NEMC 2016

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Overcoming Legacy Obstacles

Richard Burrows
TestAmerica Inc.

What is required to overcome a problem in Environmental Analysis?

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1. Someone has to realize that there is a problem
2. Someone has to decide that something needs to be done about it
3. The existence of the problem has to be communicated in such a way that momentum builds around the idea that a change is needed
4. Data has to be generated to prove that the problem is real and significant
5. Then the hard work starts……

Examples – Past, Present and Future

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- Exorcising Demons from the past
  - Is there a huge data quality problem that can be fixed with a little gizmo?
- Slaying Bugbears of the present
  - Are there fundamental problems affecting all methods that can be fixed with a different mathematical approach, also applicable to all methods?
- Hobgoblins to be dealt with in the future
  - Are there problems that should be fixed by using new analytical technology?

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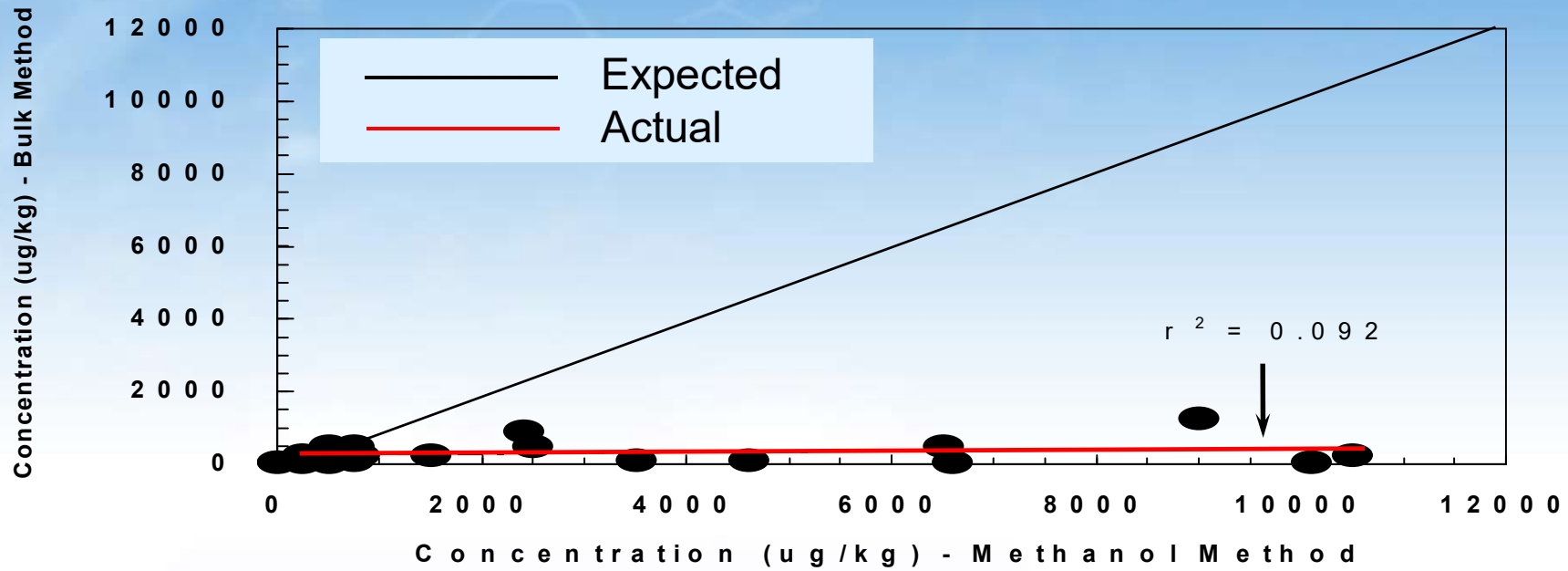
Example: Soil volatiles analysis

Significant Bias Between Methanol Preserved and Nonpreserved Samples



Volatile Organic Compounds: Comparison of Two Sample Collection and Preservation Methods, Liikala, T.; Olsen, K.; Teel, S.; and Lanigan, D., November 1996.

