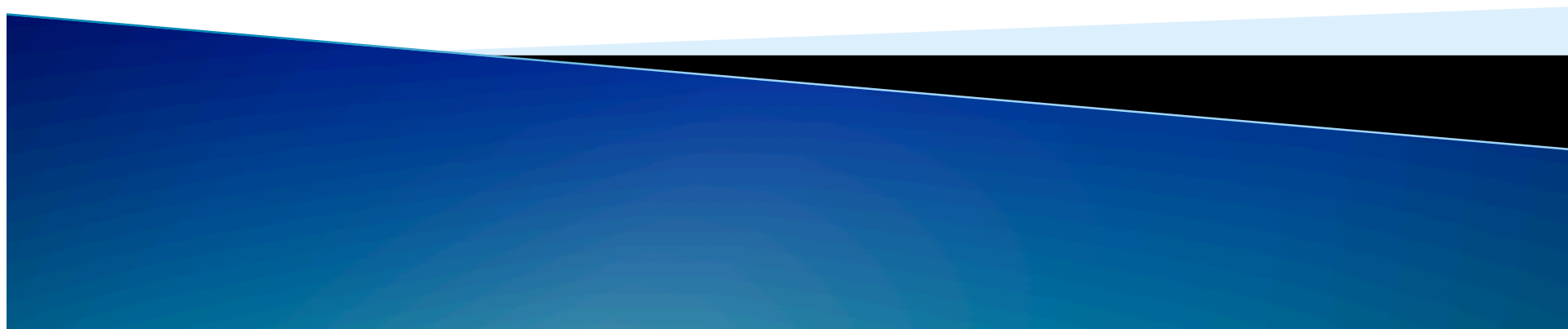




Solvent Emission Reduction in the Modern Environmental Laboratory

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Outline



- ▶ **Clean Air Act, Title V Permits**
- ▶ **Solvent Reduction Backgrounder**
- ▶ **Reducing Solvent Emissions**
 - Reduce Sample Size
 - Increase Detection Sensitivity
 - Reduce Solvent Consumption
 - Employ Solvent Recovery
- ▶ **LLE to SPE**
- ▶ **Solvent Recovery**
- ▶ **Conclusions**



Solvent Reduction Background



▶ **Clean Air Act, Title V Permits**

- Emissions of Hazardous Air Pollutants (HAP) has a stated potential limit of 10 tons per year and a combined HAP potential maximum of 25 tons per year.

▶ **Individual State Regulations**

- Most states have adopted Title V amounts but others have implemented their own limits.
- MA requires a single HAP potential emission of 1 ton per year.

▶ **Environmental Analysis Labs**

- A major concern is Dichloromethane (DCM) among other HAP solvents.

▶ **Extremely Small HAP Emitters**

- No permit is required if they are not at risk of exceeding the individual state limits.



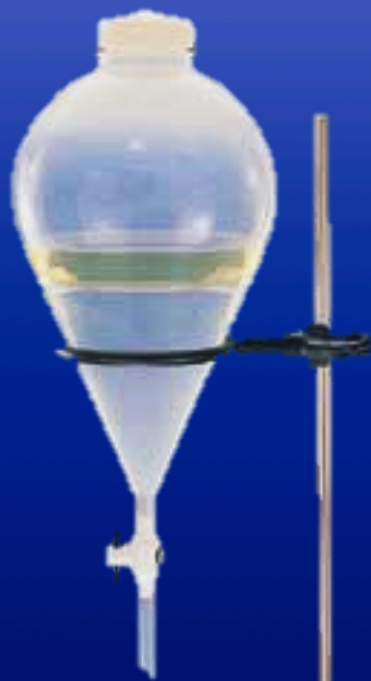
Penalties for Exceeding HAP Emission Limit



- ▶ In 2014, four labs in Massachusetts were fined for exceeding the HAP emission limit, without a valid permit.
- ▶ The fine was \$350K per site.
- ▶ The concern is that other states will become more stringent. In which case, a reduction in solvent use and/or more effective recovery would be required.



Liquid-Liquid Extraction



Separatory
Funnel

- Water sample (1 Liter)
- Extract at basic pH with 60 mL of DCM three times
- Extract at acid pH with 60 mL of DCM three times
- Dry extract over sodium sulfate
- Evaporate over 360 mL DCM down to 1 mL
- Add Int. Std. and transfer to GC vial
- Inject 1 μ L into GC/MS, with split

- **Over 360 mL DCM per sample**
- 1 ton DCM ~ 1895 samples (~ 7 samples/day for year)

How to Reduce Solvent Emissions?



