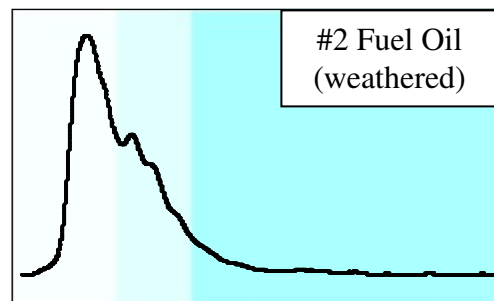
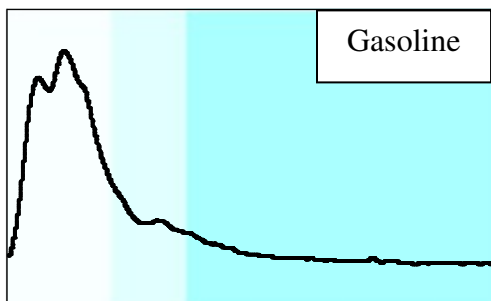


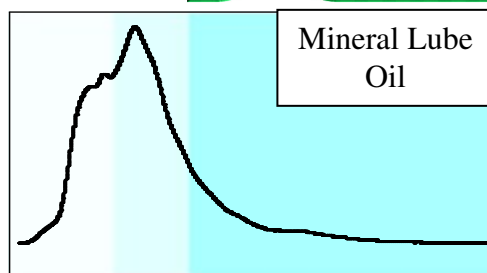
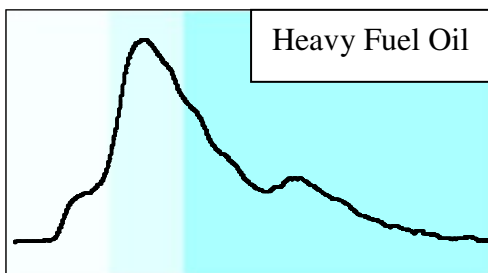
Hydrocarbon Identification and Analysis using the QED Hydrocarbon Analyser

The QED HC-1 hydrocarbon analyser from QROS Limited is the first of a new generation of advanced on site analysers. The QED has been developed in house by QROS Environmental Development and gives QROS chemists the ability to identify and accurately quantify most hydrocarbon types, on site, within minutes of taking the sample.



QED uses a significant modification of the proven UV fluorescence method as validated in the US EPA Environmental Technology Verification program. In this method, sample extracts are exposed to UV light (UV light is between 200nm and 400nm) and the analyser captures the UV light that is generated when the sample fluoresces. The light energy at various wavelengths is measured and the data is manipulated via a series of algorithms and converted into a fingerprint that gives a visual pattern corresponding to the hydrocarbon type.





Examples of the QED generated finger prints .

QED measures fluorescence, so can only detect compounds that fluoresce. The most commonly occurring compounds that fluoresce in the UV region are the aromatic hydrocarbons that include benzene, toluene, phenol, poly aromatic hydrocarbons, dibenzthiophenes, carbazoles and other similar compounds. These compounds are predominantly found in crude oil and refined crude oil products. They are also present in coal and coal products. For a contaminated site, any fluorescence is most certainly due to the aromatics found in petroleum or coal tar products.

As QED cannot directly measure the aliphatic and non fluorescing hydrocarbons, these components are calculated by using an appropriate calibrator made from a formulated petroleum product such as #2 fuel oil, heavy oil, lube oil etc.

Laboratory analysers are calibrated with diesel and fuel oil reference calibrators and the calibration used depends on the hydrocarbon found in the sample. The problem for “test kits” and first generation on site analysers is that they cannot identify the hydrocarbon being analysed. To calibrate these systems, assumptions have to be made about the hydrocarbon type used to make the calibration. An incorrect choice of calibrator can significantly change the results obtained. Unfortunately, for most hydrocarbon contaminated sites the hydrocarbon originally identified by a desk study is often different when the sample is analysed and weathering often alters the basic characteristics as well. A “general purpose” calibrator is usually supplied with test kits that can lead to an unacceptable rate of false positive and false negative results.

A significant advantage of using a UV fluorescence technique is that the naturally occurring hydrocarbons from plant derived material are not detected. Vegetable oils such as palm oil, humic and fulvic acids and waxes from leaf surfaces can be “recognised” by gas chromatography methods that are routinely used in the laboratory and reported as petroleum hydrocarbons. This can cause a significant overestimation of the TPH value, especially in the C25+ range. QED does not suffer from this problem.

