Automation of Extractable Petroleum Hydrocarbons (EPH) Method from Soils and Water

Prepared by C. Wakefield[1], J. Zymuntowicz[1], T. Dobbs[2], J. Netzer[2] and J. Wiseman [2]

1 – Alpha Analytical, 8 Walkup Drive, Westborough, MA 01581

2 – J2 Scientific, 1901 Pennsylvania Drive, Suite C, Columbia, MO 65202

Contact Information: cwakefield@alphalab.com; 508-898-9220

EPH Information

- Method – Written by Massachusetts Department of Environmental Protection to support Massachusetts Contingency Plan (MCP)
- Currently in use an estimated 10 - 15 years
- Used by Licensed Site Professionals (LSP) to evaluate specific site clean-up and closure.
- Common method performed by Environmental Laboratories

Why EPH Methods?

- Petroleum Hydrocarbons composed of aliphatic (C9-C18 and C19-C36) and aromatic (C11-C22) components, both from crude oil products as well as refined.
- Long term exposure to both aliphatic and aromatic components result in adverse biological effects including carcinogenicity.
- Contamination from Petroleum hydrocarbons in soil and water arises from many sources and must be monitored.

Extractable Petroleum Hydrocarbons (EPH) from Soil and Water MADEP 2004

- Method measures extractable aliphatic and aromatic hydrocarbons in soil and water matrices
- Core features of Method:
  - Extraction of sample with DCM
  - Dry and concentrate DCM extract
  - Exchange DCM extraction solvent into hexane
  - Fractionate aliphatic and aromatic components using silica gel cartridge and eluting first with hexane, then with DCM.
- Each fraction is collected separately and concentrated for analysis by GC/FID.

Potential Problem Concerns of MA DEP Method

- Sample prep of either water (separatory funnel) or soil (soxhlet or microwave) extraction is labor intensive
- Different analysts will yield different results in an extensive extraction procedure requiring 2 concentration steps, a hexane exchange step and a fractionation step.
- Fractionation steps require great attention to detail in order to achieve accurate and reproducible results (Silica gel activity, elution volumes, etc.)

It Would be Nice IF???

- Could set up multiple samples which could be run unattended.
- We could split the initial extract and have a “back-up” sample which would avoid need for re-extraction if problems were found.
- All the samples could be treated the same with no operator bias.

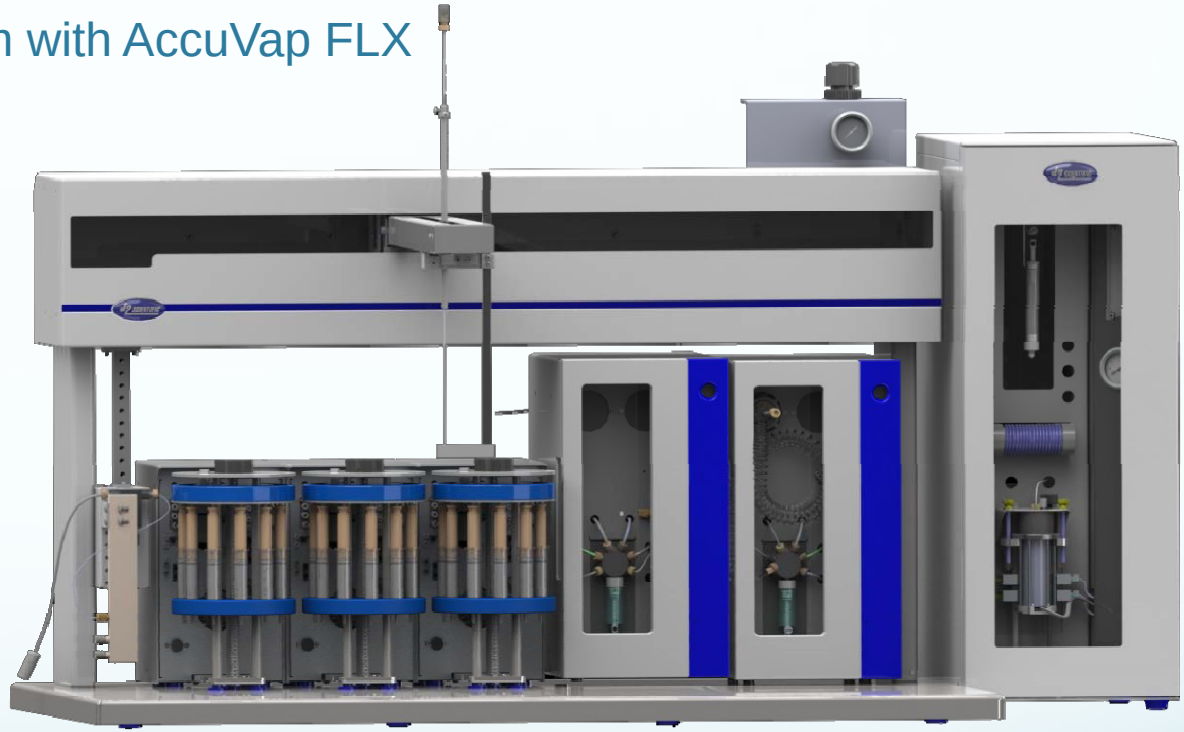
Steps to be Automated:

- DCM Extract (ca 200 mLs) concentrated
- Solvent exchanged from DCM to Hexane
- Addition of Fractionation Surrogate compounds
- Output the concentrate into two vials:
  - (1) Archive Sample
  - (2) Sample to be separated by Silica SPE
- Collect and concentrate Hexane fraction containing aliphatic compounds and output to GC vial
- Collect and concentrate a DCM fraction containing aromatic compounds and output to GC vial

An Automated Solution

PrepLinc SPEi System with AccuVap FLX

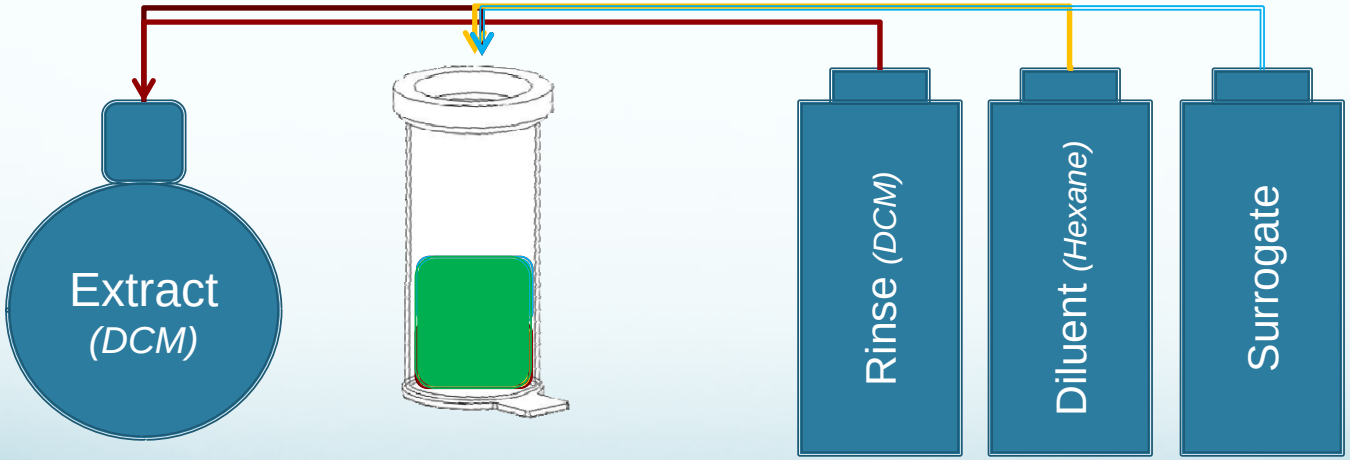
- Evaporation and Exchange of extract via the AccuVap
- Introduction of concentrated sample to SPE column
- Programmable positive pressure SPE
- Automated fractionation of elutions with transfer to AccuVap for concentration
- Collection of each concentrated fraction in separate GC vials for analysis