California Split Spoon?

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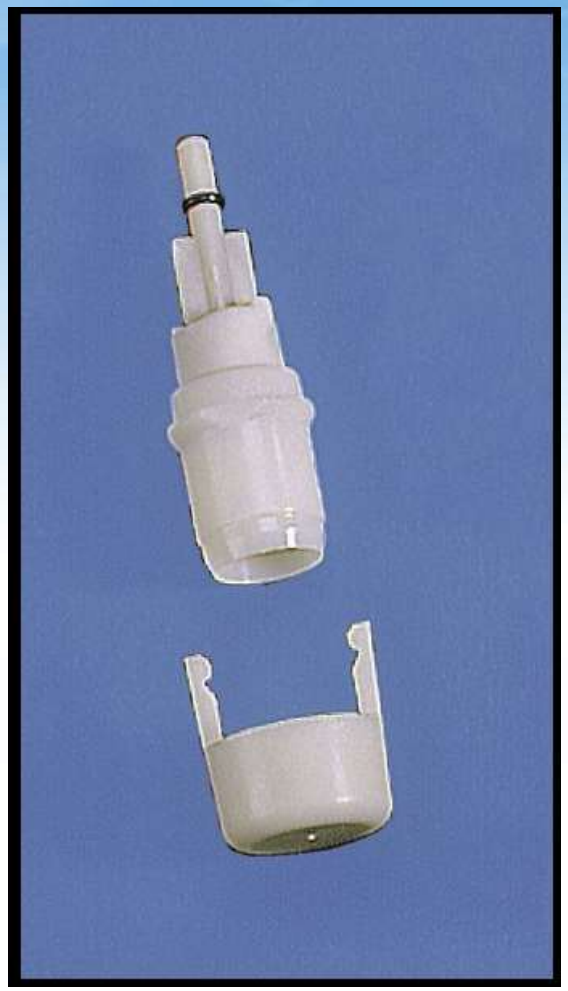
TCE Recovery after 5 days at 4C

- 4% (Aluminum lined cap)
- 5% (PTFE cap)

Alan D. Hewitt and Nicole J E Lukash, American Env. Lab., August 1996, Page 15

The Gizmo!



Another gizmo

Timeline

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Sw846 Update III

June 13 1997 – Method 5035

What did it take?

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Some states still accepting bulk sampling methods today, 19 years later

Example 2
Calibration evaluation

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What's the problem?

Pervasive use of the Correlation Coefficient (and Coefficient of Determination)

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Van Arendonk and Skogerboe, Anal. Chem. 53, 1981, 2349-2350

"One practice that should be discouraged is the use of the correlation coefficient as a means of evaluating goodness of fit of linear models"

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Taylor, Statistical Techniques for Data Analysis, 1990

"The author has seen cases where a correlation coefficient of 0.997 was believed to be a better fit than 0.996 of a 5 point calibration curve. One can even find requirements in quality assurance plans to recalibrate if the correlation coefficient is less than 0.995!"

Correlation coefficient

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IUPAC, 1998
Guidelines for Calibration in Analytical Chemistry

The correlation coefficient, which is a measure of two random variables, has no meaning in calibration because the values x are not random quantities

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Meier and Zund, Statistical Methods in Analytical Chemistry, 2000

For most applications, and calibration curves in particular, the correlation coefficient must be regarded as a relic of the past

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WTQA '98 - 14th Annual Waste Testing & Quality Assurance Symposium

