Analysis of Low Concentrations of PAH and Alkyl PAH in Environmental Samples

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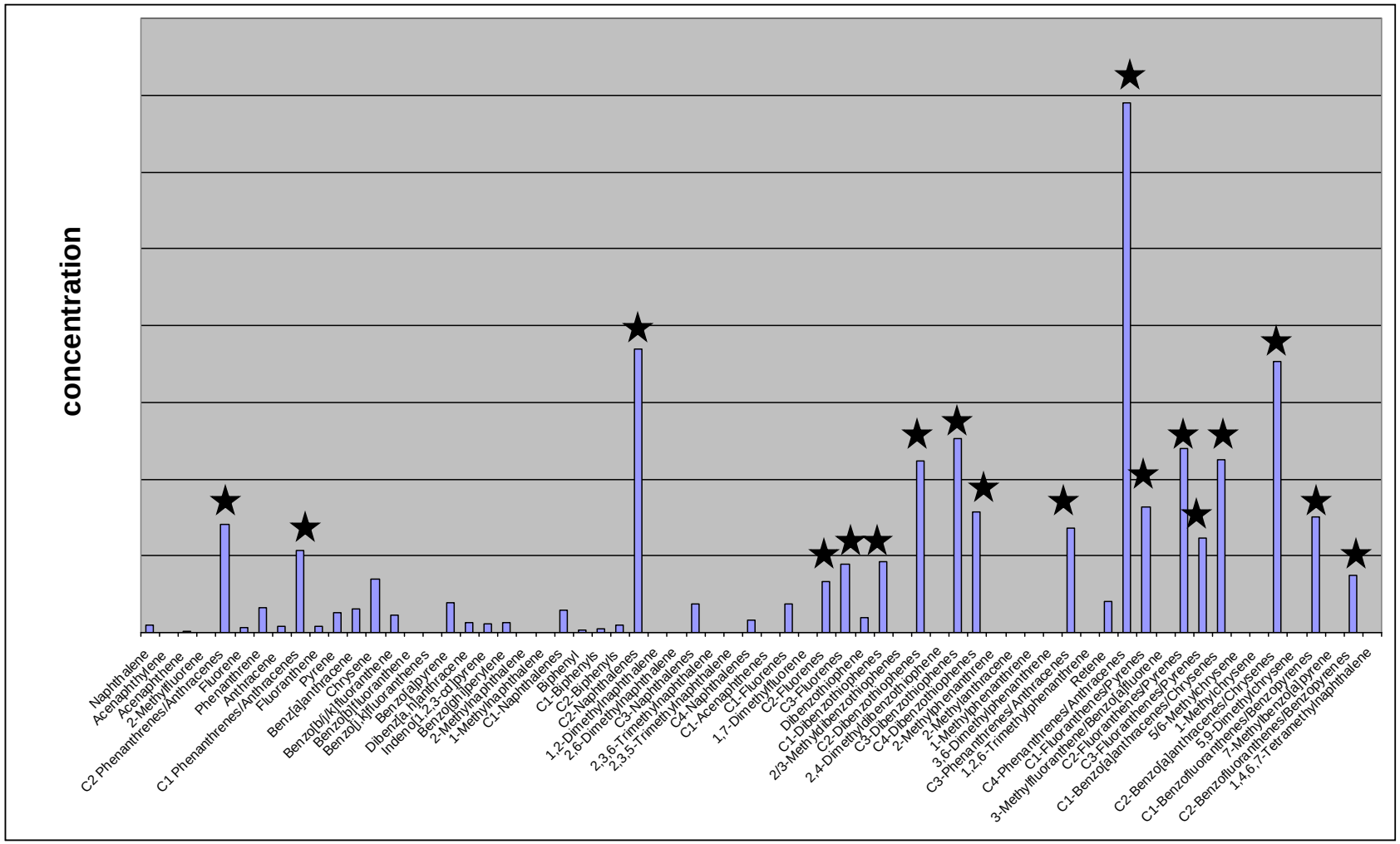
AXYS Analytical Services Ltd.

