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PERFORMANCE STUDY

TESTING PAHS & BENZO[A]PYRENE IN RECLAIMED ASPHALT USING UVF

Introduction

Sitelab's UVF analyzers are very sensitive to polycyclic aromatic hydrocarbons (PAHs), abundant in coal tars and contaminated asphalts, described here in this study. Table 1 shows how fluorescence varies depending on the size and shape of each compound and which instrument is used for analysis calibrated to Sitelab's PAH standard.

Table 1

Fluorescence Response Comparing Polycyclic Aromatic Hydrocarbon Compounds

Example Compounds in the C10 to C20 Carbon Range	Molecular Weight ($g \bullet mol^{-1}$)	Aromatic Rings per Compound	UVF-Trilogy Fluorescence Response (%)	UVF-500D Fluorescence Response (%)
Naphthalene, C10	128	2 Rings	0.1	0.0
Phenanthrene, C14	178	3 Rings	11.7	0.4
Anthracene, C14	178	3 Rings	475	46
Fluoranthene, C16	202	4 Rings	12.5	60
Pyrene, C16	202	4 Rings	13.8	0.3
Benzo[a]Anthracene, C18	228	4 Rings	94	2.7
Benzo[k]Fluoranthene, C20	252	5 Rings	645	710
Benzo[a]Pyrene, C20	252	5 Rings	330	280
Sitelab PAH Standard, 17 Compound Mixture:			100	100
16 Compound PAH Standard for Comparison:			93	105

PAH compounds provided in methanol, purchased from AccuStandard, Inc. (New Haven, CT).
Note: Ultraviolet Fluorescence (UVF) detects PAHs as the sum of EPA's regulated compounds.

Sitelab UVF-Trilogy
Part No. 7200-004-PAHS
Benchtop analyzer, uses
255-nm LED light source

Sitelab UVF-500D
Part No. 50200
Handheld analyzer, uses
375-nm LED light source

PAH Calibration Standards:
UVF-Trilogy: CAL-060M
UVF-500D: CAL-061M-500D

Benzo[a]Pyrene Standards:
CAL-BAP-COALTAR
Use with either analyzer

Performance Testing PAH in Soil Proficiency Sample

Certified Reference Materials (CRMs) used to validate laboratory GC methods for proficiency studies can be useful to validate UV fluorescence-based methods. Environmental Resource Associates (ERA) 722 Soil is spiked with 16 PAH compounds, which vary in composition from lot to lot. Concentrations are in ppb (ug/Kg).

This sample was extracted for 24 hours using 10 grams of soil with 20 mL of methanol and measured using Sitelab's UVF-500D and UVF-Trilogy analyzers and standards. Table 2 shows good accuracy with Recoveries >50%, testing PAHs compared to the certified lab value. Table 3 shows Benzo[a]Pyrene performance using Sitelab's BaP standard developed for coal tar contaminates. In this case, results do not meet ERA's acceptance limits. This is expected due to the low content of this compound compared to the soil's other spiked compounds, as illustrated in Table 4. Despite this, however, Relative Percent Difference (RPD) values exhibited were <50% in this lot, including ERA's Study Mean result.

Currently, ERA and other CRM providers only make proficiency products for PAHs in soil, sediment and water, not in asphalt.

Table 2

Soil Proficiency Sample, ERA 722 Low-Level PAHs, Lot No. D115-722	Test Result ug/Kg	Certified Value ug/Kg	Recovery %
UVF-Trilogy Analyzer PAHs:	4,700	5,838	81%
UVF-500D Analyzer PAHs:	5,803	5,838	99%
Total 16 PAHS, Study Mean: (Based on 39 lab tests)	4,029	5,838	69%

ERA does not provide acceptance criteria for Total PAHs; only individual compounds are reported, illustrated in Table 3 below.

Table 3

Benzo[a]Pyrene Using BaP Coal Tar Standard	Test Result ug/Kg	Certified Value ug/Kg	Recovery %	RPD %
UVF-Trilogy Analyzer:	235	194	121%	19%
UVF-500D Analyzer:	290	194	150%	40%
BaP Study Mean:	126	194	65%	43%
ERA Acceptance Limits:		48 – 213		

Benzo[a]Pyrene measured using CAL-BAP-COALTAR. This product fluoresces stronger and always produces concentrations 20 times lower compared to UVF PAH results in Table 2.

