Environmental

VPH by GC/MS
May 31, 2017
LSPA Training

VPH by GC/MS

Some of the Details

the devil's
in the details

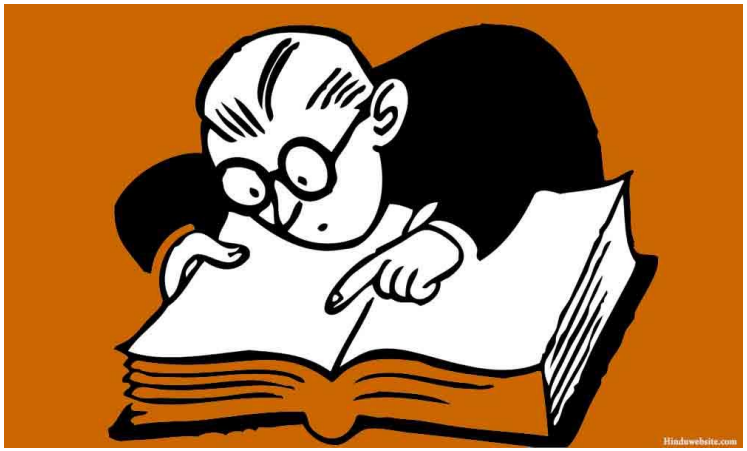
Definitions

- Definitions in VPH by GC/MS are similar to the definitions in the VPH by GC/PID/FID method.
- Hydrocarbon range definitions have not changed.

3.5 **C_5 through C_8 Aliphatic Hydrocarbons** are defined as all aliphatic petroleum hydrocarbon compounds that elute from just before n-pentane to just before n-nonane (C_9). C_5 through C_8 aliphatic hydrocarbons are determined using the total ion chromatogram.

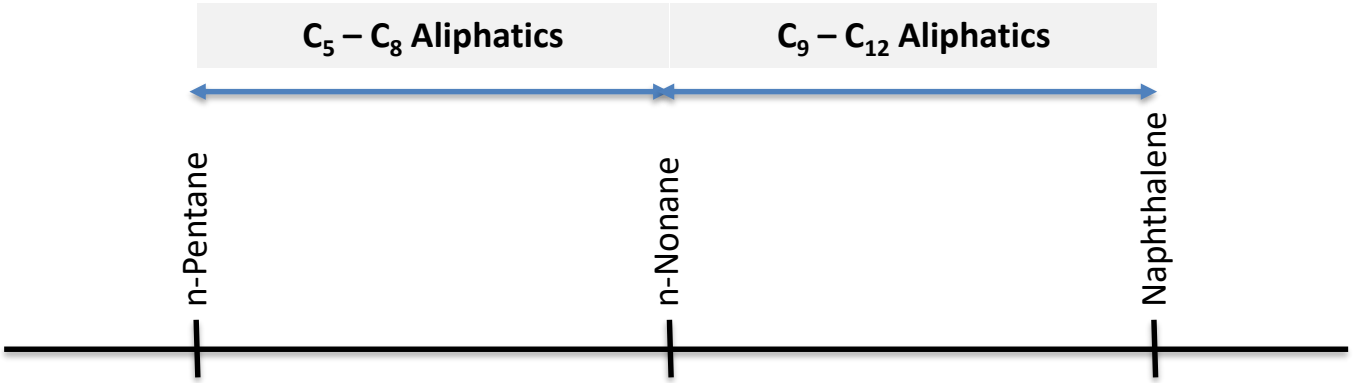
3.6 **C_9 through C_{12} Aliphatic Hydrocarbons** are defined as all aliphatic petroleum hydrocarbon compounds that elute from just before n-nonane to just before naphthalene. C_9 through C_{12} aliphatic hydrocarbons are determined using the total ion chromatogram.

3.7 **C_9 through C_{10} Aromatic Hydrocarbons** are defined as all aromatic petroleum hydrocarbon compounds that elute from just after o-xylene to just before naphthalene. Although naphthalene is an aromatic compound with 10 carbon atoms, it is excluded from this range because it is evaluated as a separate Target VPH Analyte. C_9 through C_{10} aromatic hydrocarbons are determined using the extracted ions 120 and 134.

