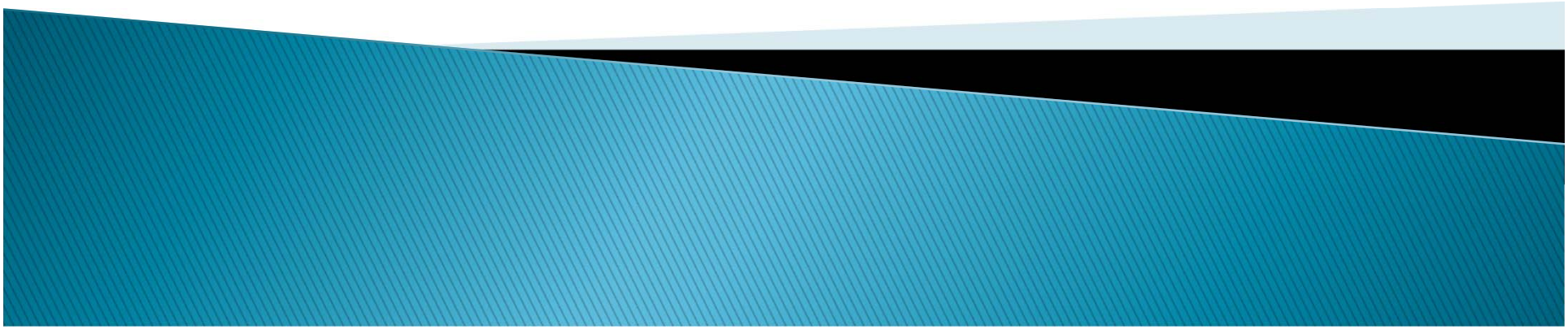
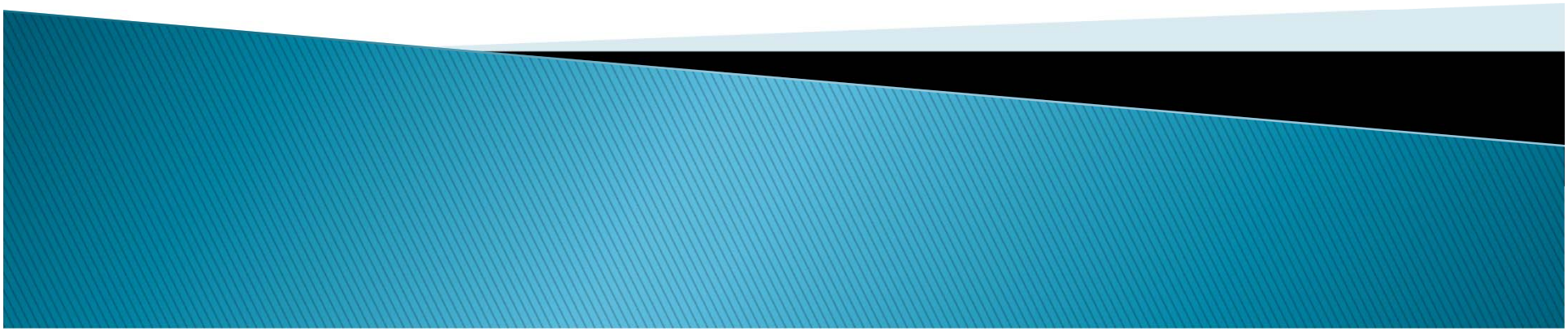
Informatics Data Processing ~~of Outliers~~ of MDLs in NPDES Permits

