A Green Approach to Semi-Volatile Analysis

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What is Green Chemistry?

As defined by the EPA……

- "Green chemistry consists of **environmentally friendly, sustainable chemicals and processes** whose use results in **reduced waste, safer outputs, and reduced or eliminated pollution and environmental damage**. Green chemistry **encourages innovation** and **promotes the creation of products that are both environmentally and economically sustainable**."

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Environmental Lab Output

Estimated 2.8 Million lbs/yr of Methylene Chloride emitted into the air from the env. lab industry for semi-volatile extraction techniques!

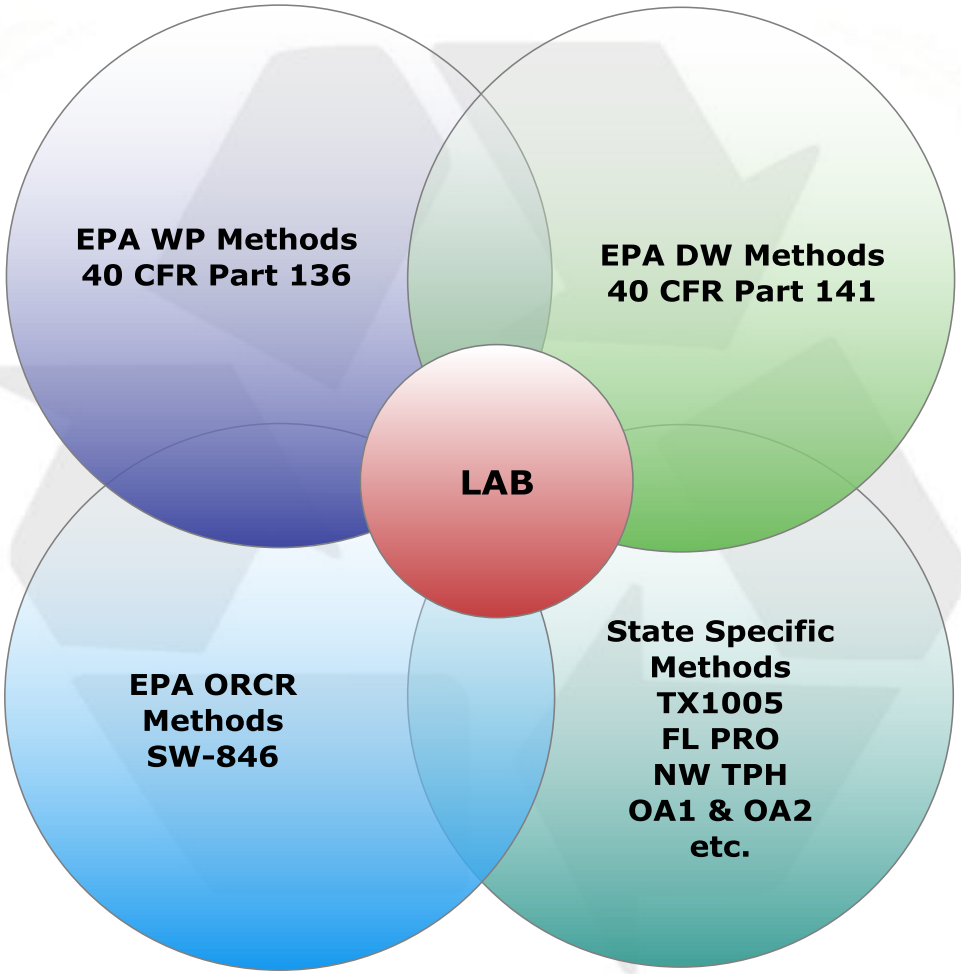
The First Attempt at Solvent Reduction

In 2003 ESC begin Methylene Chloride recollection. In an effort to reduce solvent emission ESC made an investment of 1 million dollars into solvent recollection. This invest resulted in a 90% reduction in solvent emitted in to the atmosphere by ESC.

