

A New On Site Analysis Method for Poly Aromatic Hydrocarbons

ENVIRONMENTAL
ANALYSIS

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The cost of bringing contaminated land back into use is constantly increasing. One of the biggest costs is the excavation, treatment and disposal of the contaminated soil. The ability to classify the soil as clean, contaminated or hazardous in real time can create significant cost savings as only the contaminated soil is excavated and treated or sent to landfill. For on site treatments of contaminated soil, the process can be regularly monitored allowing optimisation of the cleaning procedure.

On-Site chemical analysis is the only way contaminated soil can be classified in real time. Several on site analytical methods are available for petroleum hydrocarbons and heavy metals, but an easy to use and reliable Poly Aromatic Hydrocarbon method has not been available until now. This article describes the introduction of a new analysis method that allows accurate and reliable PAH analysis on site.

Polyaromatic Hydrocarbons are a class of chemicals that include Benzo-a-Pyrene and are known to have carcinogenic properties. They are found in diesel, jet fuel and kerosene type fuels, but most commonly in the residues and by products from manufactured gas plants and general combustion of organic material. Creosote and tar used to preserve wood were originally obtained from gas plant production waste. PAHs are also present in car exhaust. The tar used for road construction also contains high levels of PAHs. The presence of PAHs in soil and water is undesirable and many contaminated sites require PAHs to be removed to bring them back to a usable state. The currently accepted method to assess PAH contamination is to identify and quantify the sum of just 16 individual PAHs that include 2-6 ring compounds out of the hundreds of PAHs actually present.

UV Fluorescence

PAHs when exposed to high energy UV radiation fluoresce and this provides a very sensitive way to detect PAHs. This concept has been used in some early portable analysers and is also used in several on line hydrocarbon analysers. The system however needs careful calibration to specific mixtures of PAH to produce useful results. For contaminated sites the concentrations of individual PAHs in the soil often varies considerably across the site. This variation is dependent on the type of product spilled into the ground and the amount of weathering that has occurred. If the analyser is incorrectly calibrated this can lead to a significant under or over estimation of the actual PAH concentration in the soil. For example, tar from a manufactured gas plant can contain up to 40% naphthalene, but a weathered diesel spill will contain no naphthalene at all.

In order to improve the utility of fluorescence based analysis, QROS looked at the PAH ratios from hundreds of PAH containing samples and identified a novel approach to using fluorescence. The new analysis method measures specific UV emission wavelengths that correspond to the key PAHs in the sample. The method calculates the ratios of light and heavy PAHs, which is then used to select the appropriate calibration parameters. The derived ratio also indicates the possible source of the PAH.



Figure 1: Analyser outside



Figure 2: Analyser in the laboratory

Experimental Protocol

23 soils from 6 different sites, contaminated with varying concentrations of PAH were analysed. The soils ranged from top soils just under the vegetation layer to heavily contaminated tar pits from MGP sites. To mimic field conditions, the samples were analysed as received, taking care to exclude larger pieces of rock, brick and roots that were part of the soil mass. Moisture content was not factored in. Replicates were taken where the samples were very inhomogeneous.

The analytical procedure is very simple and takes under 7 minutes from sample collection. Approximately 5g of soil are extracted with 10 ml of methanol and shaken for 3 minutes or until the soil is dispersed. The methanol extract is allowed to settle (or filtered through a 2 micron filter) and diluted, usually by x1,000, x10,000 or x50,000. The diluted extract is placed in the analyser and the fluorescence is measured at 2 wavelengths, one selected to respond to all the PAHs in the sample and the other to target the 16 EPA PAHs.

The analyser used was a modified UVF-3100 fluorescence analyser. This unit is fully portable and runs from either a 12V DC or 240V AC power supply. The unit can be connected to a PC to capture the data generated or the data can be copied manually from the in built display.

Results

The quantitative result is generated by comparing the fluorescence of the sample to a 5 point calibration curve stored in the analyser. The curve is constructed using a proprietary PAH standard containing the 16 target PAHs. The ratio of the total fluorescence concentration compared to the 16 target PAH derived concentration indicates the conversion factor to be used to obtain a more accurate result.

The following results were obtained.

Old Industrial Area					
Sample	Total Fluorescence	Target 16 fluorescence	Ratio Target 16/total	Corrected result as sum of 16 EPA (mg/kg)	Lab result 16 EPA (mg/kg)
800	2899, 1373, 1713	442, 228, 300	16.2%	442, 228, 300	117
807	7964, 6018, 8680	1703, 1274, 2103	22.4%	1703, 1274, 2103	1800
918	498, 414, 1218	94, 74, 166	15.7%	94, 74, 166	219
919	2595, 1013, 1423	356, 187, 212	15.0%	356, 187, 212	400

Top soil from just below the vegetation layer from wasteground

Sample	Total Fluorescence	Target 16 fluorescence	Ratio Target 16/total	Corrected result as sum of 16 EPA (mg/kg)	Lab result 16 EPA
83	208	49	23.5%	49	144
94	520	121	23.3%	121	220
69	371	88	23.7%	88	149
93	163	42	25.8%	42	270