MDL of Multiple Analytes



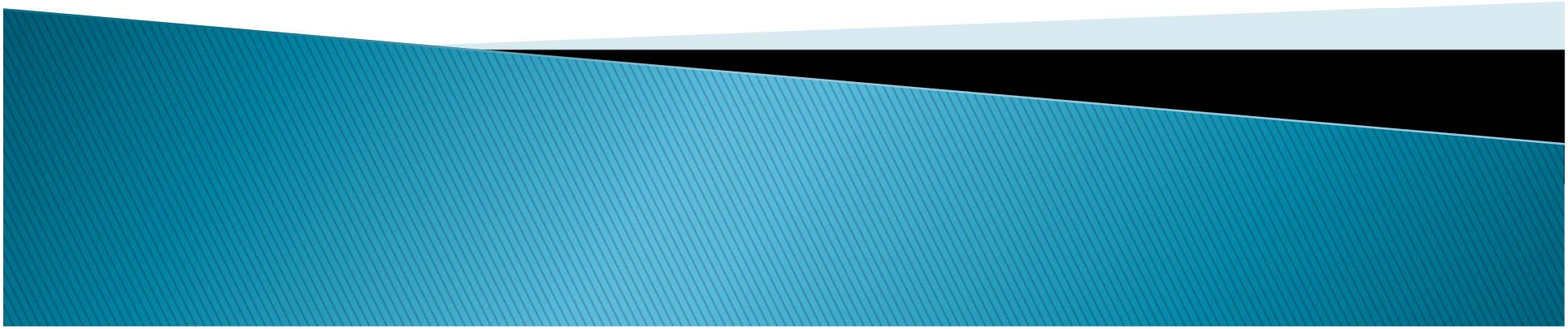
Multivariate, What Is It?

Multivariate Data Analysis refers to any statistical technique used to analyze data that arises from more than one variable.



Identification of the Problem

State NPDES Permit Writer

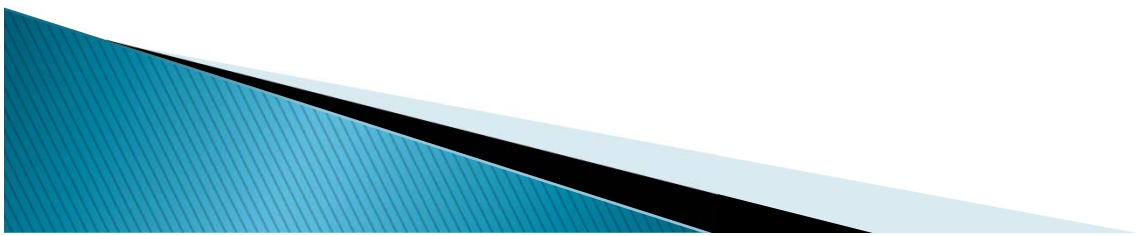


Water Quality Waste Load Allocation

- According to Table 1 of Iowa's WQS, polynuclear aromatic hydrocarbons (PAHs) include the sum of known and suspected carcinogenic PAHs which includes:
  - benzo(a)anthracene,
  - benzo(b)fluoranthene,
  - benzo(k)fluoranthene,
  - chrysene,
  - dibenzo(a,h)anthracene,
  - indeno(1,2,3-cd)pyrene.

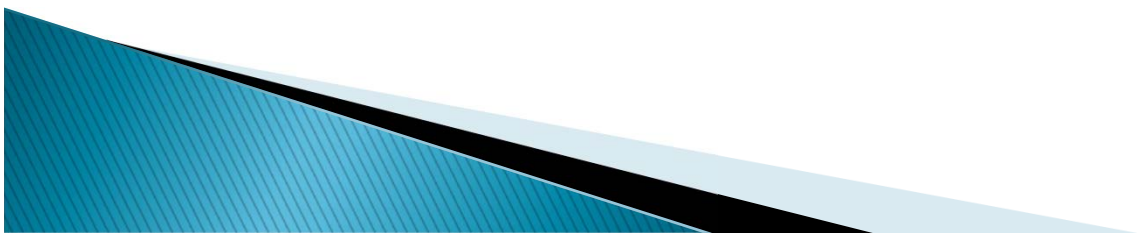
Waste Load Allocation Calculation

- A Wasteload Allocation (WLA) is the portion of a receiving water's assimilative capacity that is allocated to one of its existing or future point sources of pollution.
- WLAs establish water quality based effluent limits for point source discharge facilities.



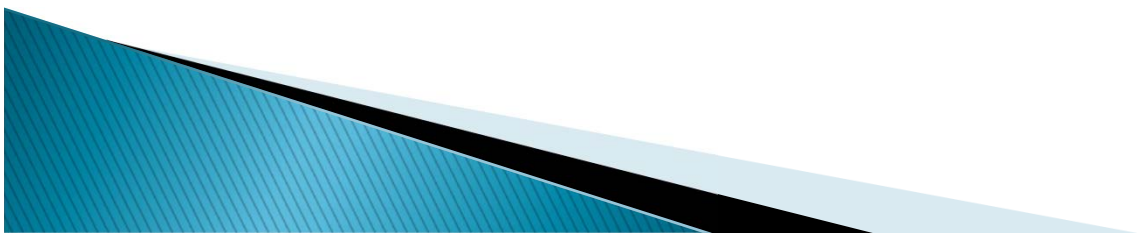
Reasonable Potential

- In instances where little data exists (less than 10 sample results) for a particular pollutant, the permit writer must use his/her best professional judgment when determining if reasonable potential exists for a pollutant to cause or contribute to a water quality standard violation.