Current Method Sources

Some Flexibility via ATP and 40 CFR Part 136.6 (method mod)

Very little flexibility



Very flexible

Some flexibility

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Trends in Method Revisions

- ✓Many method revisions are moving towards a prove it and you can use it "Performance Based" approach.
- ✓Examples 624, 625, 608, etc.
- ✓Allowance for alternate sample size, run time, extraction, carrier gas and in some cases instrumentation.
- ✓Requires proper method validation

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METHOD 3510

(Reduced Volume 100mL)

A More Modern Approach

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SW846 Method 3510C (Traditional)

- 3510C is found in SW846 and was first published in Rev.0 in 1986
- Separatory Funnel Liquid-Liquid extraction
- Uses 1000mL sample
- Requires **180mL** of solvent
- Used for methods 8270, 8081, 8082, etc.

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What is Reduced Volume 3510 Extraction

- With the use of a large volume injector you
  - ✓ Eliminate or reduce the amount of toxic solvents or reagents in current methods by 90% or more.
  - ✓ Allow traditional methods to be scaled down to much smaller sample volumes
  - ✓ Allow for new methods
  - ✓ **Reduces the overall carbon footprint for:**
    - ✯ Sample Collection
    - ✯ Analysis
    - ✯ Transportation
    - ✯ Handling
    - ✯ Disposal

3510C – Reduced Volume 100mL

"A Greener Version"

- Same as the 1000mL method
- Method is scaled to a 100mL sample
- Solvent is reduced to 18mL which is **90% less** than the original method
- Method is executed exactly as written, therefore it is **not considered** to be a **modification**
- **Instrumentation involves Large Volume Injection (LVI)**

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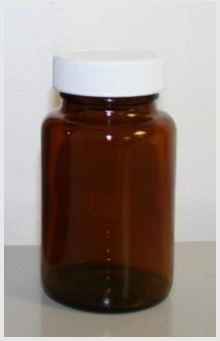
Why 3510? – Container Size Matters

Traditional Sampling/Handling	3510 Reduced Volume 100mL Sampling/Handling
1000mL Amber Glass Bottle	100mL Bottle



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Method 3511

Recently Approved Method

An Innovative approach to traditional sample extraction processes

- "The micro-scale approach minimizes sample size and solvent usage, thereby reducing the supply costs, health and safety issues, and waste generated."

  (from Method 3511 scope & application)

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What is method 3511

- Similar extraction to 8011 for EDB/DBCP
- 40mL VOA vial sampling
- 2mL of methylene chloride
- 5 minute shake
- Uses Large Volume Injection

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Why 3511? – The Environment Matters

Traditional Sampling/Handling	3511 Sampling/Handling
Extraction requires a total of **180mLs** of methylene chloride (toxic solvent)	Extraction requires a total of **2mLs** of methylene chloride (toxic solvent) **A REDUCTION OF 98.9%**

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Why 3511? – Container Size Matters

Traditional Sampling/Handling	3511 Sampling/Handling
1000mL Amber Glass Bottle	40mL VOA vial

Why 3511? – Weight

Traditional Sampling/Handling	3511 Sampling/Handling
Typically **4 Sample Sets** (8 total sample bottles) fit into the largest cooler, which is 48qt, weighs 10 lbs, takes 4 bags of ice, and the total loaded weight is approx. **60 - 80lbs**	**8 Sample Sets** (16 Vials) will fit in a 10qt cooler. Total weight **<15lbs**

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Why 3511? – Volume Matters

Traditional Sampling/Handling	3511 Sampling/Handling
Low purge well may not produce enough volume	Much easier to produce the 40mL volume needed Allows for easy collection of duplicate samples

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Technical Impressions

- ✓ 3511 has been validated and is comparable to it's larger volume counterpart 3510C.
- ✓ Combined with large volume injection there is no sacrifice to MDL's or Reporting Limits
- ✓ 3511 does not require the traditional concentration step therefore eliminating potential to compromise lighter compounds that may exist in the sample
- ✓ **Proficiency testing has been 100% acceptable!**