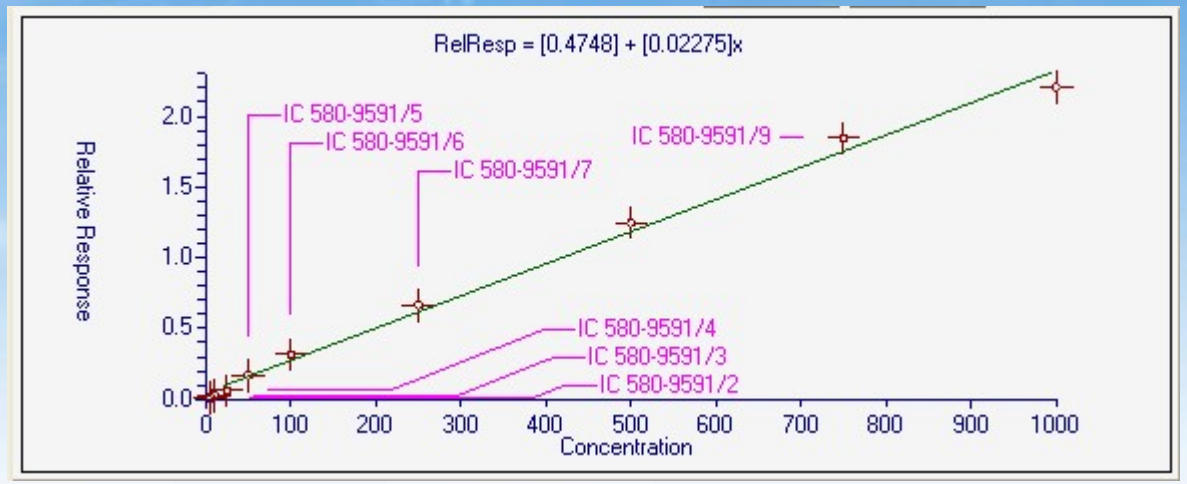
TECHNIQUES FOR IMPROVING THE ACCURACY OF CALIBRATION IN THE ENVIRONMENTAL LABORATORY

Dennis A Edgerley
Quanterra Environmental Services, 880 Riverside Parkway, West Sacramento, California 95605

First introduction of Relative Standard Error (RSE) as an option for measuring calibrations

1	0.00
2	0.00
3	0.00
4	0.00
5	0.00
10	0.00
100	10000

Calibration issues 2007



$r = 0.997$, $r^2 = 0.994$

Calibration Standard Levels

Level	Used	Amount	Area	ISArea	%Error
IC 580-9591/2	☑	5	1348	618332	421.63
IC 580-9591/3	☑	10	3250	647316	198.43
IC 580-9591/4	☑	25	7697	646400	78.87
IC 580-9591/5	☑	50	23729	700099	7.13
IC 580-9591/6	☑	100	47131	748204	17.47
IC 580-9591/7	☑	250	111297	833662	8.93
IC 580-9591/8	☑	500	229185	917698	5.52
IC 580-9591/9	☑	750	371628	1005615	5.43
IC 580-9591/10	☑	1000	499631	1131444	5.11

421.63

198.43

Nitrate MDL 0.0082		Linear unforced	Linear Forced	Linear 1/x	Linear $1/X^2$
0.05	**2247869**				
0.5	**20450323**				
2.5	**1.06E+08**				
5	**2.23E+08**				
10	**4.84E+08**				
	r				
	RSE				

RSE timeline

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- Edgerley Paper, 1998
- ACIL comments on Update 3
- Incorporated into SW-846 – Guidance memo to Update 3 (1998) and then method 8000C
- Many more presentations……
- Incorporated in CFR40 Part 136 (Wastewater methods) 2012
- Incorporated into TNI standards 2016 (as an option)

18 years and counting…..