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Composition of Benzo[a]Pyrene in Coal Tar Contaminates

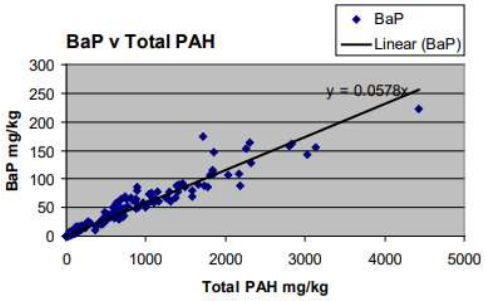
Guidelines specified by the Association of Directors of Environment, Economy, Planning & Transport (ADEPT), for managing reclaimed asphalt in the United Kingdom, referenced in Figure 1 (2019), shows the proportion of BaP to Total 16 PAHs is 5% or 20 times lower. This ratio is similar to asphalts and coal tar contaminants used in this study shown in Table 4. Phenanthrene, Fluoranthene and Pyrene are always the most abundant and always in that order, while BaP typically makes up 4 to 6 percent of the PAH contents. This is the case with all coal tar contaminates and is supported further in Environment Agency WM3 regulations. As such, response factors can be used to estimate individual compounds using UVF PAH analysis or measured directly using the BaP standard formulated for coal tar.

Table 4

Composition of 16 PAHs in Asphalts, Coal Tar, Soil and Proficiency Sample by Lab GC/MS

Most abundant PAHs and Benzo[a]Pyrene are Highlighted in Yellow	Asphalt (France) Lab 1 %PAH Content	Asphalt (France) Lab 2 %PAH Content	Asphalt (UK) %PAH Content	Coal Tar Sealcoat (US) %PAH Content	Soil with Asphalt (US) %PAH Content	ERA 722 for Comparison %PAH Content
Naphthalene	1%	1%	0.3%	4%	0%	3%
Acenaphthylene	1%	1%	0.4%	0%	1%	10%
Acenaphthene	2%	2%	2%	4%	0%	15%
Fluorene	4%	4%	1%	4%	2%	7%
Phenanthrene	21%	22%	23%	22%	16%	13%
Anthracene	5%	5%	7%	6%	4%	8%
Fluoranthene	20%	21%	18%	17%	19%	5%
Pyrene	15%	16%	13%	13%	16%	7%
Benzo[a]Anthracene	6%	6%	6%	5%	7%	7%
Chrysene	6%	5%	7%	4%	8%	6%
Benzo[b]Fluoranthene	5%	6%	5%	5%	7%	2%
Benzo[k]Fluoranthene	2%	2%	5%	2%	4%	2%
Benzo[a]Pyrene	6%	4%	5%	5%	7%	3%
Indeno[1,2,3-cd)]Pyrene	3%	2%	3%	4%	4%	2%
Dibenzo[a,h]Anthracene	1%	1%	1%	1%	1%	3%
Benzo[g,h,i]Perylene	3%	3%	3%	3%	4%	7%
Total PAHs (mg/Kg):	1,774	1,139	2,297	63,830	68	5.838
PAH to BaP Ratio:	*17X*	*23X*	*21X*	*21X*	*15X*	*30X*

Figure 1

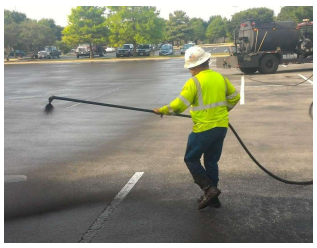


ADEPT & Construction Demolition Waste Forum, Appendix D: "50 mg/kg BaP is a good indicator of the presence of 1000 mg/kg road tar." (2019)

ERA 722 Low-Level PAHs in Soil CRM, Lot No. D115-722.

This product does not contain coal tar and it's 'PAH signature' in Table 4 is different.

Table 5 shows performance testing PAHs and BaP using Sitelab's UVF analyzers. Relative percent difference values exhibited were <50%. The sample from France in Table 4 was analyzed by two laboratories with PAHs reported as 1,774 ppm and 1,139 ppm, a difference of 44%. This variability is not uncommon for labs testing this type of material. The average PAH and BaP concentrations were used here to compare UVF-Trilogy and UVF-500D results.



Soil with asphalt fragments collected from a boring and a coal tar sealcoat brand used on parking lots show similar PAH signatures to asphalts contaminated with coal tars in Table 4.

