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Asphaltene detection using Surface Enhanced Raman Scattering (SERS)

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Surface enhanced Raman spectroscopy using a gold substrate and excitation at 514 nm can detect sub parts per million quantities of asphaltene and thereby petroleum. This simple format and sensitivity make it transformative for applications including sample triage, flow assurance, environmental protection and analysis of unique one of a kind materials.

Asphaltene is a solid precipitate or residue obtained by chemically-separating or distilling petroleum. In conventional oils it is present in low proportions relative to liquid and solid hydrocarbons. However, there are many instances where asphaltene constitutes a far greater proportion of petroleum: this includes naturally occurring oil seeps and manmade oil spills, blockages in pipelines and other infrastructure and heavy oil deposits such as Tar Sands. Asphalt and bitumen occurs widely in nature and has a long history of human use as a sculpting-media that can be easily shaped, a component compounded in medicine and adhesives and a resistant waterproof material. To those working outside the field the need for a sensitive method to detect trace quantities of asphalt and asphaltene, a commonly occurring material literally paving the streets, may be surprising. However, asphaltenes and related materials are by their nature non-volatile and chemically inert which makes the detection of trace quantities difficult. This creates a significant barrier to studying asphaltene in non-petroliferous natural systems at the organismal, ecological and even geological scales. Thus the only other approach to analyse low concentrations of asphaltene remains the use of Fourier Transform – Ion Cyclotron Resonance Mass Spectrometry (FT-ICRMS). Here we demonstrate that surface enhanced Raman spectroscopy (SERS) provides an additional method to detect low concentrations of asphaltene and thereby petroleum.

Raman spectroscopy using a green monochromatic light source has proven to be a powerful tool for characterising fossil organic matter and biological pigments in rocks and sediments. Much of the power of the technique derives from the ease with which it can be applied to different sample matrices with minimal sample processing. However, when the organic component of interest fluoresces or is present at extremely low concentrations these advantages are greatly reduced. In these situations clear Raman bands can not be identified and the characterisation and detection of the analyte is no-longer possible. Liquid fossil fuels represent a case in which both of these limiting criteria can apply – the strongly Raman active component, thought to comprise condensed aromatic nuclei, is a very small component of a conventional oil the fluorescing component greater leading causing the weaker Raman signals to be swamped. These issues are then compounded when there is only a small quantity of a sample available and the strength of any potential Raman signal further lowered. Thus while it might be desirable to apply Raman spectroscopy to the analysis of liquid-petroleum, it has infrequently been reported or repeated in comparison to the application of Raman spectroscopy to solid fossil fuels such as coal.

Surface enhanced Raman scattering (SERS) is achieved when an analyte interacts with a surface plasmon, supported on a roughened metal surface. Using a silver substrate (both silver coated beads and silver colloid) to achieve the SERS-condition previous workers reported great enhancements for molecules that are structurally related (e.g. tetraporphyrins and the PAH within hemic acids) to the larger high molecular weight and aromatised compounds found within petroleum. Thus across a range of analytical fields SERS has to come to the fore but has yet to be reported for liquid-petroleum and asphaltene.

Using a conventional Raman Microscope, a 514 nm light source and a sputter coated gold-SERS substrate we were able to detect petroleum and asphaltene at concentrations less than 50 ppm – greatly exceeding previous limits of detection for asphaltene. Full details of the method used are provided. Surface enhanced Raman spectra are shown for samples of asphaltene and whole-oil (Fig. 1, samples are described in footnotes). The key features of the spectra are broad Raman bands centred at 1367 and 1599 cm⁻¹. For comparative purposes
conventional Raman spectra are shown for samples of coal and kerogen that also have similar broad Raman bands centred at 1367 and 1599 cm⁻¹. To some extent a similarity between the surface enhanced Raman spectra of petroleum-asphaltene and kerogen would be expected as asphaltene has long been held to share structural similarities with kerogen and coal macerals—a core or nucleus comprising a condensed aromatic nucleus surrounded by covalently bound aliphatic moieties.

The absence of Raman bands at 1367 and 1599 cm⁻¹ when either the gold-substrate or asphaltene is absent (necessary conditions for SERS) is consistent with a genuine surface enhancement of an asphaltene-Raman response by many orders of magnitude. The inset of Fig. 1 displays surface enhanced Raman spectra for whole oil and maltene fractions (a deasphalted sample of oil). It is notable that bands at 1367 and 1599 cm⁻¹ are absent from the spectra of maltene fractions (deasphalted oil), even when the quantity of analyte is increased tenfold; whereas bands at 1367 and 1599 cm⁻¹ significantly increase in intensity when the concentration of whole oil is increased. This strongly indicates that it is the asphaltene fraction that is responsible for the bands at 1367 and 1599 cm⁻¹.