RSE Status

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- RSE adoption should be relatively straightforward because:
  - For the average RF calibration RSE = RSD
  - RSE essentially just allows RSD to be applied to all types of curves, instead of just Average RF
- However:
- Virtually unused
  - May increase after 2016 standards are adopted
  - Needs to be incorporated into major manufacturer instrument software
  - Needs removal of correlation coefficient option??
  - Needs champions

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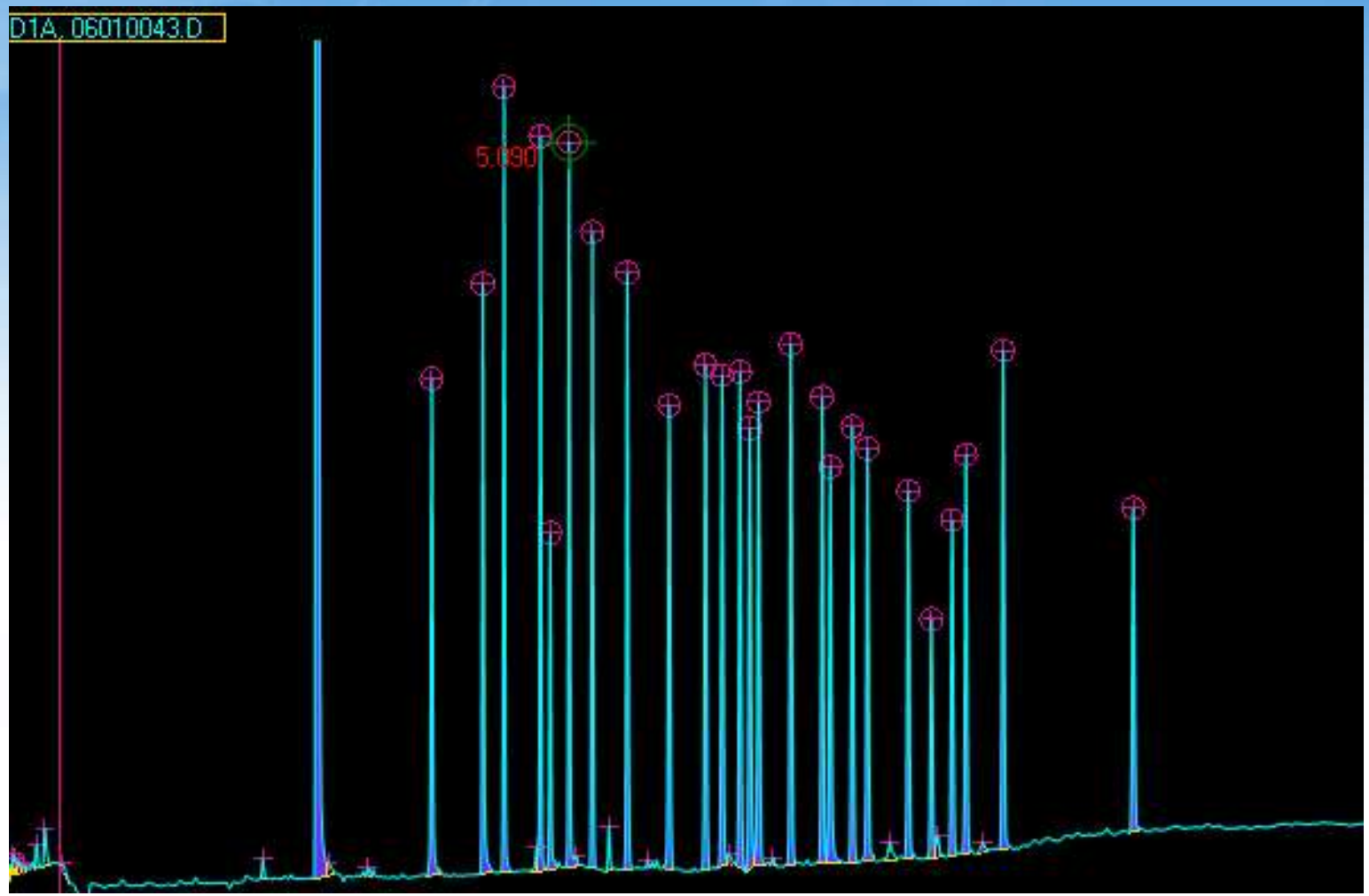
Example 3 – Something for the future

