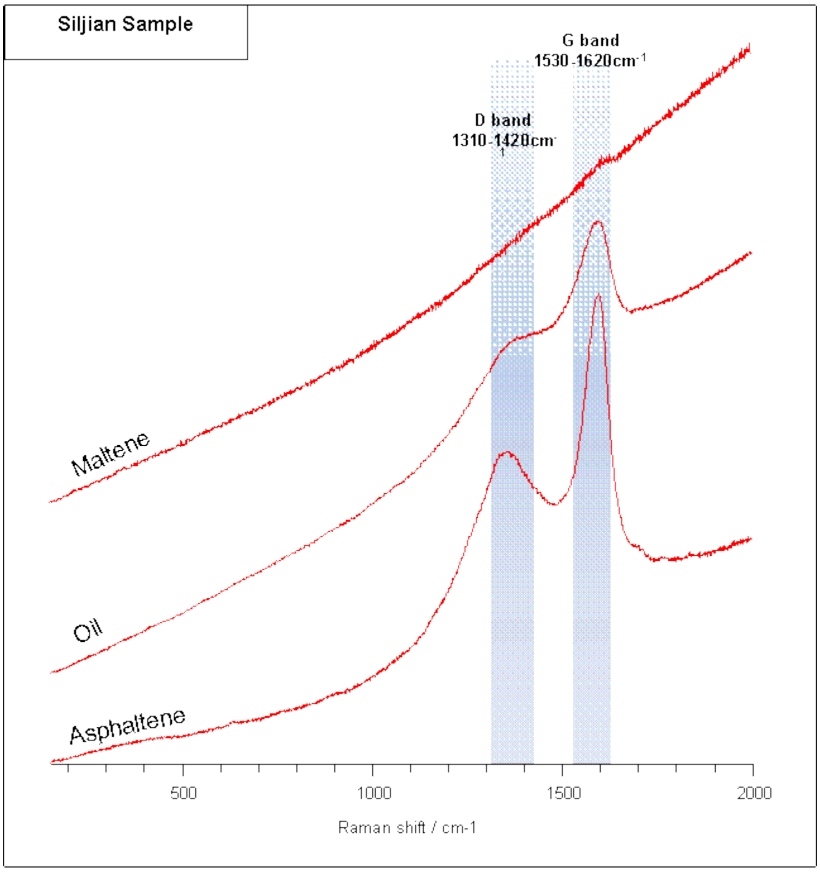
Electronic Supplementary Information 1 – Unprocessed Spectra illustrating fluorescence