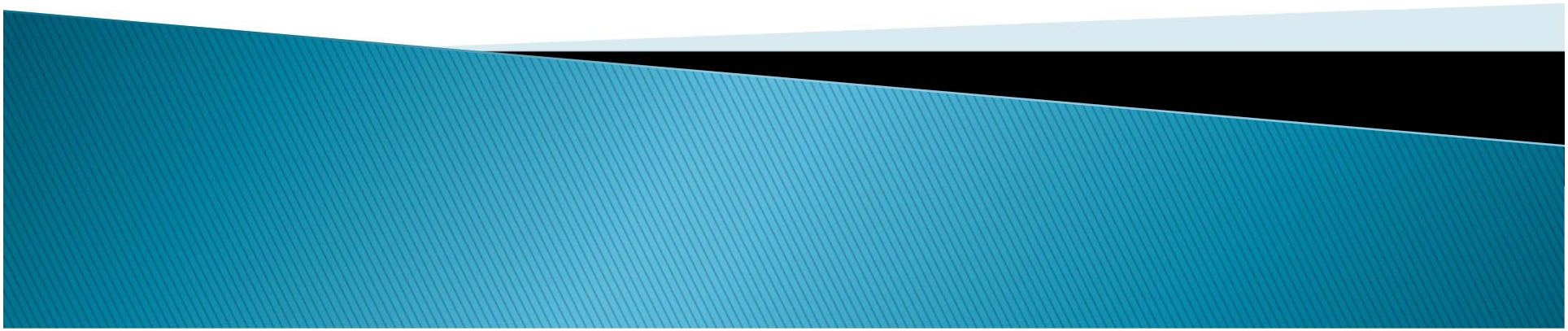


Sufficiently Sensitive Method Rule

- For the purposes of the application, “suitable method” means a method that is sufficiently sensitive to measure as close to the water quality-based standard as possible.

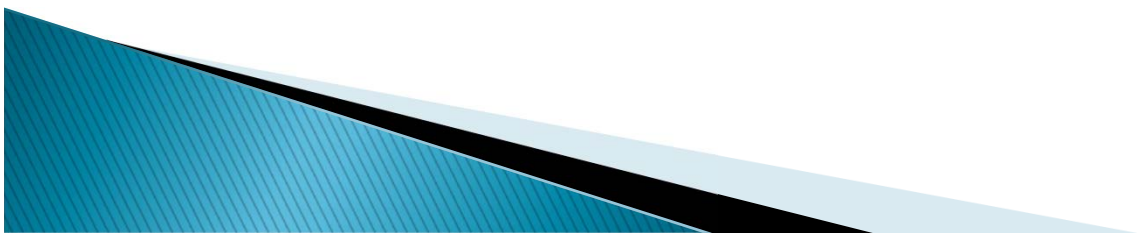


What Happened in the NPDES Permit Justification



Sufficiently Sensitive Method Rule is Enforced as:

- These six PAHs were detected in the second round of effluent testing. The MDLs associated with these results were greater than the PAHs limit calculated in the WLAs for outfalls 001 and 016, but the results were less than the reporting limits and, therefore, not quantifiable.
- Based on the above information, the permit includes monitoring for each of these six PAHs for both outfalls at a frequency of once per month based on best professional judgment to help determine if a PAHs limit may be needed in the future.