GC/ECD methods

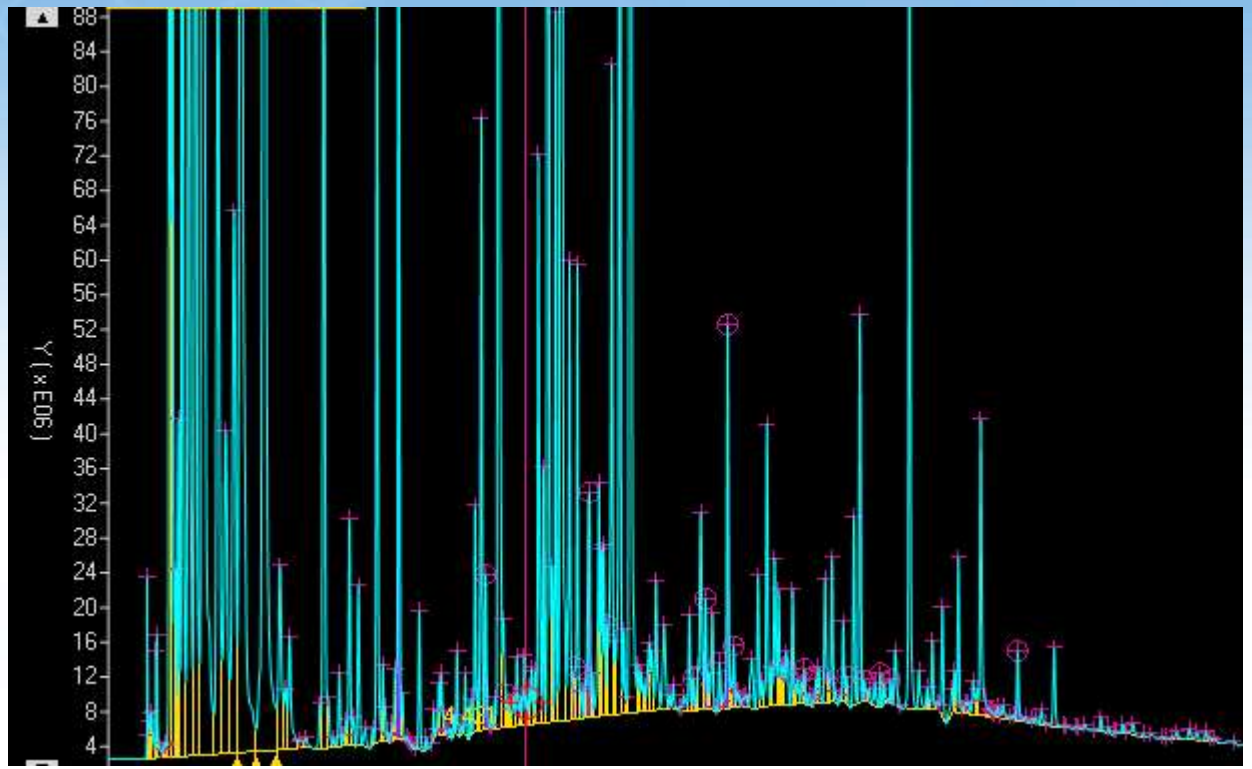
Organochlorine pesticies, 4 ng/mL

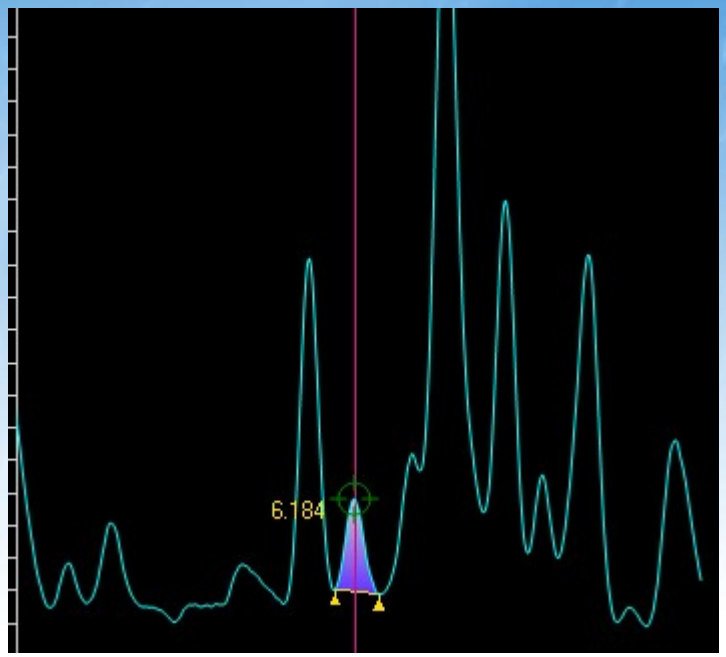