Table 5

Samples Tested by UVF for PAHs and Benzo[a]Pyrene			UVF mg/Kg	Lab GC mg/Kg	RPD %
Coal Tar Sealcoat, Brand 1 (US)	UVF-Trilogy	PAHs	70,000	63,830	9%
		BaP	3,500	3,000	15%
	UVF-500D	PAHs	58,000	63,830	10%
		BaP	2,900	3,000	3%
Asphalt (UK)	UVF-Trilogy	PAHs	2,000	2,297	14%
		BaP	100	109	9%
	UVF-500D	PAHs	2,270	2,297	1%
		BaP	114	109	4%
Asphalt using Lab Average (France)	UVF-Trilogy	PAHs	1,440	1,457	1%
		BaP	72	78	8%
	UVF-500D	PAHs	1,500	1,457	3%
		BaP	75	78	4%
Soil with Asphalt (US)	UVF-Trilogy	PAHs	61	68	11%
		BAP	3.1	4.6	39%
	UVF-500D	PAHs	85	68	22%
		BaP	4.3	4.6	7%

For comparison, UK regulatory waste limit for Benzo[a]Pyrene is 50 mg/Kg.

Method Limitations Testing PAHs in Asphalt

Due to the nature of this matrix, methanol will extract hydrocarbons more slowly compared to extracting soil or water samples using this field screening method. Studies summarized in Table 6 have show a 10 minute extraction time is sufficient, but no more than 20 minutes, to yield results similar to laboratory GC analysis for best performance. This applies to testing PAHs or Benz[a]Pyrene. Testing extracts after 24 hours will be higher and may be needed in some cases, especially for high coal tar contaminates. This is described further in Sitelab's asphalt standard operating test procedures. Visit our website to download SOPs and UVF-500D and UVF-Trilogy manuals.

Table 6

Samples Extracted in Methanol Solvent, Tested Over Time	2 Minutes mg/Kg	10 Minutes mg/Kg	20 Minutes mg/Kg	24 Hours mg/Kg	Certified Lab Result mg/Kg
1: Asphalt Planings, Site 1 (France)					
UVF-Trilogy PAHs	250	288	380	675	196
UVF-500D PAHs	324	400	490	785	
2: Asphalt Planings, Site 2 (France)					
UVF-Trilogy PAHs	235	315	380	900	377
UVF-500D PAHs	295	387	455	1,000	
3: Asphalt Planings, Site 3 (France)					
UVF-Trilogy PAHs	1,020	1,280	1,620	3,080	1,531
UVF-500D PAHs	1,000	1,390	1,450	4,400	
4: Coal Tar Sealcoat, Brand 2 (US Manufacturer)					
UVF-Trilogy PAHs	11,000	22,000		100,000	87,800
UVF-500D PAHs	10,600	19,000		62,000	
5: Asphalt-Based Sealcoat (US Manufacturer)					
UVF-Trilogy PAHs	400	820		3,200	ND <15
UVF-500D PAHs	360	720		2,460	
6: Fresh Asphalt Pavement, (Road in Massachusetts, US)					
UVF-Trilogy PAHs		108 – 130		308 – 490	Not Tested
UVF-500D PAHs		81 – 108		242 – 379	

Sample tested 4 times using 2 g and 5 g extracts plus duplicates. RPD in ranges <50%.

PAHs performed by certified laboratories using U.S. EPA Method 8270D by GC/MS

UVF detects PAHs in fresh road asphalt, made with virgin bitumen, as shown in Sample 6. UVF detects PAHs in asphalt driveway sealcoats too, as shown in Sample 5. These products contain a much higher content of asphalt compared to asphalt in pavement and as such, UVF detects higher concentrations.

Asphalts contain a variety of other PAH compounds which are not reported by the lab GC methods. This includes 'cousin' compounds, like alkylated PAHs, which co-fluoresce with UVF measurements.

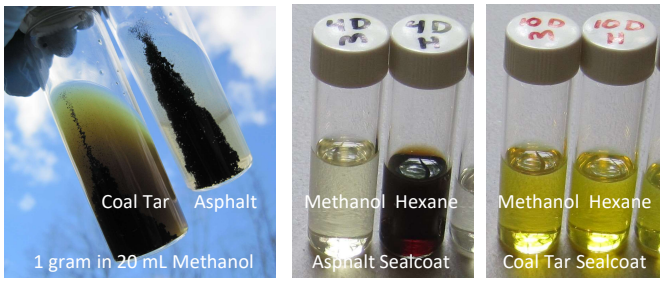
This background 'interference', as shown in Samples 5 and 6 is important to understand, since it can produce false positive results. However, testing asphalt sample extracts at 24 hours can provide helpful qualitative data useful for decision making when comparing results in samples close to the regulatory limits. In some cases, the high bias results in clean asphalts can be subtracted from results in samples of recycled asphalt mixed and diluted with contaminated coal tar material.

Photo showing asphalt samples provided by a laboratory in France, which they ground and sieved to 2 mm in size for analysis. ADEPT specifies samples be a minimum of 4 mm in size. This small particle size helps ensure samples are well homogenized and improves data quality.