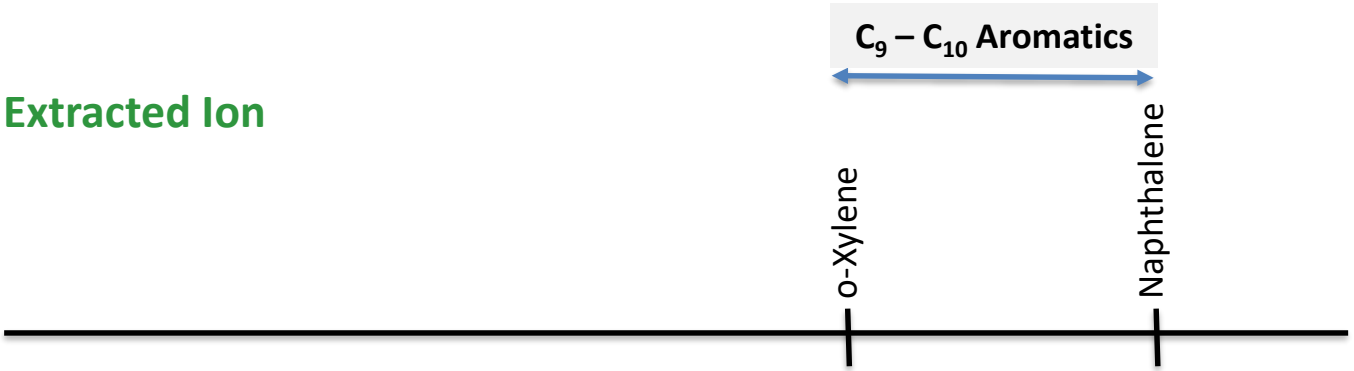


Definitions

Total Ion



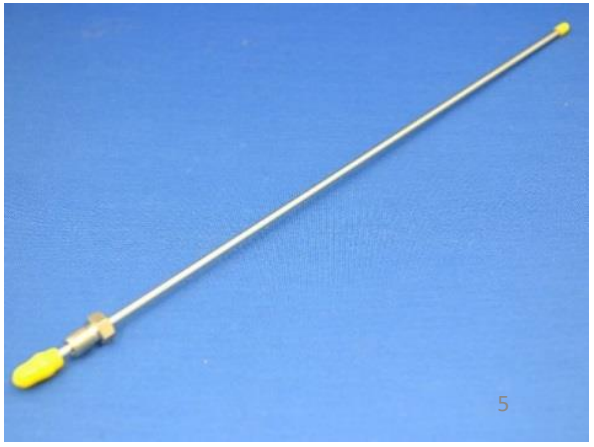
Extracted Ion



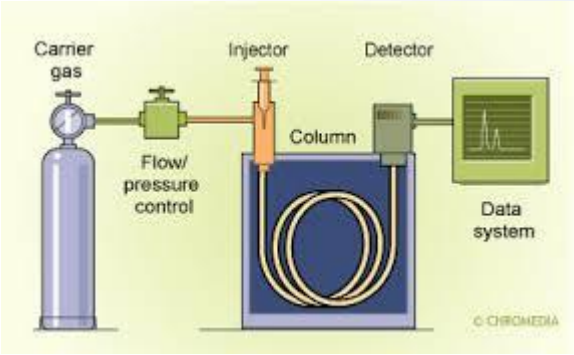
Apparatus and Materials

- Purge & trap system
- NEW: Trap Requirements
  - VOCARB 3000
  - Tekmar #9
- NEW: Must include trap used in CAM deliverable
- NEW: Trap desorption efficiency study if different trap used

- **Why do we have these new requirements?**



Apparatus and Materials



- Gas Chromatograph
- NEW: Column Requirements
  - VOCOL™: 30 m x 0.25 mm ID w/ 1.5 µm film thickness
  - RTX-502.2™: 30 m x 0.25 mm ID w/ 1.4 µm film thickness
- NEW: Must include column used in CAM deliverable
- NOT NEW: Column equivalency study if different column used