Same spike in a sample

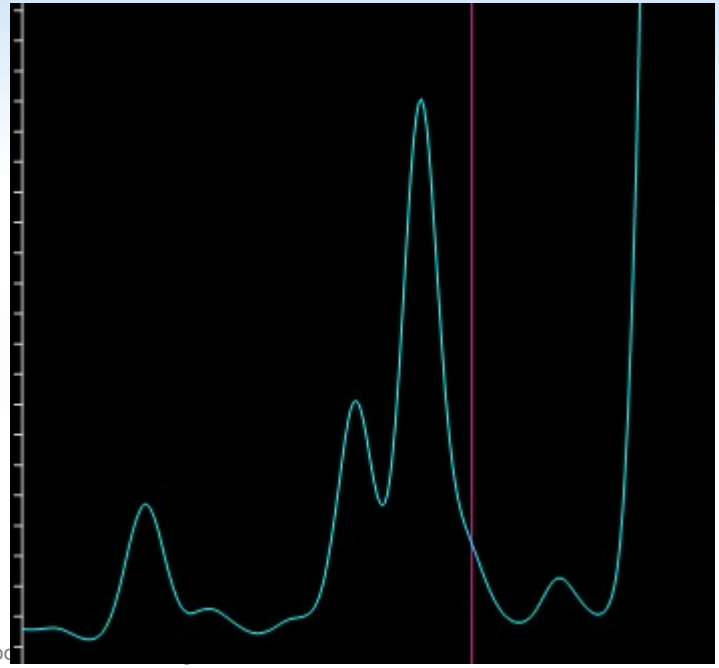
Same spike
6 false negatives

Unspiked sample
8 hits (possible false positives)