MDL Comparison for PAH's by 8270SIM

Analyte	8270 RDL ppb	3510 MDL ppb	3511 MDL ppb	3511 RDL/MDL Ratio
1-Methylnaphthalene	0.25	0.0189	0.00821	30.5
2-Chloronaphthalene	0.25	0.0165	0.0059	42.4
2-Methylnaphthalene	0.25	0.0155	0.0068	36.8
Acenaphthene	0.05	0.00823	0.00739	6.8
Acenaphthylene	0.05	0.0109	0.00588	8.5
Anthracene	0.05	0.0131	0.00601	8.3
Benzo(a)anthracene	0.05	0.0124	0.00895	5.6
Benzo(a)pyrene	0.05	0.0123	0.0116	4.3
Benzo(b)fluoranthene	0.05	0.0192	0.0138	3.6
Benzo(g,h,i)perylene	0.05	0.0194	0.0114	4.4
Benzo(k)fluoranthene	0.05	0.013	0.0136	3.7
Chrysene	0.05	0.0144	0.00923	5.4
Dibenz(a,h)anthracene	0.05	0.00454	0.00385	13.0
Fluoranthene	0.05	0.0165	0.012	4.2
Fluorene	0.05	0.00898	0.0085	5.9
Indeno(1,2,3-cd)pyrene	0.05	0.00739	0.0148	3.4
Naphthalene	0.25	0.0123	0.0198	12.6
Phenanthrene	0.05	0.0184	0.00807	6.2
Pyrene	0.05	0.013	0.0102	4.9

- Reporting limits remain the **same** regardless of prep method
- RDL/MDL ratio well within acceptance (should be 3X or greater)
- Average recovery across MDL study 101 – 130% at 0.05ppb

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LCS Recovery & Limits Comparison

Compound Name	3510C 1000mL with 8270C SIM			3511 with 8270C SIM		
	Average % Rec	LCL	UCL	Average % Rec	LCL	UCL
1-METHYLNAPHTHALENE	87	48	126	90	52	128
2-CHLORONAPHTHALENE	88	47	129	90	70	109
2-METHYLNAPHTHALENE	84	43	126	91	69	113
ACENAPHTHENE	86	51	121	91	72	111
ACENAPHTHYLENE	88	50	125	97	66	127
ANTHRACENE	97	61	133	100	68	133
BENZO(A)ANTHRACENE	91	58	123	108	71	145
BENZO(A)PYRENE	95	58	132	105	80	130
BENZO(B)FLUORANTHENE	92	53	131	95	70	119
BENZO(G,H,I)PERYLENE	96	54	139	89	62	116
BENZO(K)FLUORANTHENE	96	55	137	89	63	115
CHRYSENE	95	58	132	92	71	114
DIBENZ(A,H)ANTHRACENE	94	57	131	94	67	121
FLUORANTHENE	95	57	134	100	69	131
FLUORENE	89	52	125	92	70	114
INDENO(1,2,3-CD)PYRENE	95	56	133	95	70	120
NAPHTHALENE	82	41	122	89	73	105
PHENANTHRENE	90	54	127	91	73	110
PYRENE	95	55	135	99	74	125

LCS Recovery & Limits

- LCS recovery is consistently more accurate using 3511
- Precision (repeatability) is more consistent as shown by the tighter range of the calculated acceptance limits.
- Overall Accuracy and Precision are superior, when compared to traditional 3510C.

Proficiency Testing Results

	3511 40mL Extraction WP-198		
Analyte	**Reported Value ug/L**	**Assigned Value ug/L**	**% Recovery**
Acenaphthene	66.8	82.1	**81.4**
Acenaphthylene	24.1	28.8	**83.7**
Anthracene	89.5	91.2	**98.1**
Benzo(a)anthracene	54.0	61.1	**88.4**
Benzo(b)fluoranthene	22.4	25.8	**86.8**
Benzo(k)fluoranthene	61.4	67.7	**90.7**
Benzo(g,h,i)perylene	21	23.4	**89.7**
Benzo(a)pyrene	27.4	30.3	**90.4**
Chrysene	35.9	46.2	**77.7**
Dibenz(a,h)anthracene	24.5	28.8	**85.1**
Fluoranthene	107	110	**97.3**
Fluorene	NS	NS	
Indeno(1,2,3-cd)pyrene	NS	NS	
2-Methylnaphthalene	44.8	57.0	**78.6**
Naphthalene	NS	NS	
Phenanthrene	60	60.2	**99.7**