Low ng/sample detection limits, PAH + wide suite of alkyl PAH

Oil sands region monitoring



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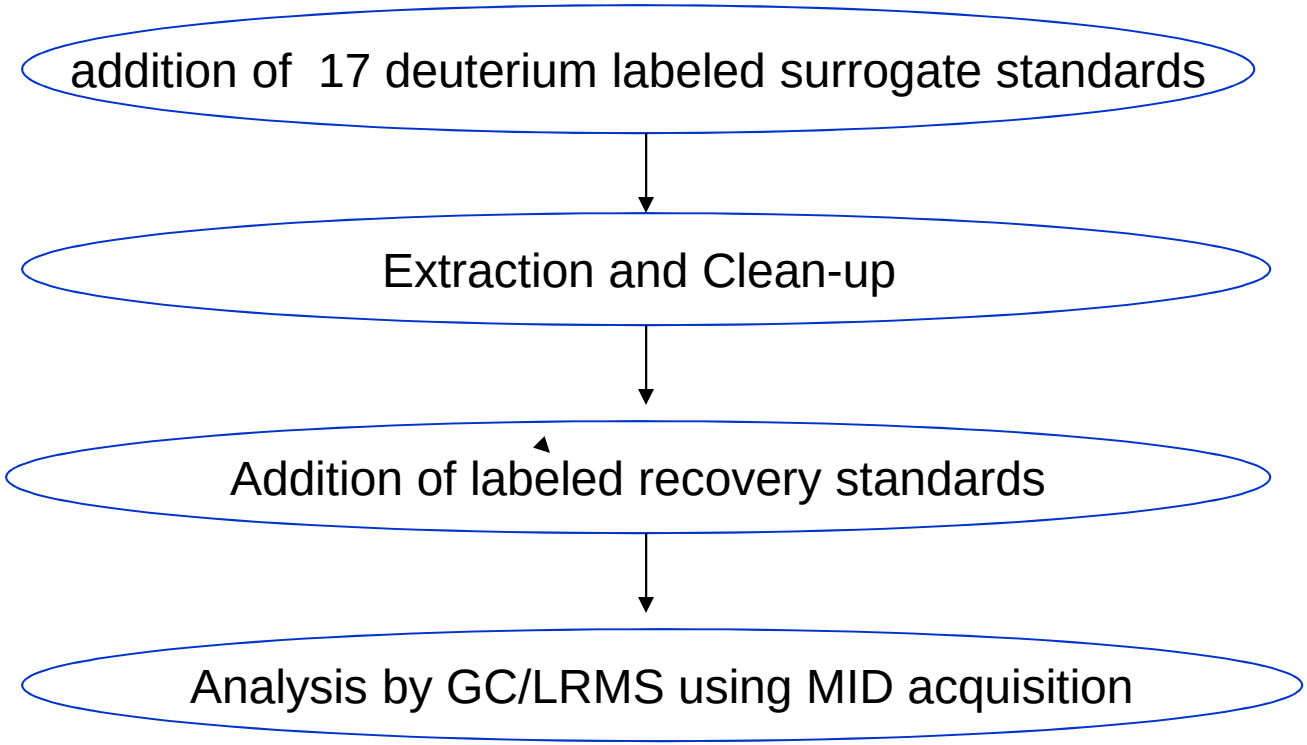
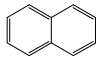
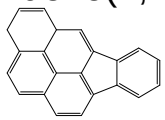
Performance based method



Parent PAH



Naphthalene
Acenaphthylene
Acenaphthene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benz(a)anthracene
Chrysene
Benzo(b)fluoranthene
Benzo(j/k)fluoranthenes
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
Dibenzo(ah)anthracene
Benzo(ghi)perylene
Indeno(1,2,3-cd)pyrene



Biphenyl
Dibenzothiophene

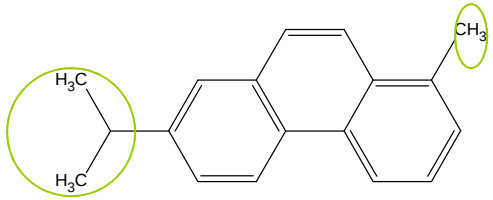
Alkyl PAH

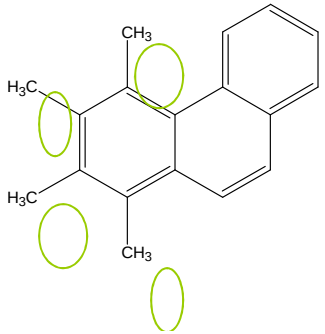
1-Methylnaphthalene
2-Methylnaphthalene
1,2-Dimethylnaphthalene
2,6-Dimethylnaphthalene
2,3,5-Trimethylnaphthalene
2,3,6-Trimethylnaphthalene
1,4,6,7-Tetramethylnaphthalene
1-Methylphenanthrene
2-Methylphenanthrene
3-Methylphenanthrene
9/4-Methylphenanthrenes
2-Methylanthracene
7-Dimethylphenanthrene
1,8-Dimethylphenanthrene
2,6-Dimethylphenanthrene
3,6-Dimethylphenanthrene
1,2,6-Trimethylphenanthrene
Retene (7-isopropyl-1-methylphenanthrene)
2-Methylfluorene
1,7-Dimethylfluorene
2/3-Methyldibenzothiophene
2,4-Dimethyldibenzothiophene
3-Methylfluoranthene/Benzo(a)fluorene
1-Methylchrysene
5/6-Methylchrysenes
5,9-Dimethylchrysene
7-Methylbenzo(a)pyrene