Non-interfered peak
No RT shift



Interfered peak
No RT shift
Masked by non-target compound

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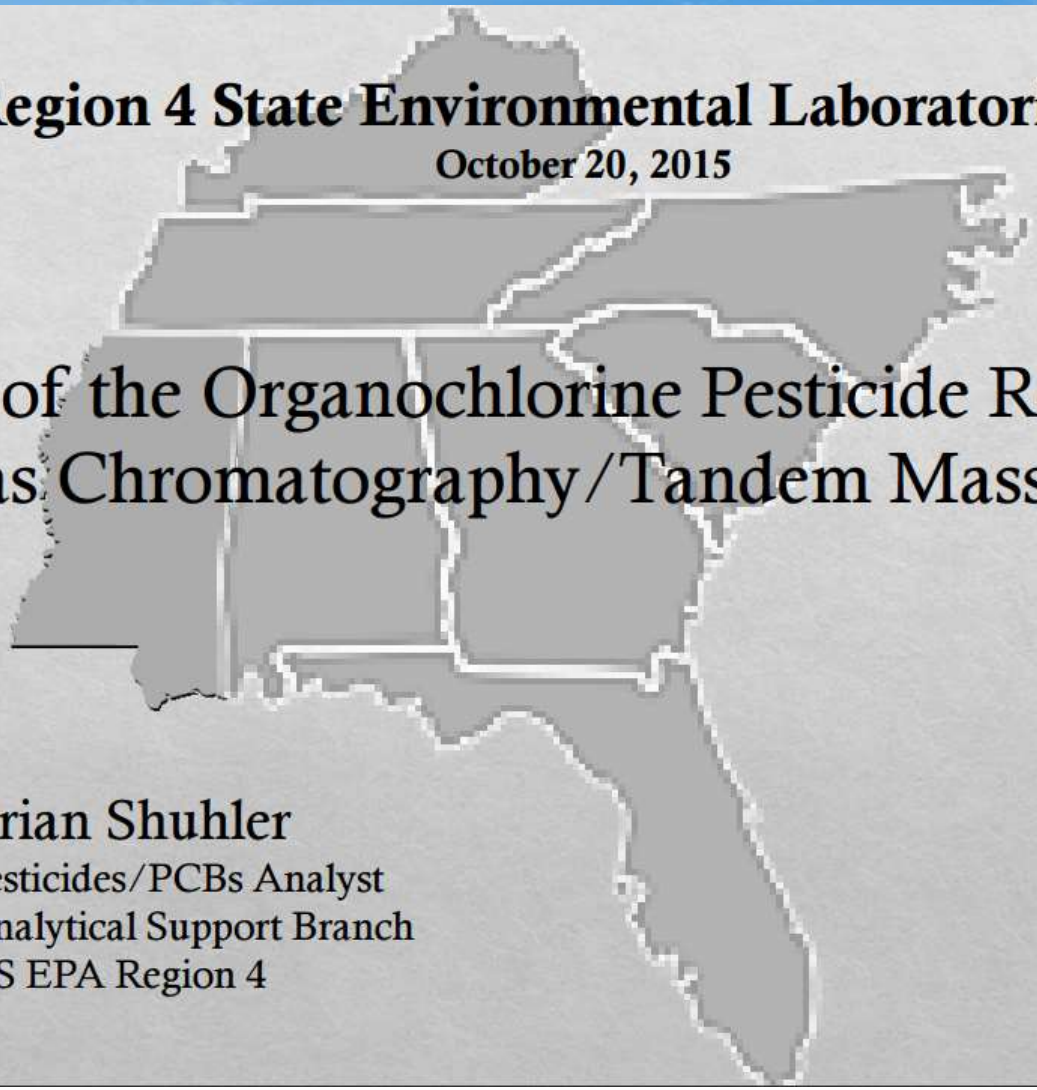
EPA Region 4 State Environmental Laboratories Meeting

October 20, 2015



Analysis of the Organochlorine Pesticide Routine Target List by Gas Chromatography/Tandem Mass Spectrometry