*NS = Not spiked

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Calculated MDL Comparison
PAH SIM by 8270C

Analyte	Conc. Used in ug/L	3510 1L MDL	3510 RV MDL	3511 MDL	Units
1-Methylnaphthalene	0.05	0.00977	0.00884	0.00821	ug/L
2-Chloronaphthalene	0.05	0.01190	0.00560	0.00590	ug/L
2-Methylnaphthalene	0.05	0.00897	0.00829	0.00680	ug/L
Acenaphthene	0.05	0.00823	0.01000	0.00739	ug/L
Acenaphthylene	0.05	0.00636	0.01190	0.00588	ug/L
Anthracene	0.05	0.00979	0.01100	0.00601	ug/L
Benzo(a)anthracene	0.05	0.01240	0.00882	0.00895	ug/L
Benzo(a)pyrene	0.05	0.01110	0.01150	0.01160	ug/L
Benzo(b)fluoranthene	0.05	0.01910	0.01170	0.01380	ug/L
Benzo(g,h,i)perylene	0.05	0.01570	0.00886	0.01140	ug/L
Benzo(k)fluoranthene	0.05	0.01300	0.01350	0.01360	ug/L
Chrysene	0.05	0.01440	0.01090	0.00923	ug/L
Dibenz(a,h)anthracene	0.01	0.00454	0.01000	0.00385	ug/L
Fluoranthene	0.05	0.01650	0.00519	0.01200	ug/L
Fluorene	0.05	0.00710	0.00976	0.00850	ug/L
Indeno(1,2,3-cd)pyrene	0.05	0.00421	0.01120	0.01480	ug/L
Naphthalene	0.05	0.01030	0.01200	0.01980	ug/L
Phenanthrene	0.05	0.01790	0.00710	0.00807	ug/L
Pyrene	0.05	0.00717	0.00811	0.01020	ug/L

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3511 Regulatory Acceptance

- ✓ 3511 Accreditation via A2LA (ISO 17025), Dept. of Defense (DOD), NELAP since 2010
- ✓ Multiple states have granted accreditation/ certification – Formal written approval has been received from **30 states**, since early 2010.
- ✓ Multiple data user divisions have granted approval - Some are states with no formal cert/accred program exists
- ✓ Well received by on-site Assessors. Assessors have been impressed at the execution, process and results from 3511.
- ✓ **……..Momentum to migrate to 3511 has increased**

Method Validation Timeline

Petroleum Related Methods

- ✓ Optimized and Validated various Diesel Range Organics methods
- ✓ Expanded into PAH and PAH SIM by 8270
- ✓ 8081 & 8082 Pesticides

Other Methods in Development

- ✓ 8270 full BNA

Several other 8000 Series Methods by the end of 2014

The Challenges of RV 3510, 3511 and large volume injection

- Initial investment of equipment
- Development time
- Longer runtimes
- Dealing with larger solvent volumes in the inlet
- Solving the complex extraction riddle? (BNA)

3510 Reduced Volume or 3511?

- Both methods achieve overall reduction in container, solvent, volume, weight.
- Both are more environmentally friendly than the traditional 1000mL counterpart
- Preference is currently driven by agency acceptance
- 3511 exhibits superior analytical performance over the traditional and scaled 3510 option.
- 3510 is readily available for all method 8000 series extractables

Conclusion

Innovation, flexibility, and availability of methods has allowed development of techniques that benefit:

- ✓The sampling process
- ✓The analytical process
- ✓The environment

3511 & 3510 100mL are viable options to shift the industry toward a more modern approach to sampling and analyses

Thank you for your time!

Any Questions?

"ESC……Saving the environment, through innovation, one method at a time"