Alkyl Group Totals

C1-Naphthalenes
C2-Naphthalenes
C3-Naphthalenes
C4-Naphthalenes
C1-Phenanthrenes/Anthracenes
C2-Phenanthrenes/Anthracenes
C3-Phenanthrenes/Anthracenes
C4-Phenanthrenes/Anthracenes
C1-Biphenyls
C2-Biphenyls
C1-Acenaphthenes
C1-Fluorenes
C2-Fluorenes
C3-Fluorenes
C1-Dibenzothiophene
C2-Dibenzothiophene
C3-Dibenzothiophene
C4-Dibenzothiophene

C1-Fluoranthenes/Pyrenes
C2-Fluoranthenes/Pyrenes
C3-Fluoranthenes/Pyrenes
C4-Fluoranthenes/Pyrenes
C1-Benz(a)anthracenes/Chrysenes
C2-Benz(a)anthracenes/Chrysenes
C3-Benz(a)anthracenes/Chrysenes
C4-Benz(a)anthracenes/Chrysenes
C1-Benzofluoranthenes/Benzopyrenes
C2-Benzofluoranthenes/Benzopyrenes





Extract Clean-up

Minimum

Silica, 5% deactivated, removes:

- compounds of differing polarity- aliphatics, phthalate esters

Additional

GPC (Biobead SX-3), removes

– lipid & other large molecules

Alumina, 2% deactivated, removes

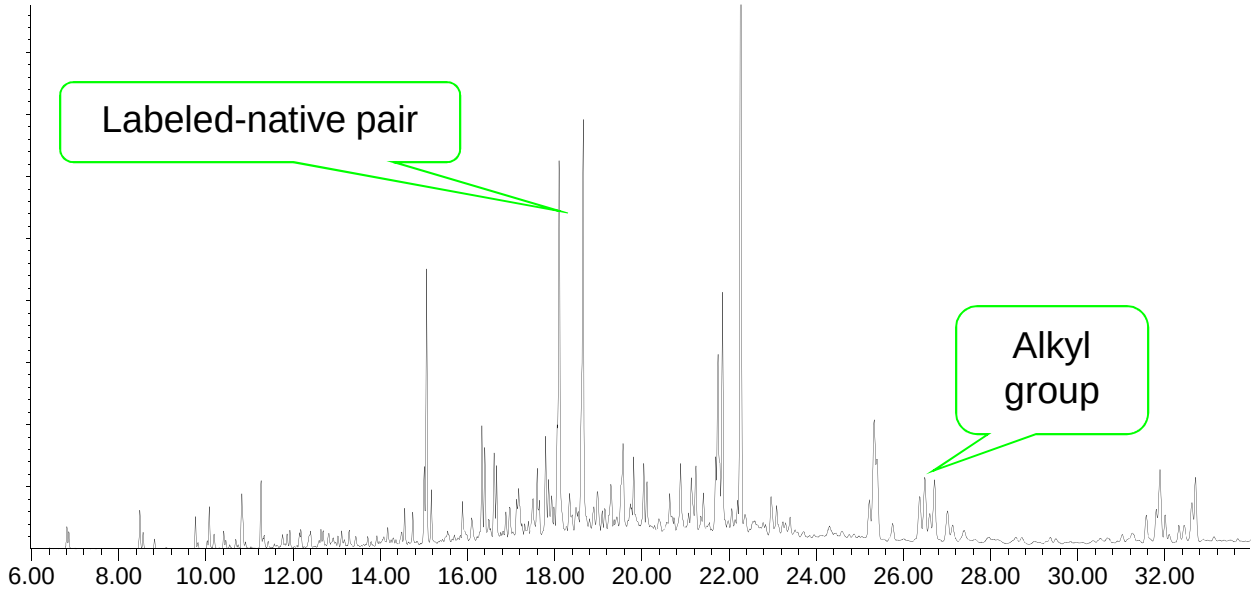
–polar compounds

Base Wash, 0.1 M NaOH, removes:

- acidic compounds

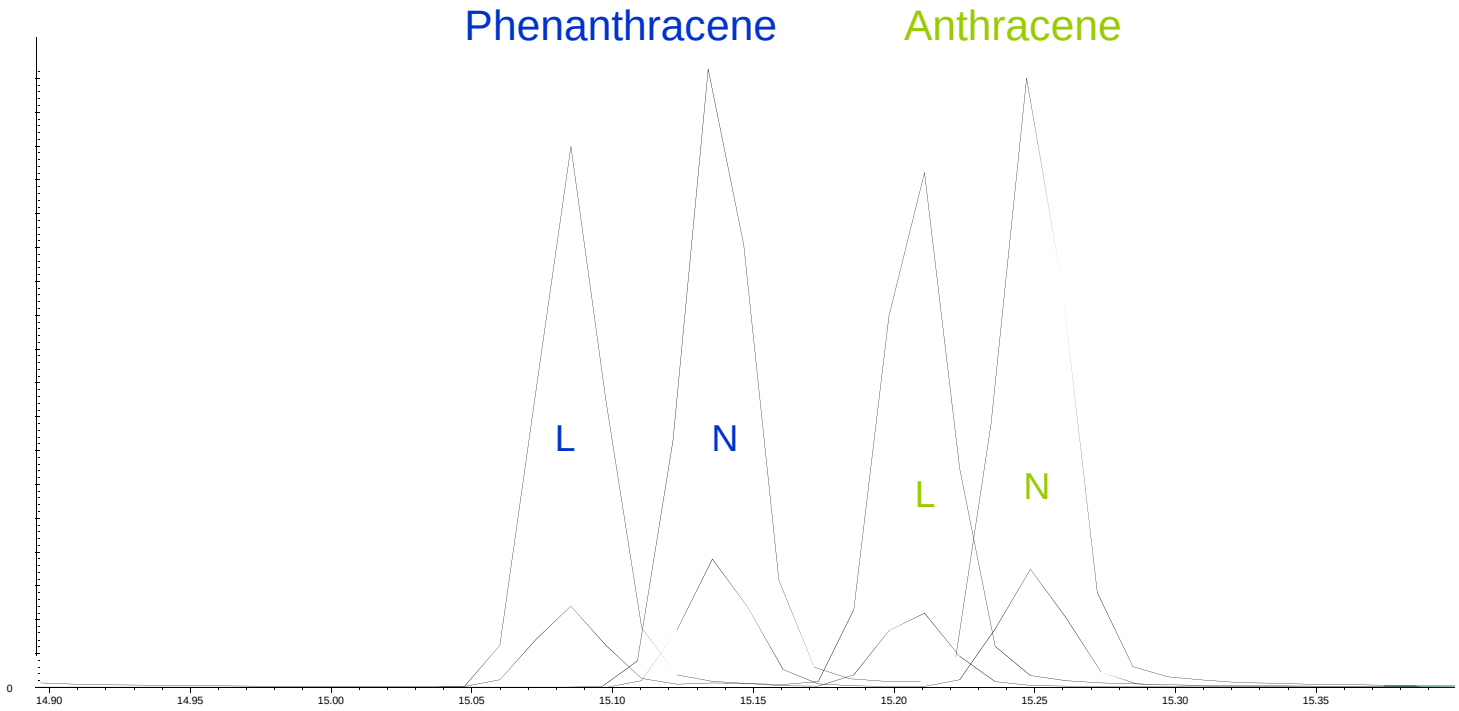
Instrumental Analysis

Split/splitless injector, 30m Restek Rtx-5 column, 60-325 ºC
Electron impact ionization, unit mass resolution
MID acquisition for sensitivity with 2 ions for specificity



Identification: PAH, Alkyl PAH

S:N, RRT window, 2 ions co-maximize, ion ratio within 20%



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Identification: Alkyl Group Totals