- ▶ Reduce sample size collected
- ▶ Reduce extraction solvent needs
- ▶ Recover solvent used



Reduce Sample Size



1-L sample size set decades ago based on:

- ▶ Sample homogeneity
 - ▶ Analytical instrument sensitivity
-
- ▶ Sample homogeneity has been shown to be less of a concern that originally thought
 - ▶ Analytical instrument sensitivity has dramatically increased
 - ▶ Benefit of lower sample shipping costs and reduced hazard
 - ▶ Possible to do additional sampling at a lower cost



Reduce Sample Size



EPA methods are acknowledging smaller samples as they are updated:

- ▶ Method 521 (2004)
 - Nitrosamines in Drinking Water, specifies **500 mL** of water sample size
- ▶ Method 535 (2005)
 - Chloroacetanilide and other Acetamide Herbicide Degradates in Drinking Water, specifies **250 mL** water sample size
- ▶ Method 522 (2008)
 - 1,4-Dioxane, specifies **100 or 500 mL** water sample size, depending upon the SPE adsorbent chosen
- ▶ Method 3511 (2002)
 - Microextraction for Selected Compounds, approximately **35 mL** sample size
- ▶ Method 625 (2014)
 - flexible sample volume based on the detection limits needed for compliance



Instrument Sensitivity Improvements



- ▶ Manufacturers have improved sensitivity over the past few decades
- ▶ Split can be changed to improve sensitivity
- ▶ SIM can be used, especially now that scanning can be used simultaneously
- ▶ Triple quad?
- ▶ Large-volume injection becoming more common, inject up to 50 μL sample



Reduce Solvent Usage



- ▶ Smaller samples require less solvent for extraction
- ▶ Solid-phase extraction (SPE) requires less solvent for analyte elution

Summary:

- ▶ Water is passed through the SPE disk and analytes are retained
- ▶ Analytes are eluted with a small volume of solvent
- ▶ Depending on sample complexity 80-180 mL of solvent are needed for elution compared to 360 for a typical acid/base neutral liquid-liquid extraction



US EPA Methods Specifying SPE for Drinking Water (1 of 2)



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 Specifying SPE for Drinking Water (2 of 2)



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)

SPE Development Efforts in Waste Water



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								✓

1 Liter Sample Volume with SPE (applied to EPA Method 625)



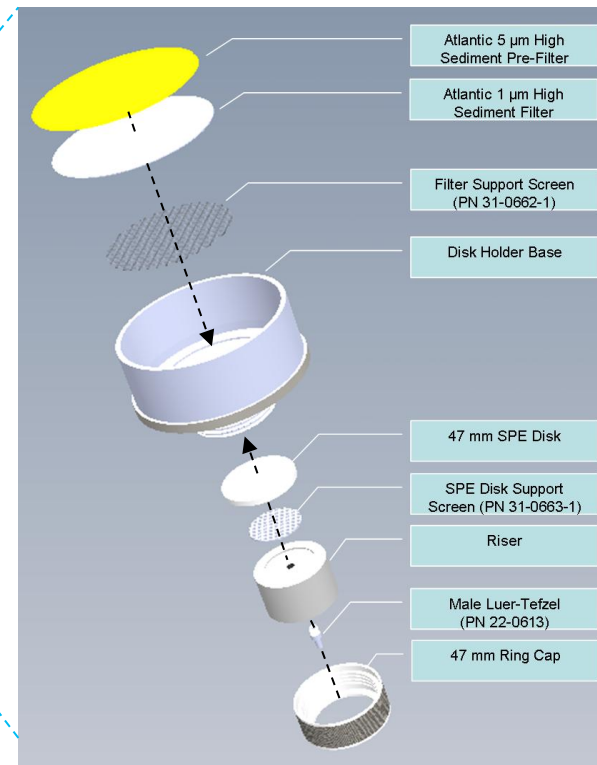
1L Sample

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



EZ Flow
Disk Holder

- 6x more filtering surface area for 47 mm disk
- Uses 100 mm pre-filters (1 and 5 μ m)



- **200 mL Extract Volume**
- **1 ton DCM ~ 3410 samples (~ 13 samples/day for a year)**

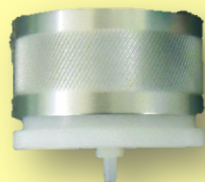
100 mL Sample Volume with SPE (applied to EPA Method 625)



- 1 μL is injected (unsplit) into the GC-MS.
- This maintains the same mass loading as the 1 Liter Sample Method.