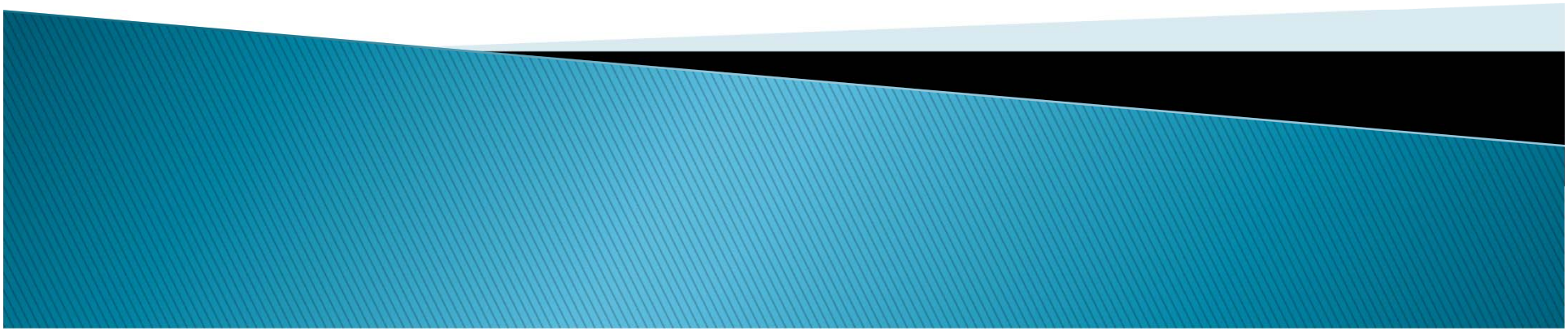


Pollutant	30-day Avg Conc Limit (mg/L)	Daily Max Conc Limit (mg/L)	Part B Scan 2 (mg/L)
benzo(a)anthracene	1.901E-04	8.529E-02	0.000379
benzo(b)fluoranthene	1.901E-04	8.529E-02	0.000451
benzo(k)fluoranthene	1.901E-04	8.529E-02	0.000459
chrysene	1.901E-04	8.529E-02	0.000303
dibenzo(a,h)anthracene	1.901E-04	8.529E-02	0.000926
indeno(1,2,3-cd)pyrene	1.901E-04	8.529E-02	0.000835
sum	1.901E-04	8.529E-02	0.003353

Pollutant	MDL (mg/L)	MDL >Avg Limit?	MDL >Max Limit?	Reasonable Potential?
benzo(a)anthracene	0.000247	Yes	No	All 6 PAHs detected in Scan 2; MDLs>Avg Limits; Results <Reporting Limits.
benzo(b)fluoranthene	0.00032	Yes	No	
benzo(k)fluoranthene	0.000206	Yes	No	
chrysene	0.000299	Yes	No	
dibenzo(a,h)anthracene	0.000258	Yes	No	
indeno(1,2,3-cd)pyrene	0.000247	Yes	No	
sum	0.001577	Yes	No	

What Could Be Done Differently?

In the LIMS

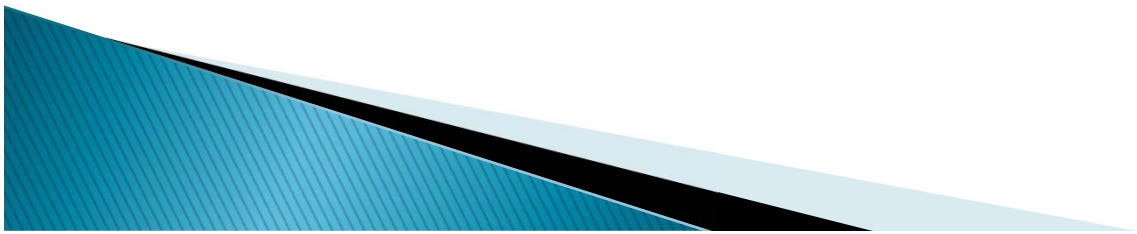


Pooled MDLs

$$MDL_{Pooled} = \sqrt{\frac{MDL^2_{(Lab\ 1)} + MDL^2_{(Lab\ 2)} + \bullet\bullet\bullet MDL^2_{(Lab\ m)}}{m}} \times \frac{a}{b}$$