PREPLINC
J2 SCIENTIFIC

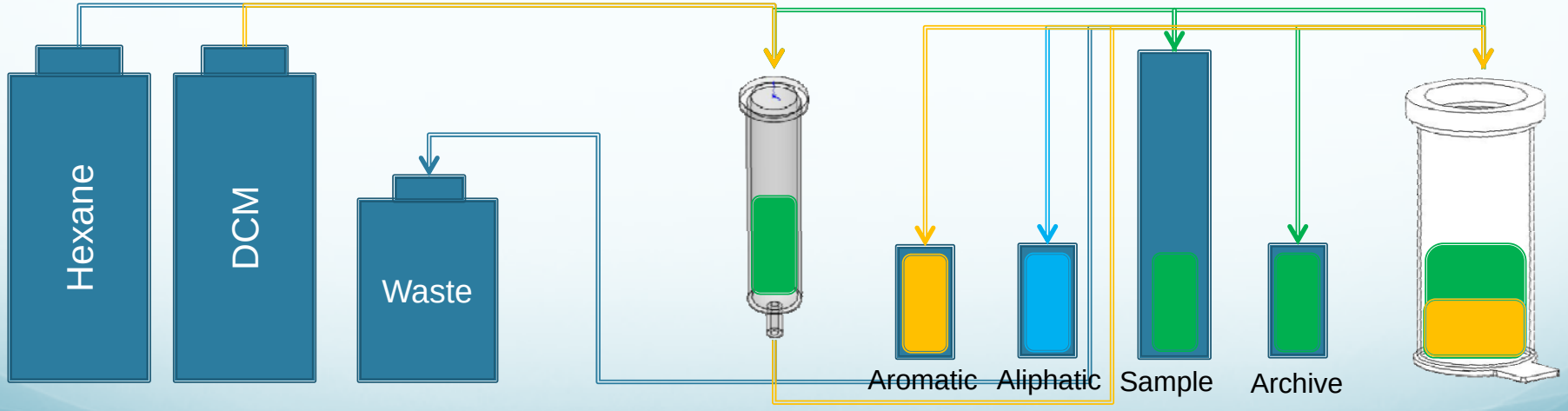
The Method – Step 1

- Concentration and solvent exchange of extract
  - Extract is added to the evaporation chamber at user defined rate. Concentration starts immediately, according to programmed parameters. Sample is not allowed to go dry or overflow chamber.
  - When all sample is added to chamber, rinse of extract vial is performed and the rinsate is also added to the chamber.
  - The extract is then exchanged from DCM to Hexane.
  - Concentration continues until the sample reaches the lower level sensor that has been calibrated to 1.0mL.
  - 1mL of surrogate recovery standard is added to the chamber and the sample is mixed via bubbling.
  - Sample is ready for further processing.



The Method – Step 2

- Transfer of Archive and SPE Processing
  - Half of the exchanged sample is transferred to a GC vial to save as an archive.
  - Half of the exchanged sample is transferred to a vial for SPE fractionation.
  - The silica gel cartridge on the SPE column module is conditioned with Hexane.
  - Sample is added to the conditioned SPE column and allowed to equilibrate for 3 minutes.
  - 21.5 mLs of Hexane is eluted through the column to the AccuVap chamber. The elution is concentrated to 1mL and transferred to a GC vial. This is the aliphatic fraction.
  - 22 mLs of DCM is eluted through the column to the AccVap chamber. The elution is concentrated to 1mL and transferred to a GC vial. This is the aromatic fraction.
  - The automated process gives three fractions: archive, aliphatic and aromatic.



End result is three GC vials containing:

- The “Archive Sample”
- The Aliphatic Fraction ready for GC Analysis.
- The Aromatic Fraction ready for GC Analysis.

Data Results:

Water Sample#1	Manual Process (ug/L)	Automated Process (ug/L)
Naphthalene	200	87
2-Methylnaphthalene	28.6	11
Acenaphthene	33.6	23.6
Fluorene	23.9	22.4
Phenanthrene	43.6	42
Fluoranthene	29.2	28
Pyrene	25	22.4
C9 – C18 Aliphatic HC	ND	ND
C19 – C36 Aliphatic HC	ND	ND
C11 – C22 Aromatic HC	1420	744
C11 – C22 Aromatic HC, Adjusted	1040	518

Data Results:

Soil Sample#2	Manual Process (mg/Kg)	Automated Process (mg/Kg)
Fluorene	4.92	3.78
Phenanthrene	6.89	6.36
C9 – C18 Aliphatic HC	2210	2426
C19 – C36 Aliphatic HC	4180	4868
C11 -- C22 Aromatic HC	4160	3716
C11 -- C22 Aromatic HC, Adjusted	4150	3706

Data Results:

Soil Sample#3	Manual Process (mg/Kg)	Automated Process (mg/Kg)
C9 – C18 Aliphatic HC	47.9	34
C19 – C36 Aliphatic HC	2170	1946
C11 – C22 Aromatic HC	460	832
C11 -- C22 Aromatic HC, Adjusted	460	832

Data Results:

Soil Sample#4	Manual Process (mg/Kg)	Automated Process (mg/Kg)
C9 – C18 Aliphatic HC	38.4	59.4
C19 – C36 Aliphatic HC	1360	1716
C11 – C22 Aromatic HC	436	532
C11 -- C22 Aromatic HC, Adjusted	436	532

Results and Conclusions

- The system developed by J2 Scientific is a move forward towards automating the EPH fractionation procedure. Other then the actual extraction which is dependent upon sample matrices and laboratory procedures/equipment, the J2 automated process includes a hexane exchange, multiple concentrations and fractionation.
- When finalized, this will give a reproducible procedure for the extensive extraction procedure of EPH.