Brian Shuhler
Pesticides/PCBs Analyst
Analytical Support Branch
US EPA Region 4

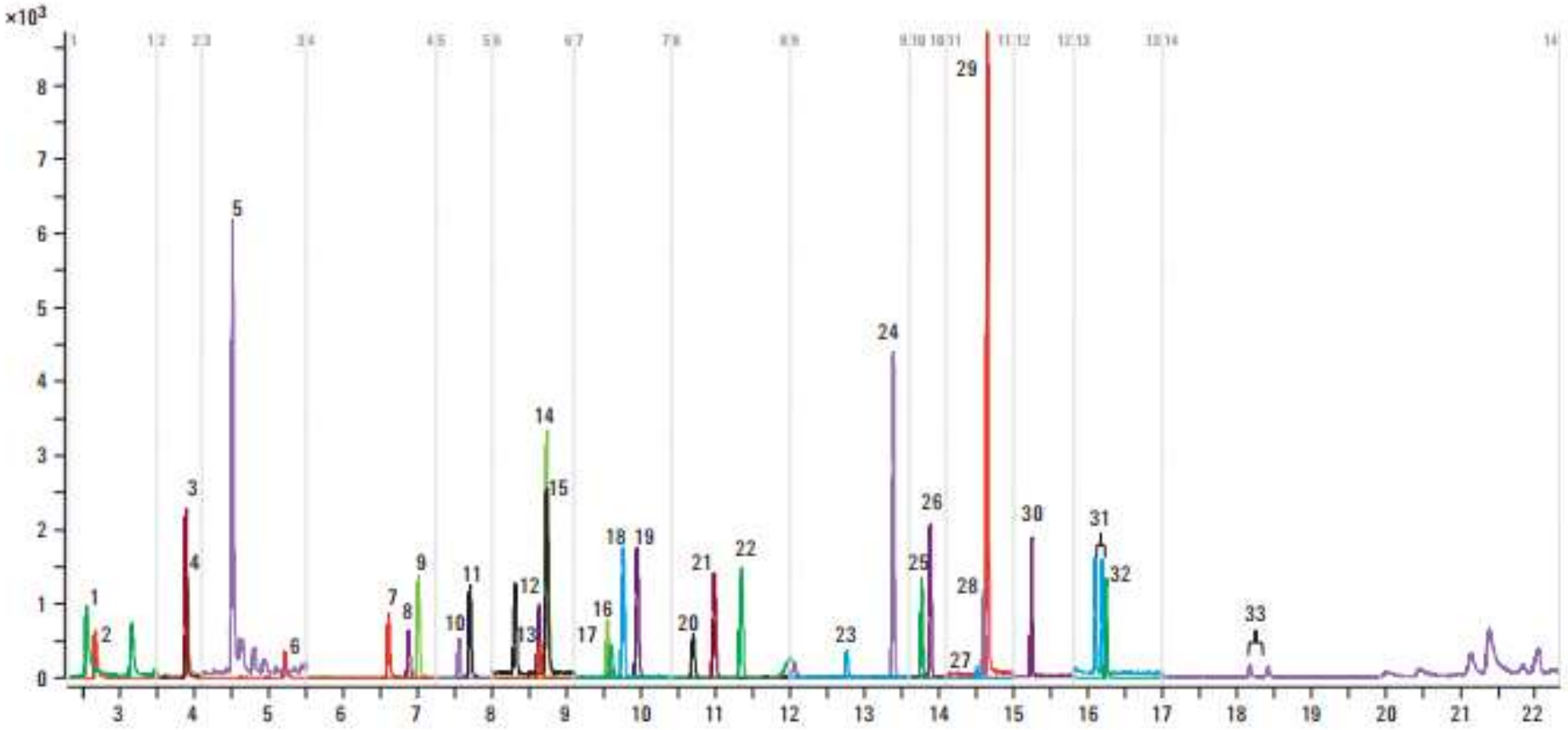


Figure 1. GC/MS/MS chromatogram (MRM) for 10 ppb spiked QuEChERS sample using Ultra Inert liner with wool (p/n 5190-2293). Peak identification: 1. Methamidophos, 2. Dichlorvos, 3. Mevinphos, 4. Acephate, 5. σ-Phenylphenol, 6. Omenthoate, 7. Dimenthoate, 8. Altrazine, 9. Lindane, 10. Diazinon, 11. Chlorothalonil, 12. Chloropyrifos methyl, 13. Vinclozolin, 14, Carbaryl, 15, Tolclofos methyl, 16. Dichlorfluanid, 17. Aldrin, 18. Malathion, 19. Dichlorobenzophenone, 20. Pirimiphos ethyl, 21. Tolyfluanid, 22 Procymidone, 23. Endrin, 24. Ethion, 25. Endosulfan sulfate, 26. DDT, 27. Endrin ketone, 28. Iprodione, 29. Phosmet, 30. Phosalone, 31. Permethrin isomers, 32. Coumaphos, 33. Deltamethrin isomers.

GC/MS/MS pesticides status

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Widely used in food and medical testing

Very seldom used in environmental testing (<1% ECD)

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Questions?