$a = 2.55$ for 3 Laboratories, 2.41 for 9 Laboratories

$b = 3.14$



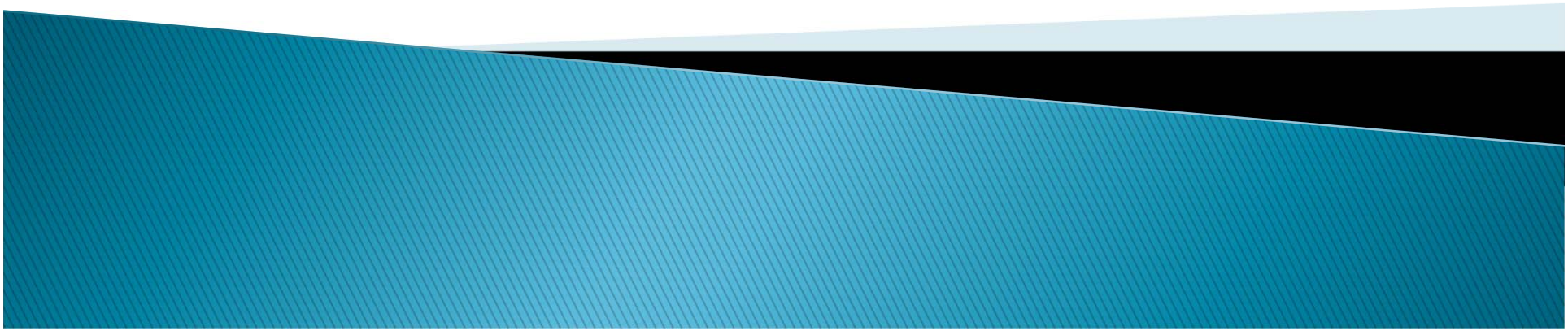
Pooled MDLs Results

Individual PAH MDL	Pooled PAH MDL
0.000247	0.000204
0.000320	
0.000206	
0.000299	
0.000258	
0.000247	

Comparison

MDL	MDL (mg/L)	MDL >Avg Limit?	MDL >Max Limit?
Iowa DNR Sum	0.001577	Yes	No
Pooled	0.000204	Yes	No

Other Options

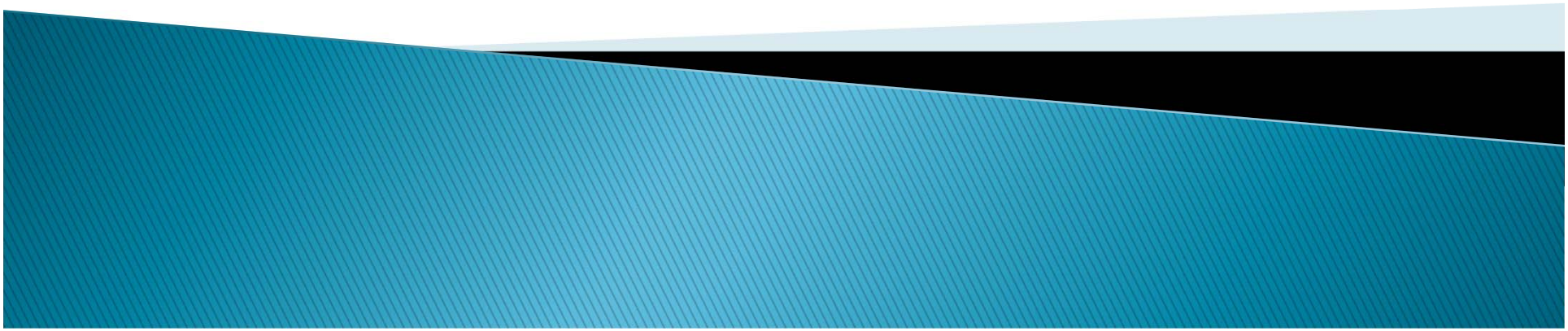


What is a Multiple MDL ?

- 40 CFR §136 Appendix B
  - If more than 100 method blanks are available, set MDL_b to the level that is no less than the 99th percentile of the method blank.
- IUPAC-Consistent Approach, Analytical Chemistry

$$LOD = \left(t_{a,v} + t_{b,v} \right) \mathrm{var}(y_{MDL})^{1/2}$$

What Finally Happened



Review the Mass Spectra as per EPA 625

Report Date: 19-Apr-2017 08:00:52 Chrom Revision: 2.2 18-Apr-2017 07:43:58

TestAmerica Cedar Falls

Data File: \\ChromNA\CedarFalls\ChromData\Milli\20170418-36501.b\J9059.D

Injection Date:	18-Apr-2017 19:35:30	Instrument ID:	Milli		
Lims ID:	310-103589-B-2-A	Lab Sample ID:	310-103589-2		
Client ID:	Final Effluent Composite				
Operator ID:		ALS Bottle#:	23	Worklist Smp#:	22
Injection Vol:	1.0 ul	Dil. Factor:	1.0000		
Method:	MILLI BNA	Limit Group:	MSS 625 ICAL		
Column:		Detector	MS SCAN		