- **Why do we have these new (and not new) requirements?**

Calibration Components for Hydrocarbon Ranges

Hydrocarbon Range	GC/PID/FID	GC/MS
C_5-C_8 Aliphatics	**n-pentane** 2-methylpentane 2,2,4-trimethylpentane	**n-pentane** n-hexane cyclohexane 2,3-dimethylpentane n-heptane n-octane
C_9-C_{12} Aliphatics	**n-nonane** n-decane butylcyclohexane	2,3-dimethylheptane **n-nonane** n-decane n-undecane n-dodecane butylcyclohexane
C_9-C_{10} Aromatics	1,2,4-trimethylbenzene	isopropylbenzene 1-methyl-3-ethylbenzene 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene p-isopropyltoluene

Marker compounds for aliphatic ranges

Sample Collection, Preservation and Handling

NO CHANGES HERE FROM PID/FID METHOD except:

- Provided better clarification on use of TSP for aqueous samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples (using ambient temperature purge)	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl to pH < 2; cool to 0-6ºC	14 days
Aqueous Samples (using heated purge)[1]	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 0.40 to 0.44 grams of trisodium phosphate dodecahydrate to pH >11; cool to 0-6ºC	14 days
Soil/Sediment Samples[2]	VOC vials w/ Teflon-lined septa screw caps. 60-mL vials: add 25 g soil/sediment 40-mL vials: add 15 g soil/sediment	1 mL methanol for every g soil/sediment; add before or at time of sampling; cool to 0-6ºC	28 days

[1] Heated purge is considered a significant modification to the method, as per Section 11.3.1.
[2] Refer to Appendix 3 for details on sample collection or optional collection/storage devices.

QUESTION

Have you ever used trisodium phosphate dodecahydrate for preservation of aqueous VOC samples?

YES

NO

Retention Time Windows

- Same as VPH by PID/FID

Hydrocarbon Range	Beginning Marker	Ending Marker
C_5-C_8 Aliphatic Hydrocarbons	0.1 min before n-Pentane	0.01 min before n-Nonane
C_9-C_{12} Aliphatic Hydrocarbons	0.01 min before n-Nonane	0.1 min before Naphthalene[1]
C_9-C_{10} Aromatic Hydrocarbons	0.1 min after o-Xylene	0.1 min before Naphthalene

[1] The retention time for Dodecane (C_{12}) is approximately 1-2 minutes less than the retention time for naphthalene, using the column and chromatographic conditions recommended for this method. For simplicity, naphthalene is used as the ending marker for the C_9 - C_{12} Aliphatic Hydrocarbon range.

C_5-C_8 Aliphatics Quantitation in Samples

Step 1
Integration of Range using total ion area at baseline

Step 2
Subtract total area of IS and surrogate (if applicable) from total area of range)

Step 3
If directed by data user: subtract total area of any non-VPH compounds. (will discuss more later)

Step 4
Calculate "Unadjusted" C_5-C_8 Aliphatic Hydrocarbons

Step 5
Calculate C_5-C_8 Aliphatic Hydrocarbons

C_9-C_{10} Aromatics Quantitation in Samples

Step 1
Integration of range using extracted ion m/z 120 at baseline

Step 2
Integration of range using extracted ion m/z 134 at baseline

Step 3
Sum areas from Steps 1 & 2

Step 4
Calculate conc. C_9-C_{10} Aromatic Hydrocarbons

C_9-C_{12} Aliphatics Quantitation in Samples

Step 1
Integration of Range using total ion areas at baseline

Step 2
Subtract total area of IS and surrogate (if applicable)

Step 3
If directed by data user: subtract total area of any non-VPH compounds. (will discuss more later)