Quantification with QED is achieved by selecting a calibrator that most closely matches the sample fingerprint obtained. QED can store up to 6 calibration curves, allowing several hydrocarbon types to be recognised and quantified. The calibration curve is constructed using 5 different concentrations of each calibrator. The calibration is deemed to be successful if the calibration curve meets the expected r^2 value and the curve is the correct shape. The QED software monitors the calibration curve data and flags up warnings if the calibrator is incorrect. QED can also check if the calibrator has become contaminated or has degraded. During the sample analysis QED initiates a self diagnostic on every run and will flag up baseline drift, excitation source output degradation and several other possible error states to ensure the sample analysis is as good as possible. At the end of a run, QED performance is checked by running the low and high concentration calibrator to ensure the calibration data is still the same as at the start of the analysis.

The hydrocarbons found on site are often a mixture of types. A fuel station may be contaminated with petrol and diesel and an industrial site with heating oil and lubricating oil. QED can be used to resolve the hydrocarbon mixtures to provide a more realistic quantification of the hydrocarbons present. The QED software can be used to overlay over the sample fingerprint a standard fingerprint for the various hydrocarbon types expected on site

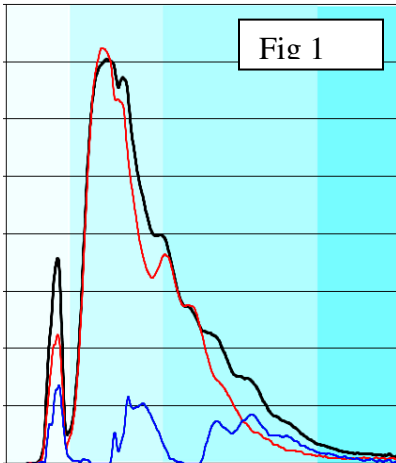


Fig 1 shows a sample fingerprint (black line) with a typical #2 fuel oil fingerprint (red line) overlaid. The blue line is the residual hydrocarbon remaining after the #2 fuel oil hydrocarbons have been subtracted from the sample hydrocarbon. The residual hydrocarbon is quantified as PAH.

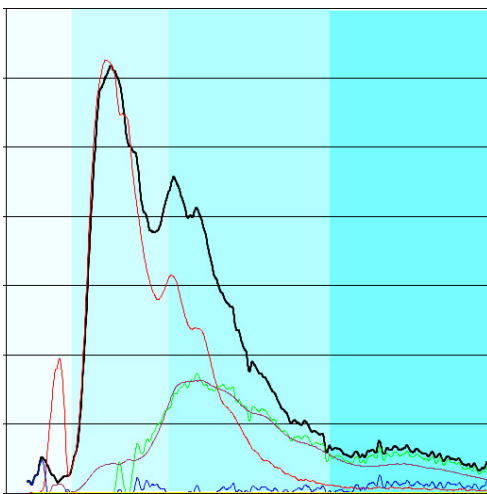
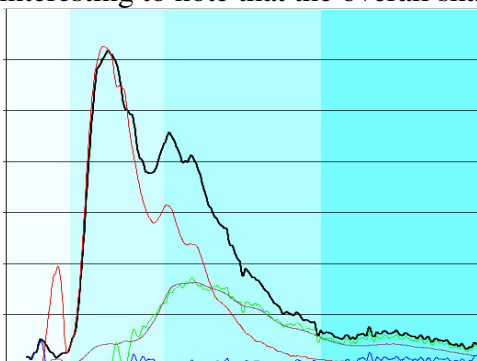
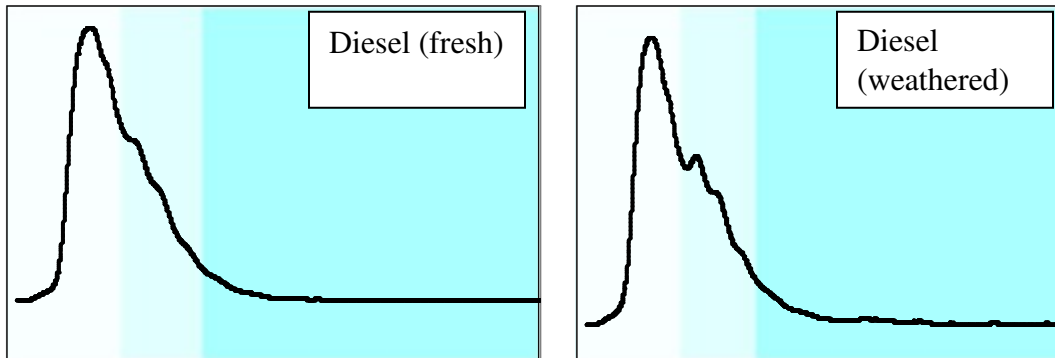


Fig 2 shows a black sample trace that has been overlaid with a #2 fuel oil fingerprint (red trace) leaving a green residual trace. A heavy oil fingerprint (purple) matches the green trace leaving a blue trace as the residual hydrocarbon. The #2 fuel oil proportion is calibrated with a #2 oil type calibrator and the heavy oil with a heavy oil type calibrator. The 2 values are added together to give a total TPH value. This technique identifies the sample as a mixture and applies the correct calibration.