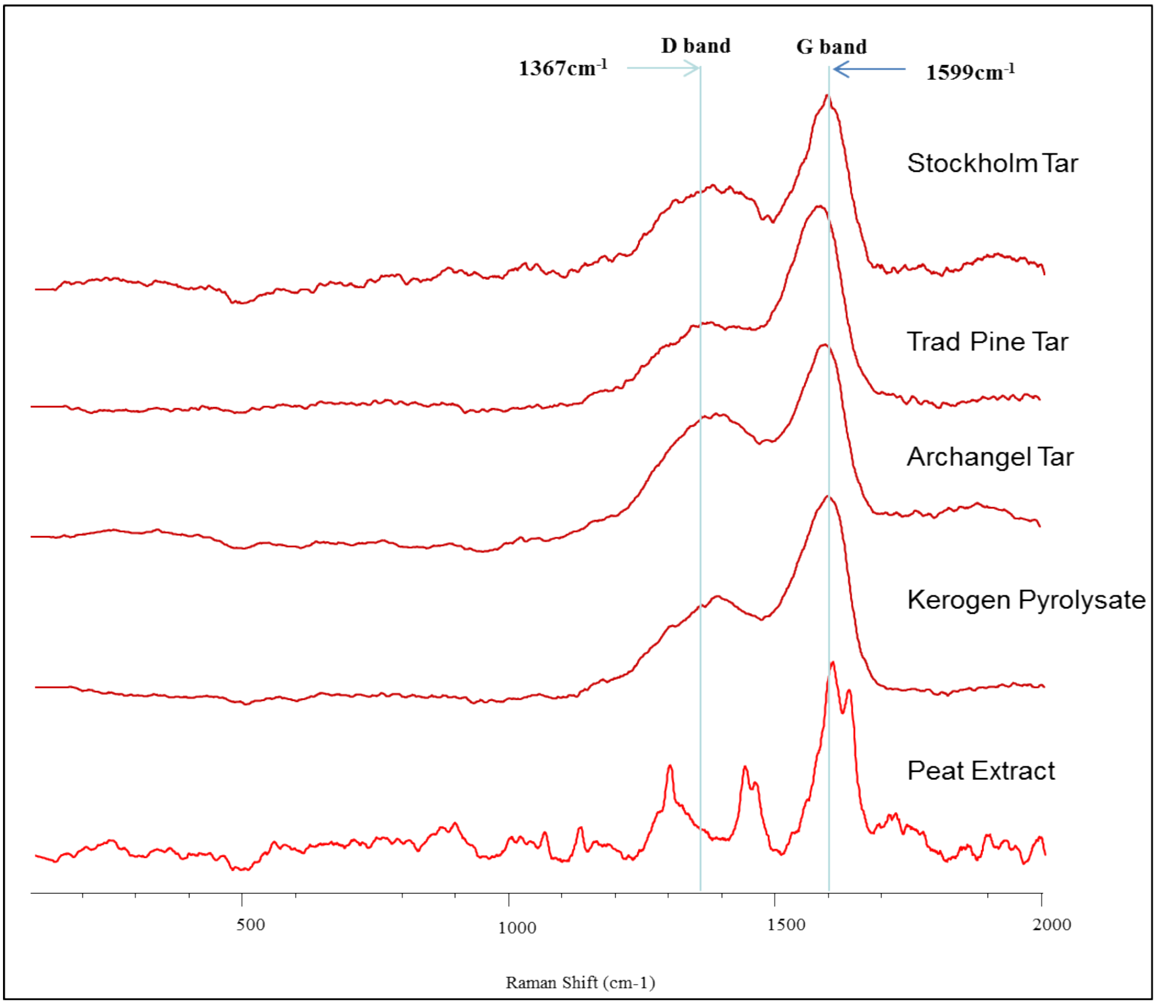


Fluorescence is a common component of the Raman spectra of petroleum, coal and related materials. For the above example it can be seen that asphaltene fraction fluoresces least and the maltene fraction the most. The effects of fluorescence can be overcome by subtracting a background value. However this can lead to numerical artefacts such as alterations to the apparent Raman shift of peaks and bands.

Electronic Supplementary Information 2 - Analysis of structurally related materials

Asphaltenes are the highest molecular weight component of liquid petroleum, produced when fossil organic matter undergoes pyrolysis in the subsurface as sedimentary rocks are buried. There are other carbonaceous materials that are structurally related to asphaltenes found in the heaviest fractions of tars produced when lignin-like materials are pyrolysed or partially combusted. Wood-tars are manufactured by pyrolysing resinous wood from pine trees such as *Pinus sylvestris L.* A similar material is the pyrolysis-tar generated by retorting of oil-shale to artificially produce petroleum. During this study it was found that the surface enhanced Raman spectra of both of tar-types is very similar to petroleum in that the main features are Raman bands at 1367 and 1599 cm^{-1}.The main difference between both of these materials and other petroleum tar and oil samples analysed in this study is the tendency for the D-band to be broader and more pronounced relative to the G-band.