Step 4
Calculate "Unadjusted" C_9-C_{12} Aliphatic Hydrocarbons

Step 5
Calculate C_9-C_{12} Aliphatic Hydrocarbons

Additional Rules for Data Adjustments

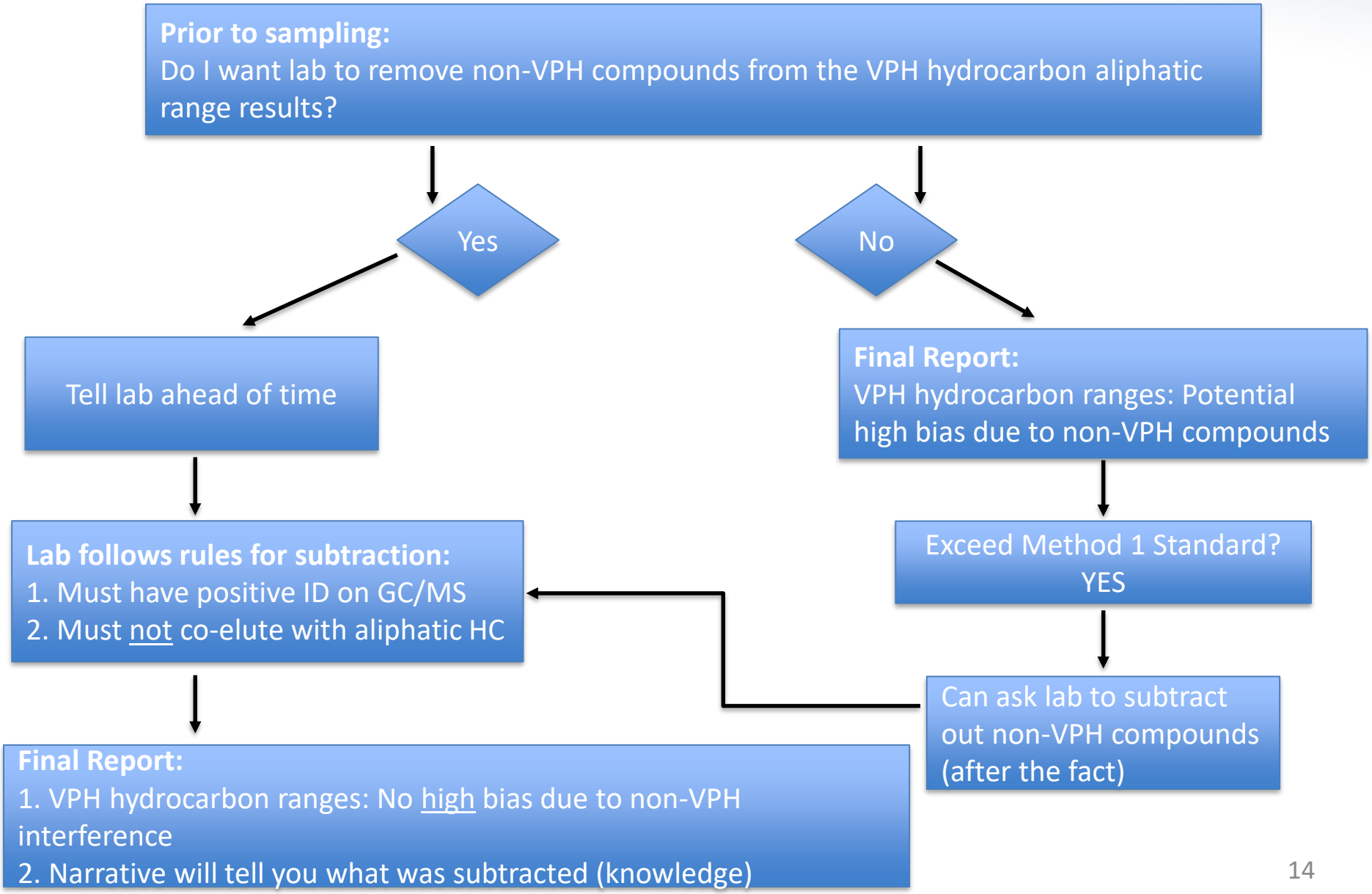
- If conc. of Target VPH Analyte (e.g., 0.7 J ug/L) is <RL (1 ug/L), do not subtract conc. from appropriate range.
- If conc. of C_9-C_{10} aromatics (e.g., 50 J ug/L) is <RL (100 ug/L), do not subtract conc. from C_9-C_{12} aliphatics.
- Non-VPH compounds: subtract from range only if all of the below circumstances exist:
  1. Requested by data user
  2. It does not co-elute with aliphatic petroleum hydrocarbon
  3. Meets requirements for positive GC/MS identification

NOTE: The identification of the non-VPH compound must be disclosed in the lab narrative, if subtracted.