Fig 2

The fingerprint can also show how much weathering may have taken place. The trace below shows the difference between fresh diesel and diesel that has lost 80% of its original mass through weathering. It is interesting to note that the overall shape of the fingerprint remains the same, demonstrating the utility of the





The traces show subtle differences and these differences can be quantified and used to approximate the amount of weathering the hydrocarbon has experienced. The quantification algorithms will factor this in when generating the results. The coloured bands in the fingerprint traces indicate the approximate position of the carbon numbers. The lightest band shows compounds in the C6 – C10 range, the mid band the >C10 – C18 and the darkest band >C18+. The results report these parameters as percentages of light, mid and heavy hydrocarbon.

The above techniques can be used to identify the hydrocarbon type and to quantify it as TPH, DRO, GRO or total BTEX, depending on the hydrocarbon type found. The detection limits are approximately 0.1 mg/kg for DRO, TPH and GRO and 0.25 mg/kg for BTEX

The QED detects most petroleum derived aromatics, so can also quantify PAHs, providing a sum of the 16 target PAHs as well as a total PAH (equivalent to the aromatics EPH) value. The algorithms used can also derive a Benzo-a-Pyrene value that correlates with conventional laboratory analysis.

The detection limit for total PAH is approximately 0.05 mg/kg.

Analysis Protocol for QED

Approximately 10g of a soil sample is accurately weighed into a sample jar containing 20ml of high purity Methanol. The soil weight is recorded in the QED software. The soil sample is vigorously shaken until the soil particles have been dispersed in the methanol. Clay samples may require the use of a field shaker to disperse the clay. The sample is allowed to settle, or if the particulate is too fine to settle, is filtered to produce a clear extract.

QED is calibrated by running the appropriate calibrators. The hydrocarbon fingerprint for the samples can be obtained by running a diluted sample in QED before calibration in order to select the appropriate calibrator types.

Calibration requires a baseline to be measured using a dark blank. The dark is placed in QED and the dark measurement button pressed. A measurement is made and the dark is stored. The calibrator type is selected in the software and the 5 calibrators are then measured. The software checks the validity of each calibrator and constructs a calibration curve for that calibrator. The calibration is successful if the r2 is better than 0.95 and the curve shape correct for the hydrocarbon type. A graph showing the calibration curve and the variation from the QED HC-1 Analyser



predicted values are shown. If the calibrator gives an incorrect predicted value, a red warning shows. It is possible to re-run the calibrator to confirm if an error has been made. If the new run is successful the red warning is removed. It is possible to run and store 5 more calibration types, but typically just BTEX, PAH and TPH calibrations are made. Custom calibrations are also possible.

A solvent blank is measured before the sample is analysed. At least 3ml of the methanol used for extraction and dilution is placed in QED and measured. If a blank is not measured before a sample is analysed, the software will call for a blank to be measured. Between 50 microlitres and 3ml of the sample extract is either placed directly into QED or diluted into clean methanol before measurement. The total volume placed in QED should be above 3ml. The volumes used to make the dilutions are entered into the software. Values for soil weights, extraction and dilution volumes are checked to ensure they are within range. An unexpected value will cause a red warning to show. An expected value shows green.

The analyse sample button is pressed and QED will measure the extract within a few seconds. A fingerprint will show on the software. If the fingerprint falls between the green and red line in the fingerprint window, the dilution is correct. If the highest point of the fingerprint is above the red line, the sample is too concentrated and should be diluted and measured again. If the highest point is below the green line, the extract should be concentrated if any dilutions had been made.

The quantification parameters should be set. The various library fingerprints stored in QED can be selected and matched to the sample fingerprint. It may require 2 hydrocarbon types to obtain the best matches. Once the best matches have been selected QED will retain these parameters for all subsequent samples. It is possible to set parameters for each sample individually if required.

Providing the sample gives a fingerprint within the correct range and that the quantification parameters have been set, QED will calculate the hydrocarbon concentration in the sample. The ratio data will also be provided.