive liquid– …
M Shamsipur, N Fattahi, Y Assadi, M Sadeghi… - Talanta, 2014 - Elsevier
Abstract A **solid phase extraction** (SPE) coupled with dispersive liquid–liquid microextraction based on the solidification of floating organic drop (DLLME-SFO) method, using diethyldithiphosphate (DDTP) as a proper chelating agent, has been developed as an **...**
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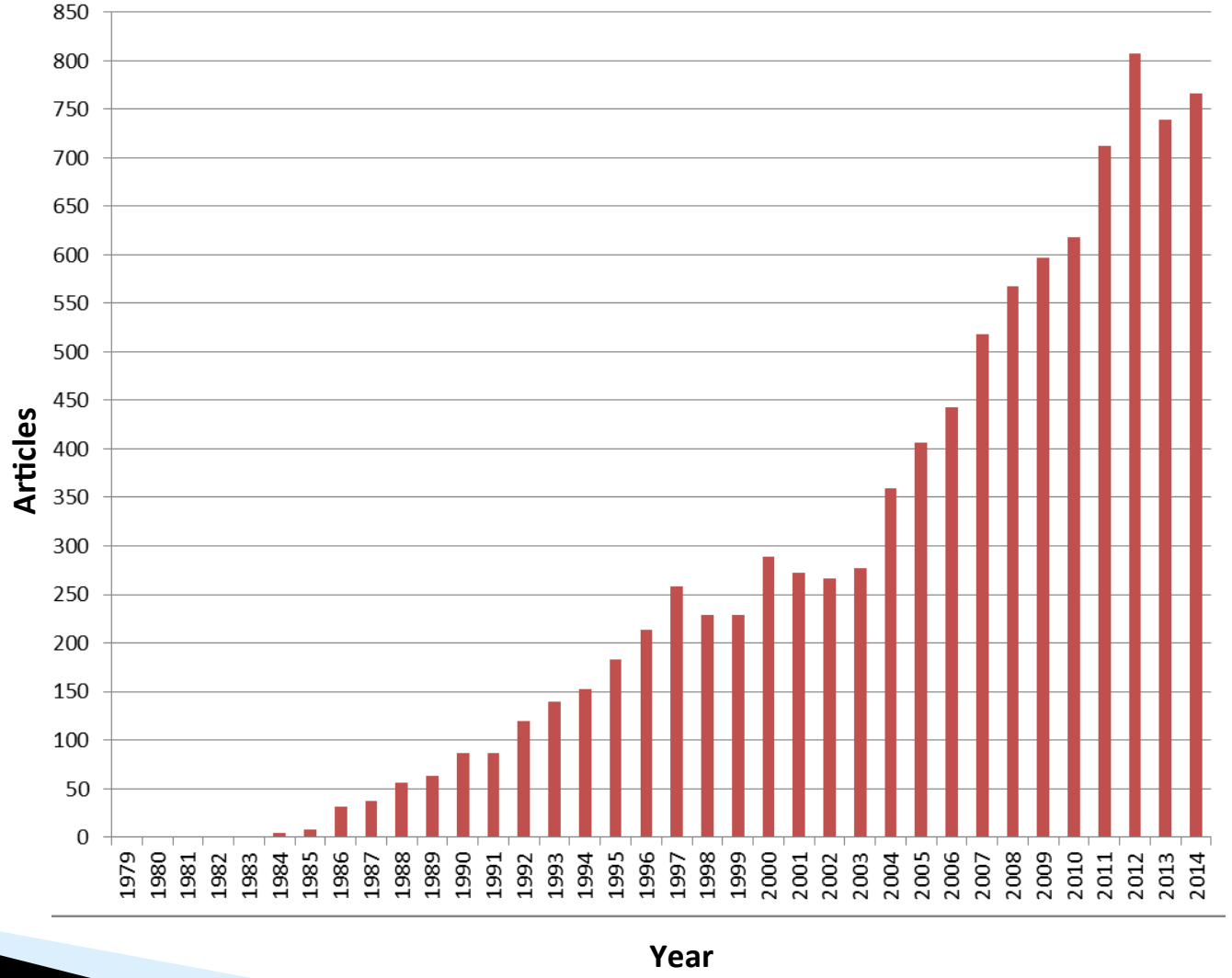
Supported liquid membrane-protected molecularly imprinted beads for micro-**solid phase extraction** of sulfonamides in environmental waters
M Díaz-Álvarez, F Barahona, E Turiel… - … of Chromatography A, 2014 - Elsevier
Abstract In this work, molecularly imprinted polymer (MIP) beads have been prepared and evaluated for the development of a supported liquid membrane-protected micro-**solid phase extraction** method for the analysis of sulfonamides (SAs) in aqueous samples. The **...**
Cited by 5 Related articles All 4 versions Cite Save