S:N, group RRT window

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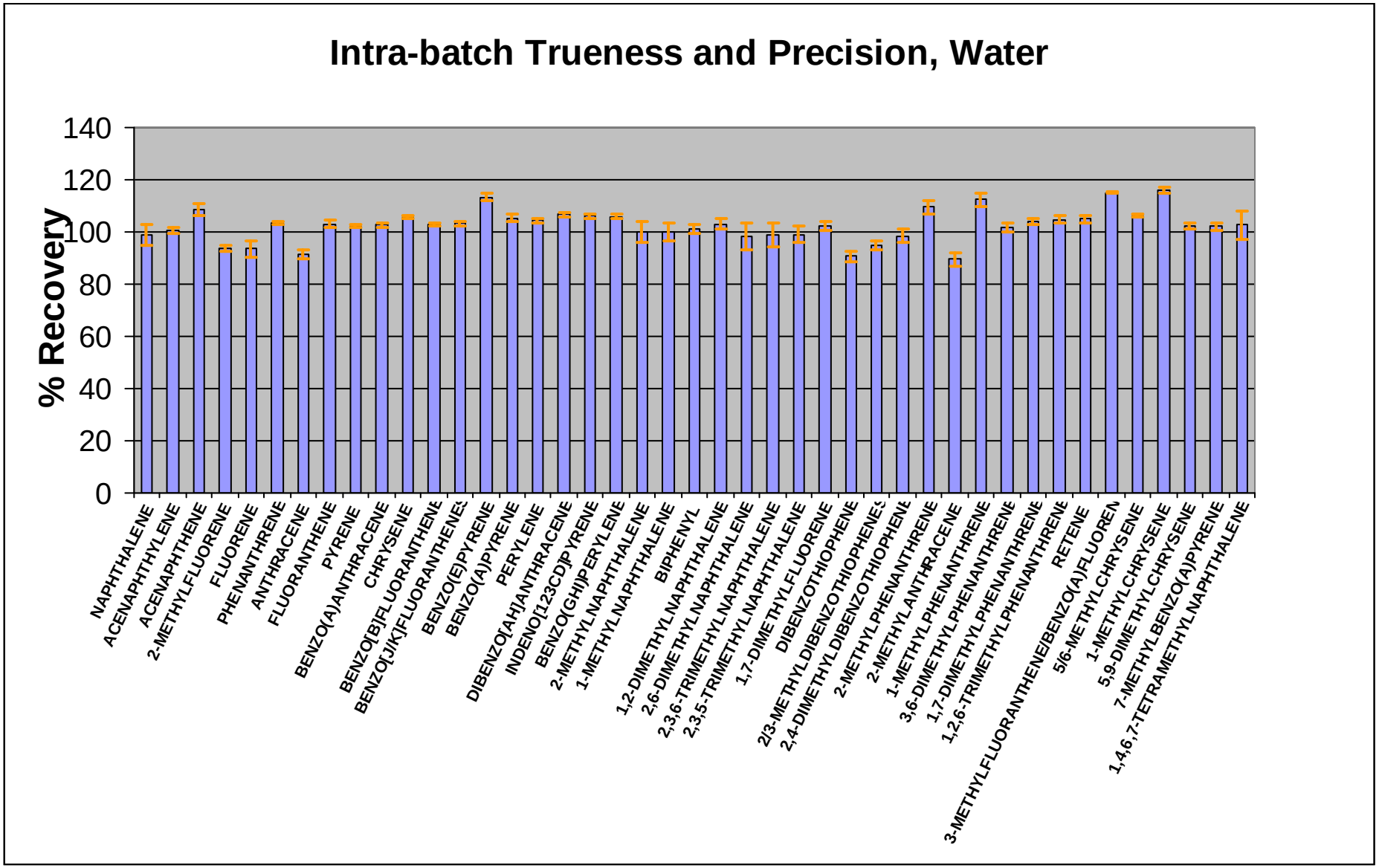
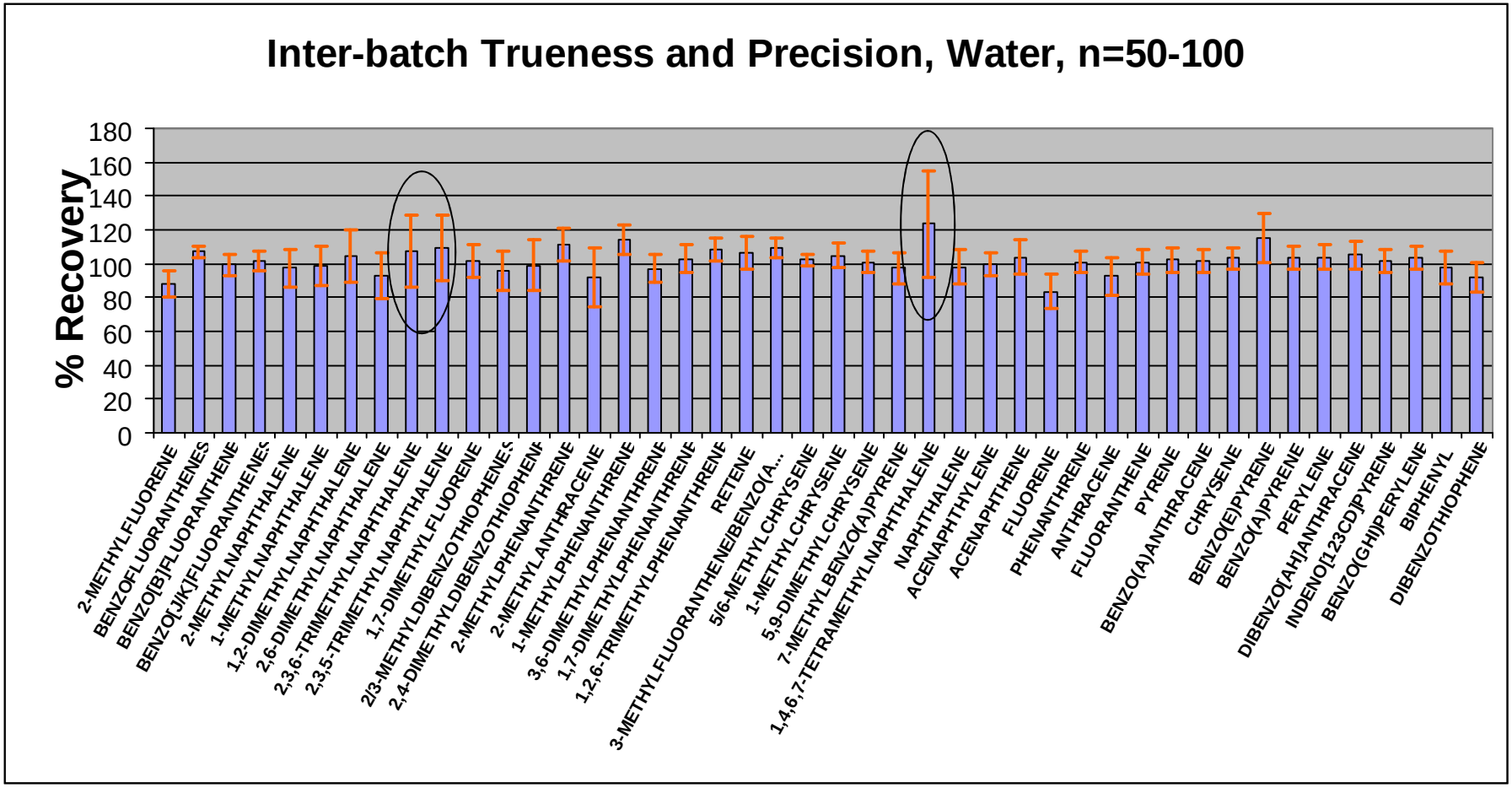
Quantification