Non-Petroleum Hydrocarbons

Hydrocarbon Range	Potential Non-VPH Compounds
C_5-C_8 Aliphatic Hydrocarbons	Acetone may co-elute/interfere with isopentane. Isopropyl alcohol, methyl ethyl ketone, trichloroethene, tetrachloroethene, tetrahydrofuran, hexanal, 1-butanol, hexamethylsiloxane
C_9-C_{12} Aliphatic Hydrocarbons	Terpenes (e.g., a-pinene, d-limonene), phenol, benzaldehyde, n-chain aldehydes, 2-ethyl-1-hexanol, siloxanes, dichlorobenzenes
C_9-C_{10} Aromatic Hydrocarbons	Siloxanes, a-pinene, and d-limonene may slightly interfere (contribute to the area of ions 120/134) if present at high concentrations.

Rules of Engagement



Example: Subtraction of non-VPH Compounds

Example	Before Subtraction		After Subtraction
	Sample #1 (mg/kg)	S-1/GW-1 (mg/kg)	Sample #1 (mg/kg)
$C_5 – C_8$ Aliphatics	350	100	75
$C_9 – C_{12}$ Aliphatics	520	1000	520
$C_9 – C_{10}$ Aromatics	75	100	75

After Subtraction Narrative Text:
Non-petroleum hydrocarbons were not included in the VPH aliphatic hydrocarbon range concentrations. Sample #1 contains acetone and trichloroethene.

Reporting Limits

- Based on concentration of lowest standard
- 1 µg/L: lowest standard
  - RL of Target VPH Analytes: 1 µg/L
  - RL of Hydrocarbon Ranges = 100x lowest standard or 100 µg/L

	RL-Water	RL-Soil*
BTEX/MTBE/Naphthalene	1.0 µg/L	0.05 mg/kg
C_5-C_8 Aliphatics	100 µg/L	5 mg/kg
C_9-C_{12} Aliphatics	100 µg/L	5 mg/kg
C_9-C_{10} Aromatics	100 µg/L	5 mg/kg

*Assumes the following:

- 10 g soil/10 mL MeOH
- 100 µL methanol extract/5 mL water

Significant Modifications (Question E)

- The use of other than a purge-and-trap sample preparation procedure.
- The use of a heated purge.
- The use of alternative detectors other than GC/MS to quantify Target VPH Analytes and/or hydrocarbon range concentrations.
- The use of extracted ions other than m/z 120 and 134 to quantify C_9-C_{10} aromatic hydrocarbons.
- The use of non-linear regression (i.e., quadratic equations) for calibration.
- Failure to provide all of the data and information presented in Appendix 2 as well as the required method deliverables.

The CAM Deliverable: What to Expect

Deliverable Item	VPH by FID/PID	VPH by GC/MS
Presumptive Certainty Form	X	X
Lab Narrative	X	X
Sample Results	X	X
Reporting Limits	X	X
Dilution Factors	X	X
Date Preserved (if EnCore® samplers used)	X	X
Date Analyzed	X	X
Method Blanks	X	X
Lab Control Samples	X	X
Surrogates	X	X
MS/MSD	X (if requested)	X (if requested)
Matrix Duplicate	X (if requested)	X (if requested)
Internal Standards	NA	
Column Used	X	X
Trap Used	X	X
Identification of non-VPH Compounds	NA	X (if requested)
Reanalyses/Dilutions	X	X

Reanalyses/Dilutions: Rules for Reporting

- If reanalysis due to internal standard or surrogate issues yields similar non-conformances (i.e., still outside criteria), the laboratory must report results of both analyses.
- If reanalysis due to internal standard or surrogate issues is performed outside of holding time and yields acceptable internal standard or surrogate recoveries, the laboratory must report results of both analyses.
- If sample is not reanalyzed for internal standard or surrogate issues due to obvious interference, the laboratory must provide the chromatogram in the data report.
- If diluted and undiluted analyses are performed, the laboratory must report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., LMBs, LCS, etc.) for each analysis must be reported. This may result in more than one analysis per sample being reported.