120 Benzo[b]fluoranthene, CAS: 205-99-2

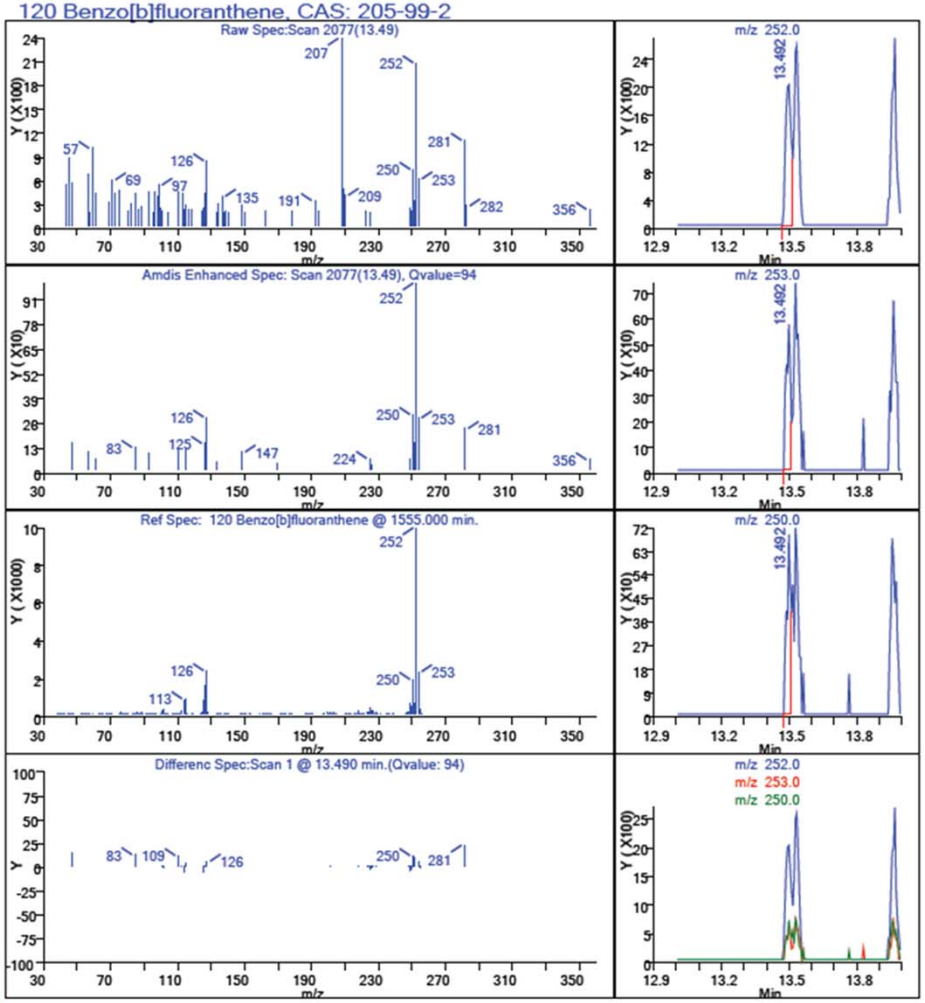


Table 3: Three Characteristic Ions-EPA 625 Confirmation Ions vs. Test America Ions				
	Table 4 EPA 625, Primary Ion (M/Z)	Table 4 EPA 625, Secondary Ions (M/Z)	3rd Party Lab, Primary Ion (M/Z)	Test America, Secondary Ions (M/Z)
Indeno[1,2,3-cd]pyrene	276	138, 277	*281*	*276, 207*
Chrysene	228	226, 229	*281*	*228, 207*
Dibenz(a,h)anthracene	278	139, 279	*280*	*278, 207*
Benzo[a]anthracene	228	229, 226	*240*	*236, 120*
3,4-Benzofluoranthene or Benzo[b]fluroanthene	252	253, 125	*356*	*252, 207*
Benzo[k]fluoranthene	252	253, 125	*281*	*252, 207*

Questions