100 mL
Sample



47 mm
Disk Holder



- **80 mL Extract Volume**
- 1 ton DCM ~ 8526 samples (~ 33 samples/day for a year)

Solvent Recovery

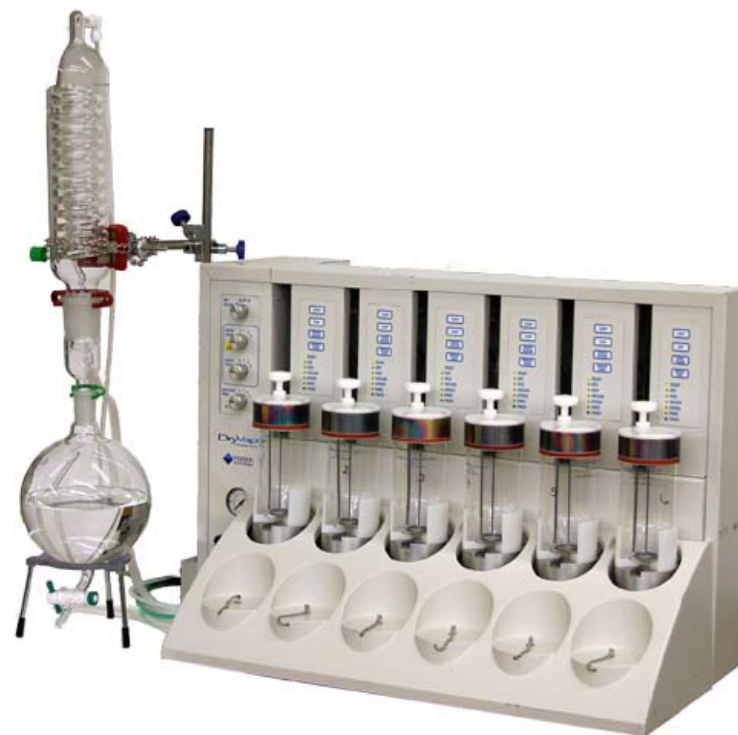


- ▶ The less solvent that needs to be evaporated to obtain the sensitivity needed in the analytical step, the less that might be emitted
- ▶ Recovery of evaporated solvent is the last step to consider in the full process
- ▶ Consider the potential for recovery when purchasing evaporators
- ▶ Evaporators that combine water vapor with solvent vapor will make recovery challenging



Closed Evaporation System

- ▶ DryVap Evaporation System
 - Evaporate up to 6 samples at once
- ▶ SolventTrap_{SVOC} Condensing Kit
 - The cooled glass column condenses more than 95% of a variety of solvents



- LLE's 1 ton DCM ~ 7 samples/day for a year without solvent recovery
- Or ~ 146 samples/day for a year with solvent recovery

Recovery of DCM

Experimental Conditions

- ▶ 1200 mL DCM Total
- ▶ 200 mL per Evaporation Tube
- ▶ Operating Conditions
 - Heat Power 5
 - Vacuum -5 in Hg
 - Chiller @ 0°C
 - Nitrogen Sparge @ 0 psig during heat state
 - Nitrogen Sparge @ 20 psig during Sparge state
 - Sparge Heat enabled
 - Evaporate to 0.9 mL endpoint
- ▶ Run time under 50 minutes



- **97.4% Recovery of DCM**
- **Std. Dev . of 0.270**
- **5 runs spanning 2 days with 2 operators**

Benefits of Solvent Recollection



The SolventTrap SVOC System allows facilities to:

- ▶ Prevent harmful solvent vapors from being released to the atmosphere
- ▶ Collect solvents for proper disposal or potential redistillation and reuse
- ▶ Protect workers from exposure to harmful solvent vapors



What to Do with the Collected Solvent?



- ▶ Disposal through proper channels
- ▶ Redistill to the quality required by the lab
- ▶ Sell to another facility for different use requiring less quality (such as metal finishing, etc..)