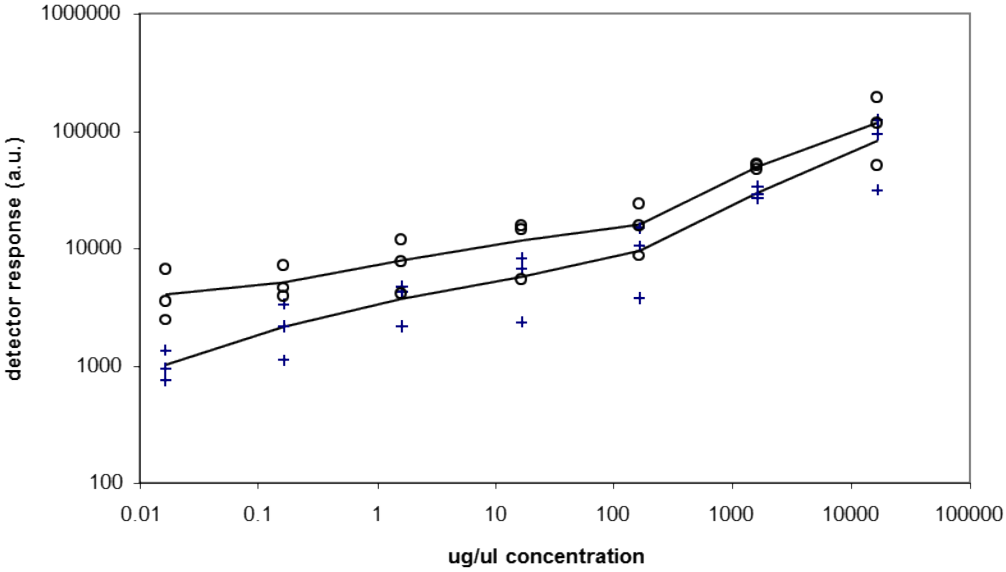
The analysis of humic acids presents similar challenges to those of asphaltenes and heavy tars: humic acids comprise large high molecular weight molecules, with aromatic elements in their structure that are poorly soluble in a range of solvents. Solvent soluble humic material was obtained by solvent extracting peat, which yielded an extract with a surface enhanced Raman spectra exhibiting bands at 1300 cm^{-1}, a doublet centred around 1450 cm^{-1} and another doublet centred around 1600 cm^{-1}. The surface enhanced Raman spectra is similar to that reported by (Vogel et al 1999) and that of chryrsene in that individual bands are generally sharp rather than borad (as seen with asphaltene).



S1 Surface enhanced Raman spectra of materials acquired using method described in text. These materials (wood tars, oil shale pyrolysates and peat extracts) are held to be structurally related to asphaltene and yield similar SERS spectra.

Electronic Supplementary Information 3 – Detection limits for asphaltene

Asphaltene fractions were prepared using the procedure described in ASTM D4124. The asphaltene fraction of petroleum is a solid precipitate formed when oil is diluted with an excess of *n*-alkane solvent or the solid residue remaining after lighter components have been evaporated (Speight 2014). Conventional oil typically contains only a few percent of asphaltene, but none the less this small quantity can form problematic precipitates capable of fouling infrastructure or forming blockages in pipelines (Speight 2014). This alone makes the direct detection of asphaltene useful for many petrochemical-related issues. Furthermore, because highly asphaltic materials are resistant to biological and chemical degradation they are also commonly encountered in other natural science fields; asphaltenes form the undegradable dense non-aqueous phase contaminant of oil spills and are abundant in naturally occurring bitumen seeps and tar-sand deposits found at the surface (Conan 1984). Additionally, asphaltene-rich bitumen is a resistant material with a long history of human exploitation and therefore an important archaeological material (Ref). Therefore, while other volatile components within petroleum are easier to characterise, the direct detect of asphaltene, aside from the detection of trace amounts of petroleum is useful for many applications.



S2 Detector response for alliquots of Siljian-asphaltene adsorbed onto SERS-substrae. Data are shown for triplicate measurements.

References for Supplementary Information Section

ASTM D4124., 2000. Standard Test Method for Separation of Asphalt into Four Fractions, American Society for Testing and Materials, West Conshohocken, PA.

J. G. Speight, The Chemistry and Technology of Petroleum, 5th edn, Taylor and Francis group, Florida, 2014.

Vogel, E., Geßner, R., Hayes, M.H.B., Kiefer, W. Characterisation of humic acid by means of SERS (1999) Journal of Molecular Structure, 482-483, pp. 195-199.

Bowden, S.A., Farrimond, P., Snape, C.E., Love, G.D. Compositional differences in biomarker constituents of the hydrocarbon, resin, asphaltene and kerogen fractions: An example from the Jet Rock (Yorkshire, UK) (2006) Organic Geochemistry, 37 (3), pp. 369-383.