SPE Articles 1979–2014

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

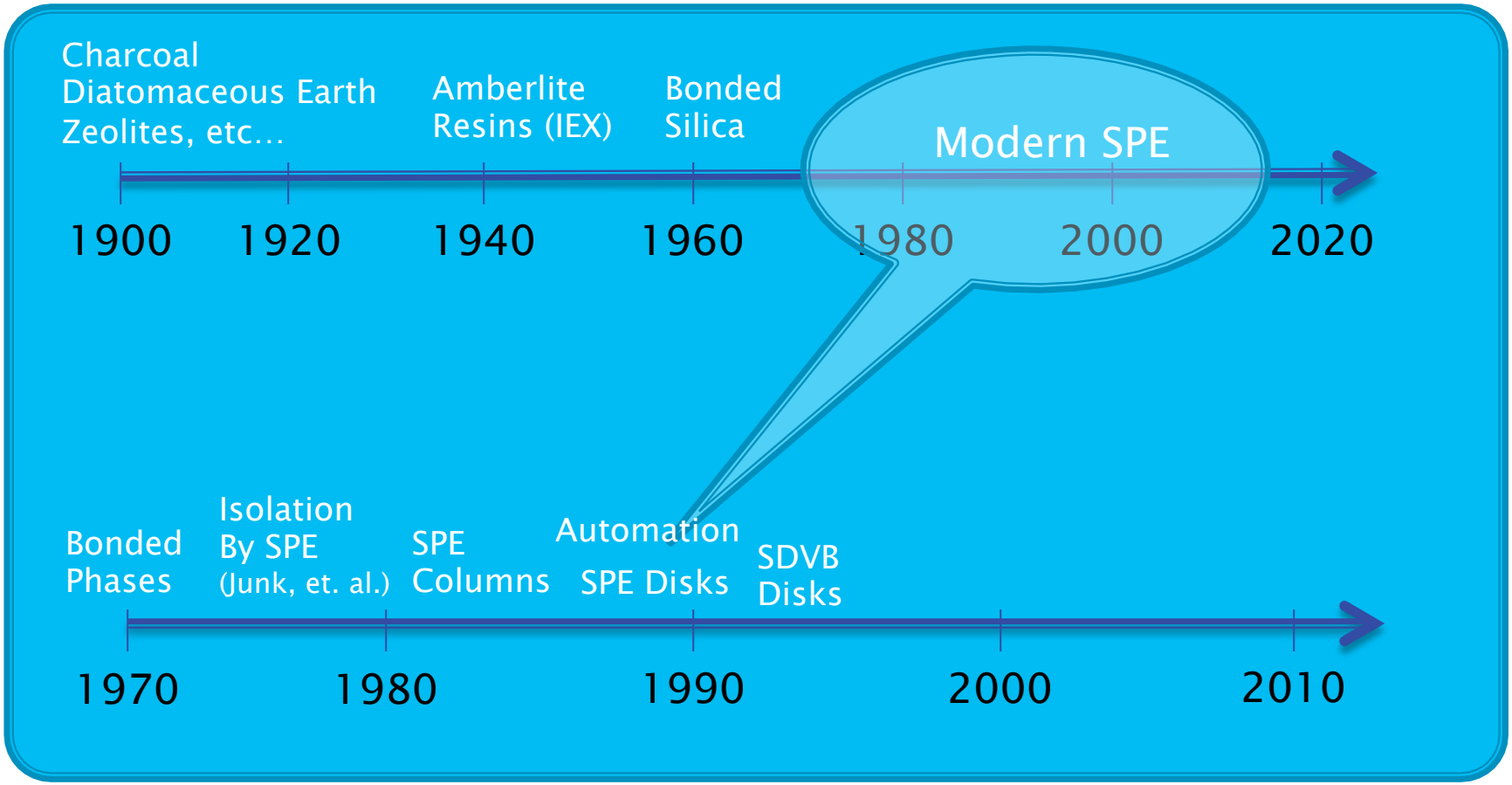


History of Solid Phase Extraction

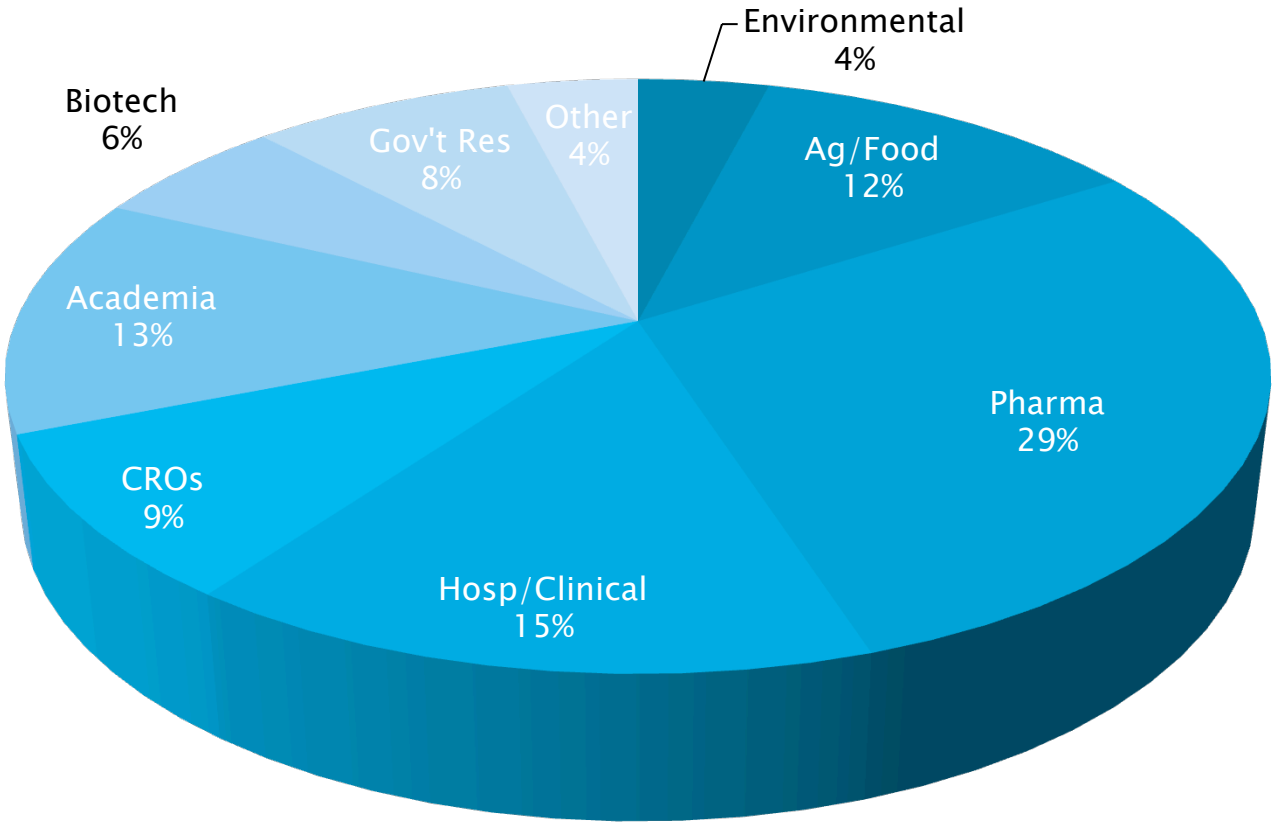
- QuEChers has brought more familiarity to the use of dispersive SPE for clean-up
- Anastassiades, Michelangelo[1]; Lehotay, Steven J.[2]; Štajnbaher, Darinka[3]; Schenck, Frank J.[4] Journal of AOAC International, Volume 86, Number 2, March 2003, pp. 412-431(20).