SolventTrap_{SVOC} Operation



DryVap/SolventTrap _{SVOC} System

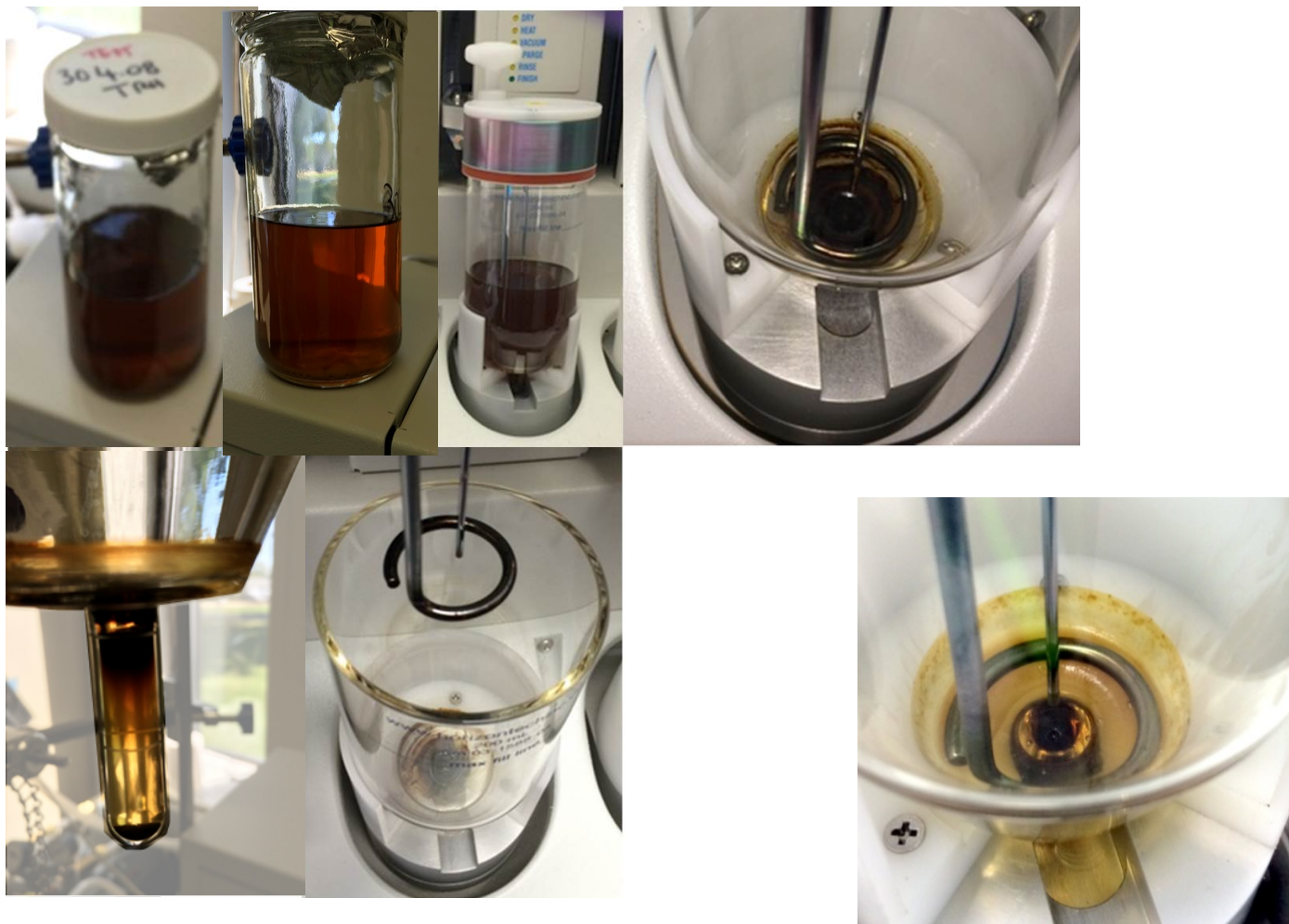


Advantages of the system include:

- ▶ Typical solvent volumes of 180-200 mL of DCM can be evaporated in 50-60 minute run times
- ▶ The end point can be automatically detected and the process ended when the endpoint is reached
- ▶ The sample can be evaporated directly into GC autosampler vials, eliminating transfer from the evaporation vessel
- ▶ Excellent solvent recovery for disposal or re-use