Gas Plant Site 1

Sample	Total Fluorescence	Target 16 fluorescence	Ratio Target 16/total	Corrected result as sum of 16 EPA (mg/kg)	Lab result 16 EPA
Tar Well 1	6690, 4145	1124, 687	16.7%	1124, 687	837
Tar Well 2	4974, 3701	846, 613	16.8%	846, 613	794
Gas Holder 1	923, 862	212, 196	22.8%	212, 196	207
Gas Holder 2	1324, 1278	334, 307	25.8%	334, 307	283

Gas Plant Site 2

Sample	Total Fluorescence	Target 16 fluorescence	Ratio Target 16/total	Corrected result as sum of 16 EPA (mg/kg)	Lab result 16 EPA
Area 1	789, 893	108, 142	14.9%	70, 92	70
Area 2	1978, 1792	347, 290	16.9%	347, 290	267
Area 3	43145, 64838	6196, 8655	13.8%	4027, 5626	4,314
Area 4	39,664, 34,531	5,284, 3,897	12.2%	3,433, 2,531	3,062
Area 5	18,846, 20,250	2,472, 2,341	12.3%	1606, 1,521	1,598

Gas Plant Site 3

Sample	Total Fluorescence	Target 16 fluorescence	Ratio Target 16/total	Corrected result as sum of 16 EPA (mg/kg)	Lab result 16 EPA
Sample 1	13,000	1,500	11.5%	1,500	1,200
Sample 2	5,000	600	12.0%	600	666
Sample 3	942	110	11.7%	110	113
Sample 4	890	90	10.1%	50	40
Sample 5	2.5	0.3	12.0%	0.3	ND

Reference Sample

Sample	Total Fluorescence	Target 16 fluorescence	Ratio Target 16/total	Corrected result as sum of 16 EPA (mg/kg)	Reference value 16 EPA (mg/kg)
LGC 6138 coal carbonisation std	6131, 5567, 5216	913, 908, 878	15.9%	913, 908, 878	693

Standards (raw fluorescence data)

Sample	Total Fluorescence	Target 16 fluorescence	Ratio Target 16/total
Creosote	241	19	7.9%
Naphthalene	195	0	0.0%
Phenanthrene	1032	53	5.1%
Pyrene	204	44	21.6%

Conclusions

The above data set indicates that on site PAH analysis by UV fluorescence is suitable for classifying soil samples during site investigation and remediation projects. For all the samples, the method would have correctly identified if they should be classified as "clean", contaminated or hazardous. Hazardous soil is generally considered to contain above 1000 ppm and background is around 100 ppm.

The difference in ratios of the total fluorescence to the fluorescence of the Target 16 PAHs is shown for the standard and various individual PAHs. Naphthalene, Phenanthrene and Pyrene are shown as they contribute the highest proportion of PAHs in most samples. The data shows how variation in the concentration of these compounds will change the ratio of the total to the Target 16 fluorescence. The ratios for creosote and the old industrial samples show a significant difference and this is expected as creosote contains a very high proportion of naphthalenes, while the samples from the industrial area contain almost no naphthalenes at all. This effect provides the method of adjusting the calibration curve so that the best calibration factor is used for the final determination of the sum of the 16 EPA target PAHs.

The ratio analysis also provides an additional valuable feature. Samples with a high Target 16 fluorescence compared to the total fluorescence contain a low concentration of the compounds amenable to bioremediation. Using the ratios could be a way of predicting how effective bioremediation or other soil treatments would be. They could also be used to monitor bioremediation, soil washing or thermal treatment as the ratio increases as the lighter PAHs are removed.

For many of the samples, the inhomogeneous nature of the soil did give a certain amount of variability between replicates. This would also be true for the laboratory analysis, but replicate analysis by the laboratory is not routinely carried out and therefore cannot be shown in this study. The on site method results obtained for the sum of the 16 EPA PAHs still correlated well with the laboratory data.

The samples from Area 1, 2 and 3 contained approximately 50% by weight of large porous stones. Area 3 had a very strong tarry odour and contained greater than 30% naphthalene. Samples of topsoil from the old industrial area and the wasteground contained a very high proportion of plant roots and organic matter. The 800 series also contained visible particles of asphalt. The results from the topsoil samples confirm that humic acids do not contribute to the result, unlike some laboratory methods. The low recoveries from these samples show how high levels of naturally occurring organics can inhibit the extraction efficiency. The data from Gas Plant site 3 was generated using an alternative set of UV filters and response factor algorithm but the same calibration curve.

This study shows that UV analysis is a very powerful tool for on site analysis. The technique has already been shown to provide excellent correlation to Gas Chromatography for TPH analysis both for Diesel Range and Gasoline Range Organics in a US EPA Environmental Technology Verification program. This study has demonstrated that PAH analysis is also possible using the same instrument, therefore providing a powerful tool for contaminated land professionals for the majority of their hydrocarbon analysis needs.

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