- QuEChers
  - Quick Easy Cheap Effective Rugged & Safe

History of SPE



Where is SPE used Today?



Where is SPE Used – Examples

Food & Beverage:

- Mycotoxin testing (Aflatoxins & Ochratoxins)
- Antibiotic measurement in food
- Beer, Wine and Juice makers

State & Government:

- Forensic and criminal labs
- Academia and other government funded labs (SPE researchers & method developers)

Pharmaceutical Companies (R&D departments):

- Sample Clean-up (volumes >1.0mL)
- Protein purification
- Drug development
- Toxicology labs

Where is SPE Used – Examples

- **Total Extractable Hydrocarbons** : C10 to C40

- **Drugs of abuse** : BZE (benzoylecgnonine = metabolite of cocaine), amphetamines, morphine's and cocaine in urine, blood, plasma and oral fluids prior to GCMS

- **Acid, basic and neutral drugs in animal urine** : horses greyhounds, bulls, camels

- **SPE Sudan I and IV additive screening** : prohibited dyes (red) in food, solvents, oils, waxes, shoes, floor polishes

Where is SPE Used – Examples

- **Organic compounds from marine sediments, soil and dust samples**: alkenones (2-nonadecanone), tetra ethers, n-alkanes, sterols and fatty acids to chart temp. changes

- **Vitamin D** or its metabolite 24,25 dihydroxyvitamin-D3 from plasma, blood and urine

- **Antibiotics** in animal feed: corn, rice, grains

- **Organic acid profiles** in wines

- **Cyclosporine** in Blood: immunosuppressant used in organ transplants

Chemistry Development Continues

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CHRONOLOGY

Technology & Chemistry	2006	2007	2008	2009	2010	2011	2012	2012
DVB Disk	✓							
HLB Disk		✓	✓	✓	✓			
Dual pH Kit			✓	✓	✓			
Carbon Cartridge & Kit				✓	✓	✓	✓	
FFSDH					✓	✓	✓	
8270 One Pass Disk						✓	✓	
MeAc/MeFm							✓	✓
8270 One Pass L Disk/ Carbon Cartridge Light								✓
8270 ANALYTES & PERFORMANCE								
Lipophilic Compounds (Neutrals & Acids)	✓	✓	✓	✓	✓	✓	✓	✓
Hydrophilic Compounds (Phenols)		✓	✓	✓	✓	✓	✓	✓
Organic Bases (Anilines)			✓	✓	✓	✓	✓	✓
Light End Organics (NDMA, methyl methane sulfonate)				✓	✓	✓	✓	✓
High Sediment Samples					✓	✓	✓	✓
M 625 Performance Requirements							✓	
1/10th sample volume lower cost disk, lower solvent consumption								✓