ADEPT Guidelines: https://adeptnet.org.uk

New guidelines published in 2024 now list UV-fluorescence based methods as an approved Rapid Measurement Technique (RMT) for screening PAHs as an alternative to PAK marker spray.

Forensic Analysis using Polar vs. Non-Polar Solvents



Photos showing asphalt and coal tar driveway sealcoats extracted in methanol and hexane solvents. Hexane dissolves all the asphaltenes into solution within minutes. The use of the two solvents is used for hydrocarbon fingerprinting analysis using the UVF-Trilogy. Once the extract is filtered, extracts are stable for months and do not increase in concentration. The difference in color using these two solvents with or without filtration can be useful for visual screening purposes.

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Differences in Sitelab's UVF Analyzers, Past & Present

Sitelab introduced the UVF-Trilogy in 2018, replacing the older UVF-3100 models after 20 years. It uses LEDs instead of a mercury vapor lamp. The optical filters used in both models are identical and both use square quartz cuvettes. The UVF-Trilogy features a touch screen interface, arrives factory calibrated and can test a wide range of contaminates.

Sitelab introduced the UVF-500D model in 2020, replacing the older TD-500D models after 15 years in production. These analyzers are used to test TPH in water or soil contaminated with crude oils and heavy fuel oils. This device is not suitable for testing PAHs in diesel, gasoline or other light-refined hydrocarbons. The UVF-500D is sold online with Sitelab Corporation's partner Obstitech in Denmark.

Visit https://uvf-500d.com/

The UVF-Trilogy performs multi-point calibrations and can store up to 18 calibration curves in memory. The analyzer uses 'snap in' UV modules available for PAHs, GRO, DRO and TPH oil range hydrocarbons. This model arrives factory calibrated to PAHs and Benzo[a]Pyrene.

The UVF-500D performs a 1-point calibration. An adjustable solid standard is available which can be tuned and tightened to read the same as the PAH or BaP solvent standards. This device is useful to check calibrations for quality control or to recalibrate the analyzer, if necessary.

Asphalt Test Procedure is Easy

Samples are typically prepared using 2 gram or 5 gram size aliquots extracted in 20 mL methanol solvent. Extracts are shaken by hand, allowed to sit for 10 minutes and then filtered to stop the extraction process. Dilutions are made using a micro-pipette and a graduated test tube. The dilution is poured into a glass cuvette and placed into the UVF for measurement. The sample reading is multiplied by the dilution factor to report the final concentration. Filtered extracts and dilutions made are reusable and are stable for months.

Summary and Conclusions

Sitelab's portable UVF analyzers are highly sensitive to PAHs with detection limits in the low ppb range. As demonstrated in this study, both PAH and Benzo[a]Pyrene results correlate well to laboratory GC methods, making this a suitable screening tool to meet ADEPT's BaP limits. In the UK, material above 50 mg/Kg is regulated as a waste.

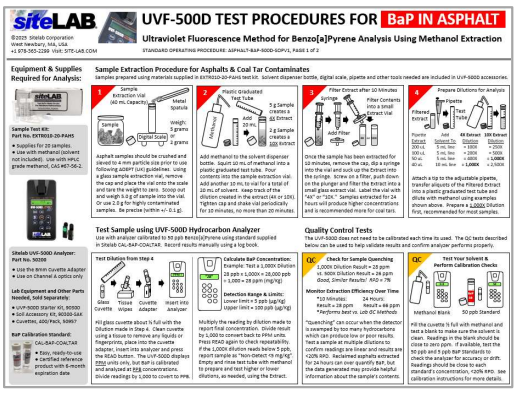
UVF methods do have their limitations for asphalt applications. Sample extraction time in methanol should be monitored. When confirmatory analysis is performed, use an accredited laboratory experienced testing reclaimed asphalts. Use a second laboratory, if necessary, when UVF results are not accurate or don't trend well.

The fluorescence and detection of PAHs and BaP in clean, coal tar free asphalts, including binders, sealcoats or other pavement products made with bitumen (CAS No. 8052-42-4), can produce false positive results. In general, however, BaP in reclaimed asphalts without coal tars will produce concentrations below 25 mg/Kg, ADEPT's lower limit, using this method.

Test Kits Available for Asphalt Analysis

20 Sample Test Kit,
Part No. EXTR010-20-PAHS
This product is compatible with all Sitelab analyzers.

Use with methanol to prepare samples for analysis. Solvent not included. Use HPLC grade methanol only.



Standard operating procedures for calibration and sample analysis can be downloaded on Sitelab's website. These SOPs were developed to meet ADEPT's RMT protocol requirements. Copies of the UVF-500D and UVF-Trilogy manuals are also available.

Visit: https://site-lab.com