



An Automated High Throughput Sample Fractionation Method for the determination of PAHs, MADEP-EPH, TNRCC Method 1005-1006

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Introduction

Polycyclic aromatic hydrocarbons (PAH) are believed to be mutagenic and contain toxic chemicals. These chemicals contain carcinogenic properties which have led to legislative restrictions on their release in the environment. Therefore, suitable monitoring methods are extremely important. PAH pollutants are present in the air, water, and soil and have been a concern for a considerable period of time. There are several ways that they can be brought into the environment. The most predominant source is from them being readily formed during pyrolysis and incomplete combustion processes (e.g. fossil fuel burning). This application describes the Automated Sample Fractionation of the Aliphatic from Aromatic Hydrocarbons after Automated Sample Extraction. This note demonstrates an approach to obtaining aliphatic and aromatic hydrocarbons separately with no interferences, GC/MS is used to determine the individual concentrations of the petroleum compounds in order to determine the toxicity of the sample.

Instrumentation

- FMS PLEtm (Pressurized Liquid Extraction System) automated extraction from Soil
- FMS PowerPreptm EPH automated sample cleanup and fractionation
- FMS Silica Gel Column
- GC/MS

Method Summary

The FMS PowerPrep EPH System is set up with a single silica gel column, The 11cm FMS 10g 5% deactivated neutral Silica column was installed on the system and pre-eluted with 100mL DCM followed by 75mL pentane. The sample extract is prepared for analysis using the automated FMS PLE system., including the addition of any internal standards needed for quantification of results. Sample extracts must be introduced to the silica gel column in an appropriate aliphatic solvent (iso-octane is strongly recommended however pentane can substitute iso-octane). If more than a few percent of a polar solvent (e.g., DCM, toluene) is present in the sample extracts, low molecular weight aromatic compounds may elute in the aliphatic fraction. Ten individual fractions, indicated in the last column of Table 1, were collected and tested for aliphatic and aromatic hydrocarbon content as follows. Deuterium labeled PAH, and Alkane standards were added to each fraction to allow quantification, then each fraction was reduced in volume in a Kuderna-Danish flask fitted with a chimney containing glass beads using a water bath at 55°C. They were then transferred using DCM rinses to a glass centrifuge tube and further reduced in volume to ~200µL using Nitrogen blow down. The concentrated extracts were then transferred to a glass GC auto-sampler vial with DCM rinses; blow down with Nitrogen to 400µL and an internal standard added to give a final volume of 500µL. Each fraction was analyzed by GC/MS for the target compounds.

Table 1. PowerPrep EPH Solvent program used to elute the hydrocarbon fractions. The individual fractions collected are indicated in the last column.

Step	Flow Rate, l/min	Volume, ml	Solvent	Operation
1.	10	100	DCM	Column Condition
2.	10	75	Pentane	Column Condition
3.	10	15	Pentane	Aliphatic. Fraction 1a
4.	10	10	Pentane	Aliphatic. Fraction 1b
5.	10	10	Pentane	Aliphatic. Fraction 1c
6.	10	12	DCM	Solvent Exchange
7.	10	25	DCM	Aromatic Fraction 2a
8.	10	25	DCM	Aromatic Fraction 2b
9.	10	25	DCM	Aromatic Fraction 2c
10.	10	25	DCM	Aromatic Fraction 2d
11.	10	50	DCM	Aromatic Fraction 2e
12.	10	70	DCM/MeOH	Aromatic Fraction 2f

Results

The aliphatic fractions were expected to be eluted with pentane, the least polar solvent. Therefore three pentane fractions were collected and analyzed for aliphatic hydrocarbons. Then the elution solvent was changed to DCM to elute the aromatics. The “solvent exchange” fraction and the first aromatic fraction were also analyzed for aliphatics to ensure that all were recovered with the pentane elution. These results, shown in Table 2, indicate that quantitative recovery of the aliphatic hydrocarbons was achieved with the second aliphatic fraction, 15 to 25 mL of pentane. Small concentrations of aliphatics were measured in the first and third pentane fractions but it is recommended that these be discarded to allow exclusion of any other organic material that might be collected in those fractions and potentially interfere with the subsequent GC analysis.

Table 2. Distribution of Targeted Aliphatic Hydrocarbons in the Fractions Collected

