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- Background
- First Investigation Details and Observations
- Follow-up Activities Details and Observations
- Outcome of Investigation
- Summary





# Background

- For a long-term monitoring project, whole-volume, double-blind performance test (PT) sample submitted semi-annually
- Polynuclear aromatic hydrocarbons (PAHs) were driving compounds
- PT sample that contained benzo(a)pyrene, benzo(b)fluoranthene, and naphthalene
- PT sample was a custom made standard



Benzo[a]pyrene

Benzo[b]fluoranthene





naphthalene



# Background

- Lab A performing well (approximately 20 years of PT sample success for all three compounds)
- Then three straight PT sample failures for benzo(a)pyrene and benzo(b)fluoranthene
- The change in PT performance sparked the investigations summarized in this presentation





- PT Vendor generated eight, 1-Liter, whole-volume custom samples
- Two 1-Liter samples were sent to Lab A for benzo(a)pyrene, benzo(b)fluoranthene, and naphthalene analysis as double-blind sample
- Six 1-Liter samples were sent to Referee Lab for benzo(a)pyrene, benzo(b)fluoranthene, and naphthalene analysis as single-blind samples
- Lab A received a whole-volume, off-the-shelf PT sample for polynuclear aromatic hydrocarbon (PAH) analysis as a single-blind sample





Sample ID	PAH	Result Pass/Fail
Custom-A	Benzo(a)pyrene	Fail Low
Custom-A	Benzo(b)fluoranthene	Fail Low
Custom-A	Naphthalene	Pass







Sample ID	PAH	Result Pass/Fail
Custom-1	Benzo(a)pyrene	Pass
Custom-1	Benzo(b)fluoranthene	Pass
Custom-1	Naphthalene	Pass
Custom-2	Benzo(a)pyrene	Pass
Custom-2	Benzo(b)fluoranthene	Pass
Custom-2	Naphthalene	Pass





Sample ID	PAH	Result Pass/Fail
Custom-3*	Benzo(a)pyrene	Fail Low
Custom-3*	Benzo(b)fluoranthene	Fail Low
Custom-3*	Naphthalene	Pass

\* Referee Lab notified of the failure, and passed benzo(a)pyrene and benzo(b)fluoranthene upon a second preparation and analysis.





- Lab A failures consistent with prior couple of sample rounds
- Referee Laboratory passed two standards indicating that the standard was correctly prepared
- Referee Laboratory failures corresponded to Lab A indicating that the failures may be related to method or chemistry of the extraction



# **Single-Blind PT Standard Results**

		Result (Pass/ Fail)	Result (Pass/Fail) Method 8270C
PAH Compound	Rings	Method 8270C	SIM
Naphthalene	2	Pass	Pass
Acenaphthene	3	Pass	Pass
Acenaphthylene	3	Pass	Pass
Fluorene	3	Pass	Pass
Phenanthrene	3	Pass	Pass
Anthracene	3	Fail low	Fail low
Pyrene	4	Pass	Fail low
Fluoranthene	4	Pass	Fail low



# **Single-Blind PT Standard Results**

		Result (Pass/	
		Fail)	Result (Pass/Fail)
PAH Compound	Rings	Method 8270C	Method 8270C SIM
Chrysene	4	Fail low	Fail low
Benzo(a)anthracene	4	Fail low	Fail low
Benzo(a)pyrene	5	Fail low	Fail low
Benzo(b)fluoranthene	5	Fail low	Fail low
Benzo(k)fluoranthene	5	Fail low	Fail low
Dibenz(a,h)anthracene	5	Fail low	Fail low
Benzo(g,h,i)perylene	6	Fail low	Fail low
Indeno(1,2,3-cd)pyrene	6	Fail low	Fail low





- Lighter (2-3 ring) PAHs recovered generally acceptably
- Heavier (4-6 ring) PAH recovered generally unacceptably
- Performance suspected of having a correlation to number of rings in the PAH
- Lighter PAHs are more likely to be in the solution
- Heavier PAHs are more likely to adhere to the container
- Standard preparation into reagent-free water, no particulates or TSS for heavier PAHs to adhere to