- RRFs, RRTs, & ion ratios from calibration (natives and labelleds)
- multi-level calibration for PAH
- alkyl PAH use multi-level or single level calibration
- verification of calibration every 12 hours and at end
- quantification against labeled surrogates added prior to analysis
- results recovery corrected, little or no bias.
- sample specific DLs account for any matrix elevation of DL
- RRF of most similar compound used for alkyl group totals

Isotope dilution



Isotope dilution



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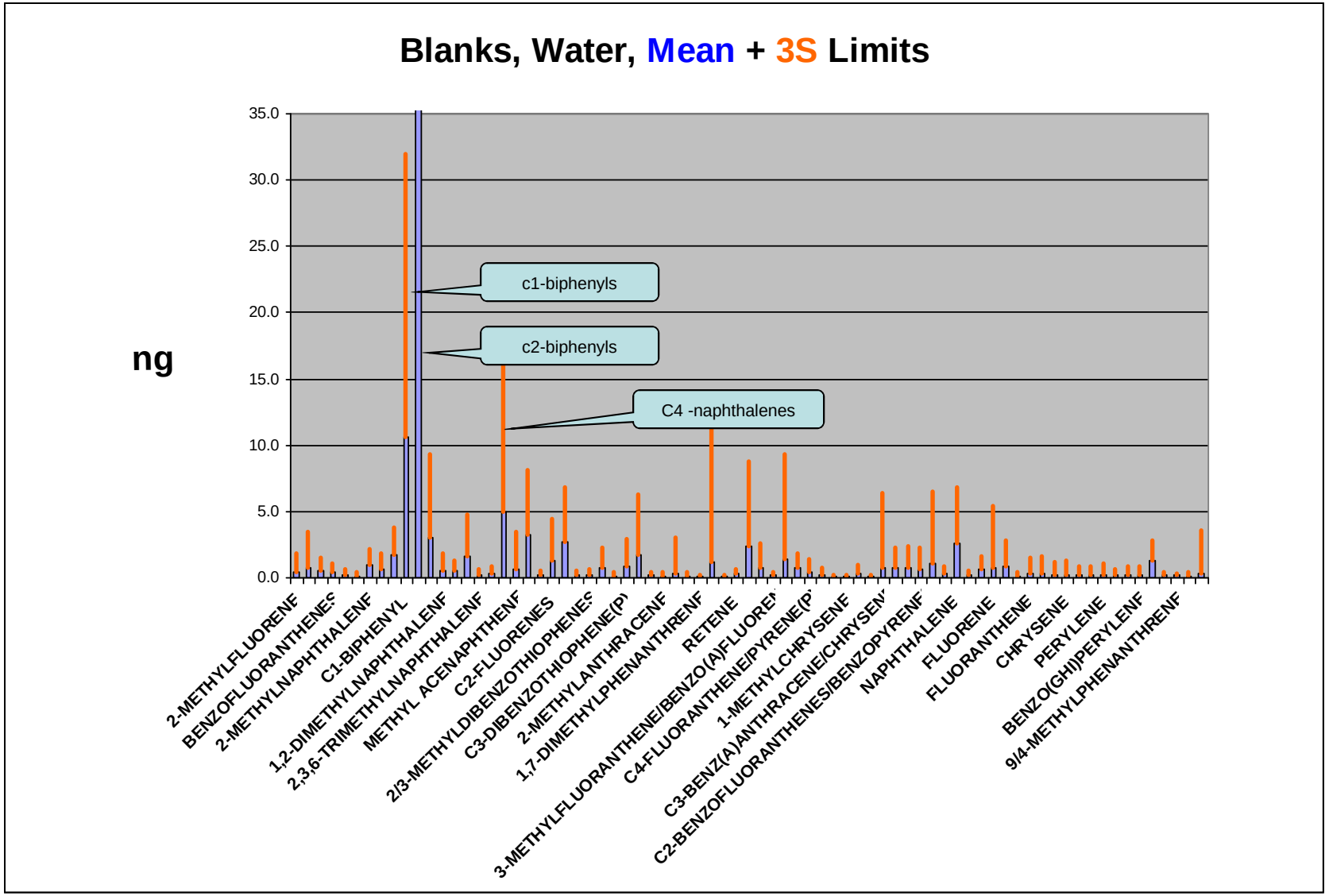
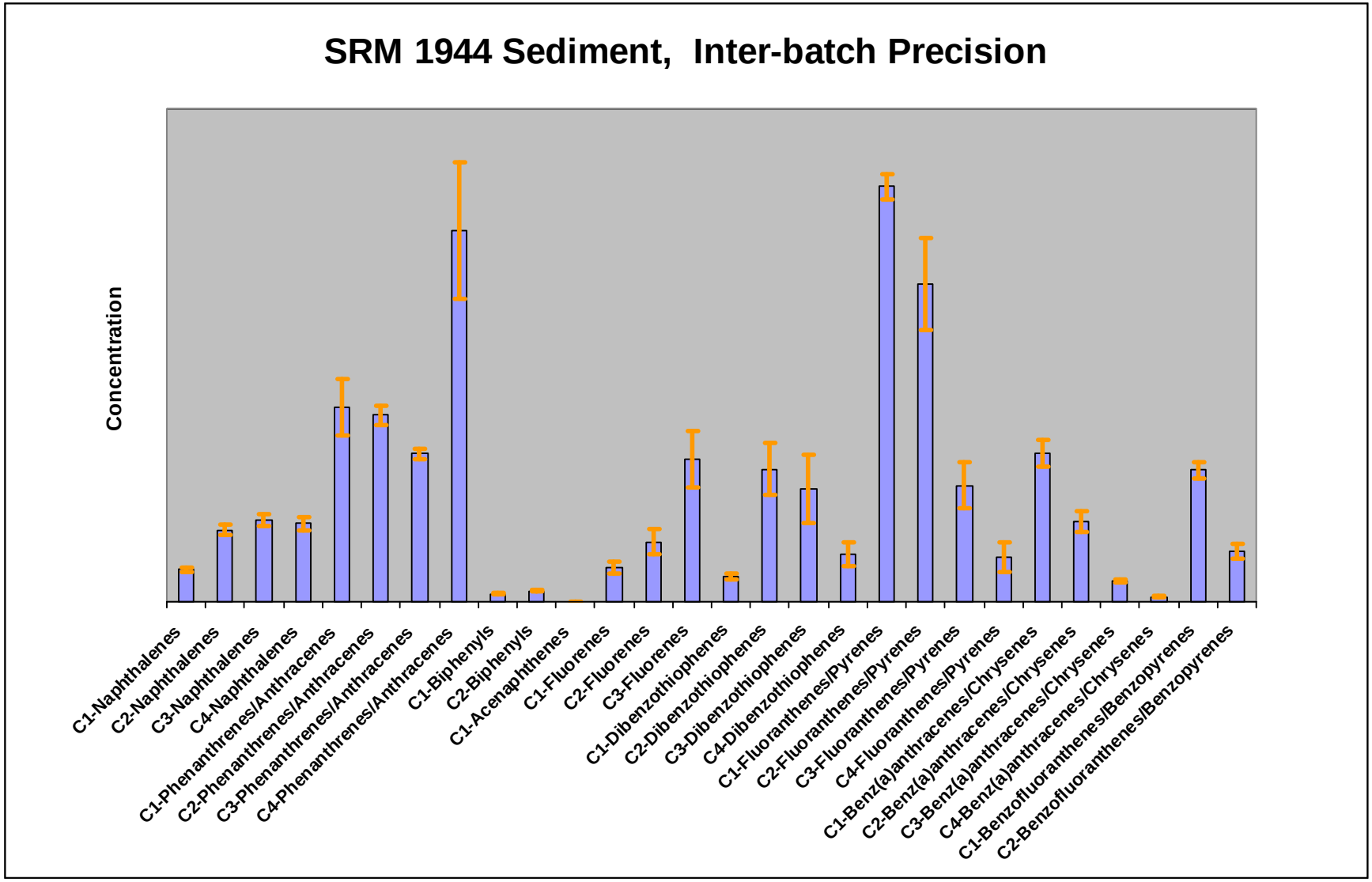
Blanks