ANALYTE	ng spiked	0-15 ml Pentane		15-25 ml Pentane		25-35 ml Pentane		12 ml DCM (Solvent Exchange)		0-25 ml DCM (The First portion of DCM Eluant)	
		Fr. 1a	%rec	Fr1b	%rec	Fr1c	% rec	SE	% rec	Fr2a	% rec
nC10	436	2.24	0.51 %	402.90	92.41%	3.49	0.80%	4.37	1.00 %	5.78	1.33%
nC12	382	0.74	0.19 %	630.88	165.15%	47.75	12.50%	0.88	0.23 %	0.86	0.23%
nC14	404	0.62	0.15 %	602.97	149.25%	39.01	9.66%	1.24	0.31 %	3.49	0.86%
nC16	429	2.68	0.62 %	434.68	101.32%	16.94	3.95%	0.40	0.09 %	8.45	1.97%
Pristane	409	1.60	0.39 %	366.17	89.53%	8.87	2.17%	1.42	0.35 %	1.93	0.47%
nC18	408	2.80	0.69 %	480.36	117.74%	19.50	4.78%	0.69	0.17 %	1.40	0.34%
nC20	420	4.50	1.07 %	453.25	107.92%	12.11	2.88%	1.55	0.37 %	3.78	0.90%
nC22	410	8.90	2.17 %	441.11	107.59%	12.76	3.11%	5.37	1.31 %	12.76	3.11%
nC24	432	20.62	4.77 %	473.12	109.52%	32.92	7.62%	11.62	2.69 %	33.85	7.83%
nC26	412	30.50	7.40 %	465.08	112.88%	46.83	11.37%	16.60	4.03 %	50.61	12.28%
nC28	412	27.48	6.67 %	491.67	119.34%	42.78	10.38%	17.65	4.28 %	49.20	11.94%
nC30	450	24.14	5.36 %	528.11	117.36%	41.58	9.24%	14.24	3.16 %	32.20	7.16%
nC32	418	17.88	4.28 %	508.34	121.61%	24.66	5.90%	7.25	1.73 %	15.02	3.59%
nC34	433	13.71	3.17 %	947.75	218.88%	59.92	13.84%	3.68	0.85 %	8.27	1.91%
nC36	424	17.37	4.10 %	396.49	93.51%	4.99	1.18%	2.12	0.50 %	3.82	0.90%

The red fraction is where most of the alkanes were found

The DCM fractions were analyzed for aromatic compounds and the results presented in Table 3 indicate that quantitative recovery of targeted compounds was achieved with fraction 2, 25 – 50 mL of DCM containing the aromatic compounds. DCM Fractions 2c to 2f and the 70mL 1:1 DCM/MeOH did not contain and alkanes or PAHs .

Table 3. Distribution of Targeted Aromatic Hydrocarbons in the Fractions Collected.

	Ng spiked	0-25 mL DCM		25-50 mL DCM	
		Fr 2a	% rec	Fr 2b	% rec
Naphthalene	2001	739.40	36.951%	1253.26	62.632%
Acenaphthylene	1960	1.91	0.097%	1939.28	98.943%
Acenaphthene	1966	8.65	0.440%	1885.08	95.884%
Fluorene	2408	0.07	0.003%	2322.34	96.443%
Phenanthrene	1958	0.30	0.015%	2033.02	103.831%
Anthracene	1976	0.02	0.001%	1899.28	96.118%
Fluoranthene	2033	0.04	0.002%	2093.06	102.954%
Pyrene	2016	0.09	0.005%	2071.38	102.747%
Benz(a)anthracene	2096	0.25	0.012%	2089.60	99.695%
Chrysene	2118	0.08	0.004%	2152.86	101.646%
Benzo(a)fluoranthene	4009	1.51	0.038%	3971.23	99.058%
Benzo(e)pyrene	2116	0.08	0.004%	2052.56	97.002%
Benzo(a)pyrene	1954	0.10	0.005%	1921.22	98.322%
Perylene	2252	0.10	0.004%	2220.03	98.581%
Dibenz(ah)anthracene	2123	0.07	0.003%	2143.67	100.973%
Indeno(1,2,3,cd)pyrene	2093	0.68	0.032%	2080.41	99.399%
Benzo(ghi)perylene	2157	0.11	0.005%	2142.09	99.309%
1-Methylphenanthrene	1982	0.22	0.011%	2104.10	106.160%
C2-Phen/Anthracene	2050	0.17	0.008%	2187.91	106.727%
Dibenzothiophene	2010	0.31	0.015%	1824.27	90.760%
Retene	2040	0.41	0.020%	2168.77	106.312%
2-Methylnaphthalene	1978	239.85	12.126%	1718.59	86.885%
1-Methylnaphthalene	2128	299.34	14.067%	1809.50	85.033%
Biphenyl	2150	0.40	0.019%	2222.49	103.372%
2,6-Dimethylnaphthalene	2176	52.39	2.408%	2074.83	95.350%
2,3,5-Trimethylnaphthalene	2215	0.06	0.003%	2322.73	104.864%

Conclusions

The FMS PowerPrep/EPH system in combination with the FMS Silica gel column is shown to automatically separate Aliphatic (Alkanes) Hydrocarbon from PAHs (Aromatic) Hydrocarbons at a high rate of speed producing excellent recoveries and reproducibility. The combination of the FMS PowerPrep EPH system and the FMS Teflon column demonstrates consistent, reproducible, reliable high throughput Automated Sample Fractionation of PAHs. The PowerPrep EPH system can fractionate up to 30 samples per hour.

For more information on the [PowerPrep EPH system](#)