- How were the PT samples made?
- Review of preparation and analytical procedures between laboratories
- Lab A requested to review changes from passing to failing results
- Items requested for review: personnel, materials, procedures, etc.
- Follow-up actions were based on outcome of the laboratory information



# PT Sample Preparation

- The PT vendor generated whole-volume samples utilizing analyte-free water
- A custom standard mixture with only benzo(a)pyrene, benzo(b)fluoranthene, and naphthalene was prepared for several rounds as a stock standard in methanol in sealed 2 mL ampules



# **PT Sample Preparation**

- 1-Liter amber bottles filled with analyte-free water were refrigerated over-night prior to the addition of the stock standard.
- On the day of shipment, the PT vendor adds the standard by injecting the standard approximately 1 inch below the surface of the water. The bottle is capped and inverted to mix the sample.





# **Preparation and Analytical Methods**

## Lab A:

- Sample extraction via SW-846 Method 3510C (Separation Funnel)
- Extract analysis via SW-846 Method 8270C Full Scan for double-blind and single-blind
- Extract analysis via SW-846 Method 8270C Selective Ion Monitoring (SIM) for single-blind



- Sample extraction via SW-846 Method 3520C (Continuous Liquid-Liquid)
- Extract analysis via SW-846 Method 8270C Full Scan







- No difference in preparation or analytical procedures
- No difference in vendors or quality of materials
- Some personnel changes but different personnel for each PT preparation and analysis
- Suspects sample transfer was the issue
- Proposed internal study to evaluate transfer issue





- Generated 2 Control Samples at 20 ug/L in 1-Liter Amber Containers
- Generated 2 Control Samples at 50 ug/L in 1-Liter Amber Containers
- Stored in refrigerator overnight until preparation via separatory funnel extraction
- 2 sample transfers included solvent rinse by swirl in the container
- 2 sample transfers included solvent rinse by cap and container inversion
- All extracts analyzed by SW-846 Method 8270C



# Sample Transfer Study Results

	20 ug/L Swirl		20 ug/L Cap	
Compound	Result	%R	Result	%R
Benzo(a)pyrene	8.9	45	17.0	85
Benzo(b)fluoranthene	9.9	50	18.2	91
Naphthalene	15.3	76	15.6	78

 Cap and invert extraction technique shows greatly improved extraction over the swirl technique.



# Sample Transfer Study Results

	50 ug/L Swirl		50 ug/L Cap	
Compound	Result	%R	Result	%R
Benzo(a)pyrene	36.9	74	49.6	99
Benzo(b)fluoranthene	40.6	81	57.4	115
Naphthalene	49.6	99	52.8	106

 Cap and invert extraction technique shows greatly improved extraction over the swirl technique.





- Based on Lab A findings, the Referee Lab evaluated its sample transfer procedure
- Referee Lab was not performing a container rinse for the SW-846 Method 3520 preparation
- Referee Lab investigated use of container rinse with SW-846 Method 3520 preparation



# **Follow-up Activities**

- The problem was identified as the sample transfer
- Lab A and Referee Lab updated procedures to be more detailed on the container rinse
- Additional whole-volume, double-blind PT samples to Lab A
- Additional whole-volume, single-blind PT samples to Referee Lab
- Both facilities have provided two rounds of acceptable PT results



# Summary

- Long term project with double-blind PT samples
- Lab A results fell out of criterion for benzo(a)pyrene and benzo(b)fluoranthene for a couple rounds
- Appears that heavier PAHs were adhering to the container
- Suspected sample transfer process
- Lab A performed a small experiment to confirm transfer was issue





- Lab A and Referee Lab updated procedures to include thorough container rinse
- The slight change produced great improvement in performance
- Investigation into PT failures can be more than just evaluation of the calibration and other system performance indicators







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