Round Robin: What We Saw

Issue	Overall Effect on Sample Result
Calibration: Incorrect procedure used for integration of total aliphatic area counts	Aliphatic results biased low
Calibration: Forcing of curve through zero when performing linear regression	Results biased low
Calibration: Use of four points for calibration of C_9-C_{12} aliphatics	Unknown
Calibration: Utilization of extracted ion area counts for aliphatic range calibrations	Aliphatic results biased high
Calibration: C_9-C_{12} aliphatics calibration did not include undecane due to coelution issues	Unknown
Calibration: C_9-C_{10} aromatics calibration not performed using all components or proper total concentration	Aromatic results biased low
Calibration: %RSDs not calculated correctly	Results biased low
Calibration: Laboratory-generated response factors were not reproducible and were recalculated during review	C_9-C_{12} aliphatic results biased high and C_9-C_{10} aromatic results biased low
Sample Calculations: incorrect calculation of reporting limits (too high)	Potential false negative results
Sample Calculations: subtraction of extracted ion area counts of internal standards and surrogates from total ion area counts for aliphatic ranges	Aliphatic results biased high
Sample Analysis: use of incorrect GC/MS scanning parameters	Aliphatic results biased high

Round Robin: What We Learned

- **GC/MS scanning range important**: 35-250 amu
- **Choice of trap important**:
  - NOT RECOMMENDED: Tenax/silica gel/charcoal trap used by 1 lab: low bias for C_9-C_{12} aliphatic hydrocarbons (heavier hydrocarbons)
  - RECOMMENDED: VOCARB 3000 & Tekmar #9 traps desorb temps of 250˚C used: all of the compounds have boiling points which were below the desorb temperature.
- **Choice of column important**: 1 lab did not use one of the recommended columns.
  - Allocation of C_5-C_8 aliphatic and C_9-C_{12} aliphatics different from other labs (although total VPH #s were generally comparable).

- Linear regression generally needed for C_9-C_{12} aliphatic hydrocarbons.
- Needed slightly higher %RSD criteria for ranges compared to target analytes.
- 1,2,4-Trimethylbenzene more appropriate to use in lieu of 1,2,3-Trimethylbenzene for calibration of C_9-C_{10} aromatics.

Environmental

How to Evaluate VPH Data

QUESTION

Have you ever asked the lab to provide you a chromatogram to help in your review of the data?

1. Yes

2. No

3. I don’t know what a chromatogram is.

4. I hope this class is almost over.

QUESTION

If naphthalene recovers at 62% in the LCS (criteria are 70-130%), which of the following is true?

A. Naphthalene concentrations in the associated samples are biased high.

B. Naphthalene concentrations in the associated samples are biased low.

C. C_9-C_{10} aromatics are biased low in the associated samples.

D. A and C.

E. B and C.

QUESTION

Running samples using VPH by PID/FID

If the recovery of the VPH surrogate on the FID is 65% (criteria are 70-130%), which of the following is true?

A. The results for BTEX, MTBE and naphthalene are potentially biased low.
B. The results for C_5-C_8 aliphatics are potentially biased low.
C. The results for C_9-C_{10} aromatics are potentially biased low.
D. The results for C_9-C_{12} aliphatics are potentially biased high.
E. All of the above.

QUESTION

Running samples using VPH by GC/MS
If the recovery of the VPH surrogate is 65% (criteria are 70-130%), which of the following is true?

A. The results for BTEX, MTBE and naphthalene are potentially biased low.
B. The results for C_5-C_8 aliphatics are potentially biased low.
C. The results for C_9-C_{10} aromatics are potentially biased low.
D. The results for C_9-C_{12} aliphatics are potentially biased low.
E. All of the above.

Thank you

Questions?

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