US EPA Methods – Drinking Water

Number	Title	Date	Compounds
508.1	Determination of Chlorinated Pesticides, Herbicides, and Organohalides by Liquid-Solid Extraction and Electron Capture Gas Chromatography	1995	Pesticides (45)
521	Determination of Nitrosamines in Drinking Water by SPE and GC with Large Volume Injection and Neg Chem Ionization MS/MS	Sept 2004	Nitrosamines (7)
522	Determination of 1,4-Dioxane in DW using SPE and GC/MS with SIM	Sept 2008	1,4-Dioxane (1)
523	Atrazine and Simazine by SPE and GC/MS	2011	Atrazine and Simazine (2)
525.3	SVOAs in DW by SPE and GC/MS	2012	Large suite
526	Selected SemiVOAs using SPE and GC/MS	June 2000	Acetochlor to nitrobenzene and 2,4,6-trichlorophenol (11)
527.0	Determination of Selected Pesticides and Flame Retardants in DW by SPE and GC/MS	Aug 2009	Atrazine to Malathion to Vinclozolin (26)
528	Determination of Phenols in DW with SPE and GC/MS	April 2000	12 phenols (12)

US EPA Methods – Drinking Water

Number	Title	Date	Compounds
529	Determination of Explosives and Related Compounds in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography/Mass Spectrometry (GC/MS).	Sept 2002	Explosives (14)
532	Determination of Phenylurea Compounds in DW with SPE and HPLC with UV Detection	June 2000	Diflubenzuron to Thidiazuron (8)
535.1	Measurement of Chloroacetanilide and Other Acetamide Herbicide Degradates in Drinking Water by Solid Phase Extraction and Liquid Chromatography/ Tandem Mass Spectrometry	2005	Degradates (12)
537	Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/ MS/MS).	Sept 2009	Perfluorinated compounds (14)
539	Determination of Hormones in DW by SPE and LC-ESI-MS/MS	Nov. 2010	Hormones (7)
549.2	Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and High Performance Liquid Chromatography with Ultraviolet Detection	June 1997	Diquat and paraquat (2)

Other Regulatory Methods

- Included in US EPA SW-846 sample prep method 3535A
- Can be coupled with methods 8270, 8081, 8082, 8061, 8141, 8330, 8095 and 8321 for the determinative step

- Currently, US EPA method 608 a wastewater method incorporating solid phase extraction (ATP for disk technology), included in MUR

- Method 1664 is a popular method incorporating SPE for Oil & Grease extraction

- Although many methods incorporate SPE, without a major wastewater method, such as 625, it is more difficult for laboratories to justify learning curve and the purchase of automation equipment

Method 1664 for O&G

- Many environmental labs in the US, ranging from refineries and power plants to wastewater treatment facilities and commercial labs, use SPE for Oil & Grease
- Automation is well accepted and implementation and learning curve is low, making good business sense

Business Considerations

- Benefits to the lab
  - Can it help with sample throughput?
  - Save cost
  - Reduce labor
    - Provide productive walk-away time
    - Provide better reproducibility for fewer re-runs
- Reduce solvent usage for less chance to emit

- What is the sample load to consider automation?

Example

Method 625

- Many of the environmental methods allow SPE and it has become established
- Method 625 included in the recent MUR (published Feb 19, 2015) will include SPE when it is through the regulatory process next year
- Business considerations
  - Once a method is developed, little technician interaction is required
  - Using SPE for this method with one-pass can help with the onerous problem of emulsions
  - 0.2-0.6 of LLE solvent usage is typical

Conclusions

- Sample preparation remains the weak link in the overall analytical process
- Solid phase extraction has a long history and is used routinely in other areas such as food and pharmaceutical
- New chemistries and formats continue to develop to make the technology more accessible and reliable
- Many environmental methods allow SPE and method 625 is on the horizon
- Method 1664 is an example of a successful implementation of both SPE and automation
- There are business considerations that each lab must evaluate before a successful implementation of SPE can take place
- SPE offers a tool for the laboratory to consider in the overall advancement of sample preparation

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