Blanks, Water, Mean + 3S Limits
ng
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
c1-biphenyls
c2-biphenyls
C4 -naphthalenes
2-METHYLFLUORENE
BENZOFLUORANTHENES
2-METHYLNAPHTHALENE
C1-BIPHENYL
1,2-DIMETHYLNAPHTHALENE
2,3,6-TRIMETHYLNAPHTHALENE
METHYL ACENAPHTHENE
C2-FLUORENES
2/3-METHYLDIBENZOTHIOPHENES
C3-DIBENZOTHIOPHENES
2-METHYLANTHRACENE
1,7-DIMETHYLPHENANTHRENE
RETENE
3-METHYLFLUORANTHENE/BENZO(A)FLUORENE
C4-FLUORANTHENE/PYRENE
1-METHYLCHRYSENE
C3-BENZ(A)ANTHRACENE/CHRYSENE
C2-BENZOFLUORANTHENES/BENZOPYRENE
NAPHTHALENE
FLUORENE
FLUORANTHENE
CHRYSENE
PERYLENE
BENZO(GHI)PERYLENE
9/4-METHYLPHENANTHRENE

Alkyl Group Precision



Interlaboratory Comparison Exercises

- 2011, NIST Deepwater Horizon NRDA- marine sediment, 33 labs
- 2011 NIST Deepwater Horizon NDRA -mussel tissue, 34 labs

  - wide suite of PAH, alkyl PAH and alkyl PAH group totals
  - alkyl PAH group total study consensus value RSDs higher than for PAH, alkyl PAH
  - overall analytical issues noted by study authors:
    - choice of representative compound used for quantification of alkyl PAH
    - different alkyl PAH RFs depending on substitution
    - choice of peaks included in summation
    - (DL effect not examined)

- 2011 Deepwater Horizon NRDA- solution, spiked blood, spiked plasma, 6 labs

  - 4 PAH, 6 alkyl PAH
  - study results within reasonable range of gravimetric for most compounds
  - agreement for solution and plasma better than for blood
  - methylnaphthalenes in blood more variable, perhaps handling losses

Conclusions

- Reliable low ppb or ppt concentration data can be obtained by careful application of standard analytical techniques.
- Determination of PAH plus wide suite of alkyl PAH compounds for oil sands monitoring applications.
- Critical components include a focus on clean blanks, labeled standards, effective interference removal and multiple ion monitoring identification.

Questions