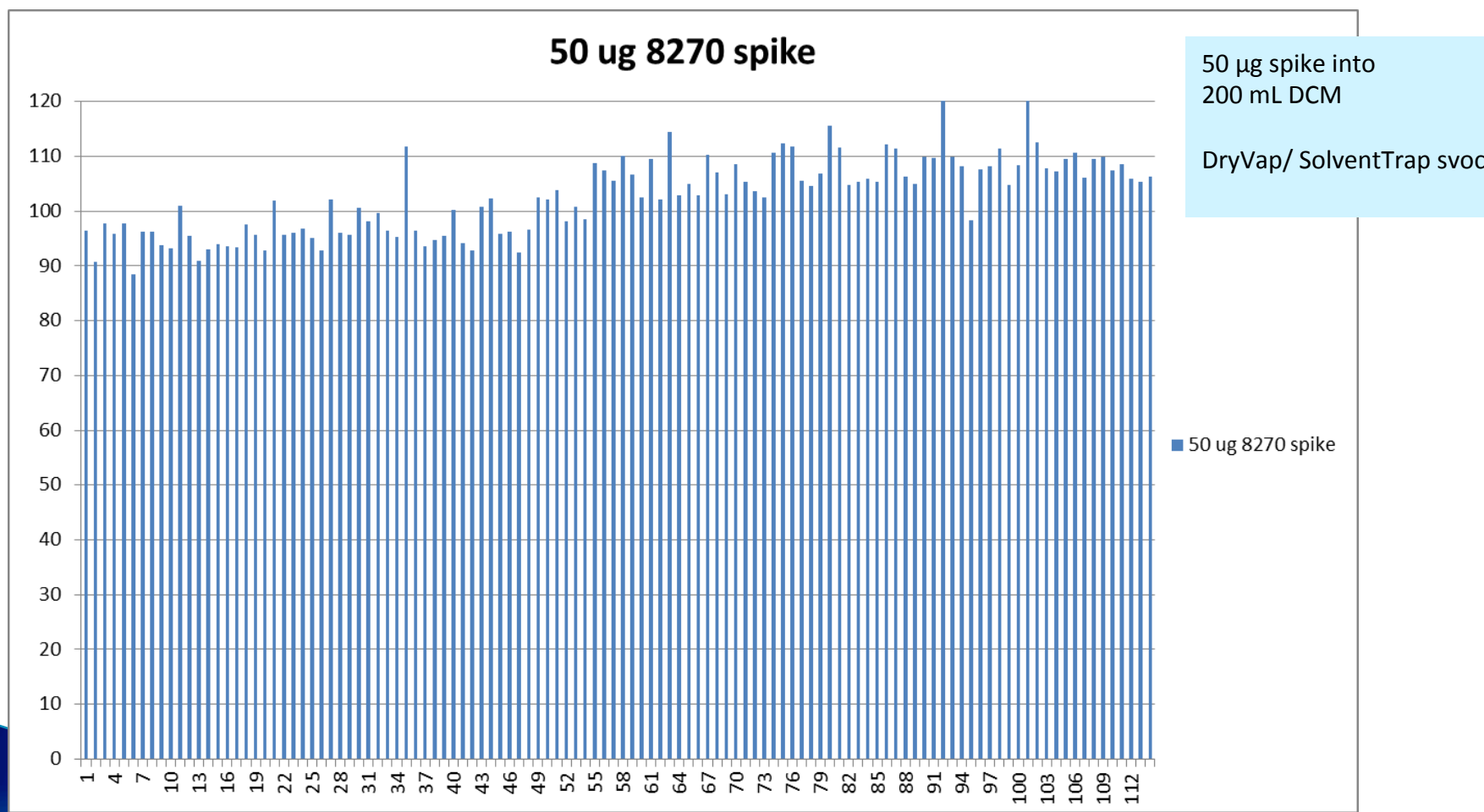
Real Samples – Soil Extracts



Excellent Solvent Recoveries

Analyte Recovery 8270 Spike

Average of n=6



Conclusion



Advances have been made that allow the reduction of solvent use in the laboratory

- ▶ Smaller sample sizes
 - Less solvent needed for efficient extraction
 - More sensitive analytical techniques reduce the need for large samples
- ▶ Solid-phase extraction reduces the solvent needed for effective extraction of small or larger samples (1L)
- ▶ Solvent recollection is feasible and instrumentation has been developed to recollect more than 95% of many solvents
- ▶ The trend of using less solvent will continue until the limit of feasibility is reached