Previous workers have noted that lipid-pigments and humic materials that fluoresce sufficiently to mask the diagnostic bands and peaks of conventional Raman spectra yield surface enhanced Raman spectra with clearly resolved peaks. In this study it is notable that the surface enhanced Raman spectra of the whole-oil exhibited D and G bands that were Raman shifted in a manner consistent with the super-positioning of the broad D and G-bands (observed for an asphaltene-isolate) onto the fluorescence dominated signal generated by the maltene fraction (see S1). Thus while the current assay appears to have increased the relative strength of key Raman bands (relative to the fluorescence background), this is not to the extent previously reported for comparable naturally occurring materials, where fluorescence was more effectively quenched.

Fossil fuel scientists, meteorite petrographers and geologists applying conventional Raman microscopy to solid carbonaceous materials (kerogen) within rocks and sediments attribute the first order Raman bands occurring at ~1585 and ~1350 cm⁻¹ to the different vibrational modes of condensed benzene-like rings. These aromatic structural-units contain variably disordered sp² carbons and give rise to varied aromatic C-C ring-stretching. The broad Raman band between 1350–1380 cm⁻¹ (termed the D-band) corresponds to the vibrational mode of a disordered graphitic lattice with an A₁g symmetry. It is thought to arise from heteroatom-containing units or other defects in graphene-layer carbon atoms that are located in close proximity to lattice disturbances. The Raman band between 1580–1615 cm⁻¹ corresponds to the in-plane vibration of aromatic carbons in carbonaceous materials that at some level have a graphitic structure, and a vibrational mode with an E₂g symmetry. Despite the existence of this considerable body of work for interpreting Raman spectra in solid fossil fuels, we also looked to standard compounds to further interpret data.

The surface enhanced Raman spectra of pyrene corresponds reasonably well to that previously published for pyrene, e.g. three diagnostic peaks obtained at Raman shifts of 1406, 1594 and 1630 cm⁻¹. However, a visual inspection of the surface enhanced Raman spectra of several PAH (Figure 2, see footnote for description of samples and materials) reveals key differences between the surface enhanced Raman spectra of asphaltene and PAH standards investigated. This includes the higher ring number PAH presented here and those from other work. The key differences between the surface enhanced Raman spectra of the PAH and petroleum are the number and position of peaks that fall within the Raman-shift range of the broad bands centred at 1367 and 1599 cm⁻¹; typically two or more individual peaks are resolved within the Raman shift range of the D and G bands. Thus while it is likely that similar PAH generate the bands at 1367 and 1599 cm⁻¹, no single PAH can easily be suggested to be responsible for the surface enhanced Raman spectra observed for asphaltene.

Samples of wood-tar (tar produced by artificially pyrolysing resinous-wood), hydro-cracked kerogen, and peat-extract, materials that are structurally related to asphaltene, were also investigated. The key differences between the surface enhanced Raman spectra of these materials (excepting the peat extract) and those of the asphaltene spectrum reveal.
...petroleum was the relative intensity of the D and G Raman bands (See S2 and ‡ for description of samples); the D Band was typically broader and of proportionally greater height.

The surface enhanced Raman spectra of liquid and solid petroleum is dominated by the asphaltene fraction and the spectra likely reflect the same vibration modes (varied C-C ring stretching) observed in larger PAH and structurally related carbonaceous materials. When analysing asphaltene by SERS low amounts can be detected, and the effects of fluorescence greatly reduced. In comparison to FT-ICRMS methods a SERS-asphaltene assay, although providing little in terms of molecular characterisation, would be better suited to sample triage and limit-tests. Furthermore, because the analytical equipment required is more common place, the assay is easy to perform and would be within the capabilities of many non-specialised laboratories and has far greater potential for miniaturisation, something that current technology is unlikely to achieve for FT-ICRMS.

A thousand fold increase in the limit of detection for asphaltenes and related materials facilitates analyses of one-of-a-kind or rare materials – examples of this could include meteoritic and archaeological samples, samples that can’t be replaced or repeated. However, the potential impact goes beyond the analytical sciences by increasing the analytical window for the most recalcitrant fractions of petroleum. Asphaltene is the undegradable fraction of petroleum, but it is unreasonable and unlikely that this “undegradable” fraction of petroleum persists indefinitely. What happens to these low concentrations of asphaltene is still poorly understood because of the difficulties inherent in assaying low concentrations, as aside from FT-ICRMS\textsuperscript{5,12}, few methods exist that can work with the low quantities of analyte found at background levels. Similarly the effect of low concentrations of asphaltene-like materials in ecological and living systems is not currently known, although based on current knowledge of the carcinogenic effects of smaller PAH found in tobacco\textsuperscript{22} and wood tars, asphaltene-like compounds that contain large PAH covalently bound within their core should be of interest.

Relative to FT-ICRMS, SERS is far more readily adapted to point of need deployment and monitoring, with the measurement of PAH in seawater amongst the most pertinent demonstrations of SERS-based systems for environmental monitoring\textsuperscript{20,23}. The broad use of flow-cells and lab-on-a-chip equivalents indicates that flow assurance monitoring for petrochemical applications should also be feasible\textsuperscript{24,25,26}. An easily and also widely applied SERS method capable of detecting very low quantities of asphaltene and heavy petroleum helps address these issues, not only increasing limits of detection, but increasing the availability of analyses and broadening the pool of scientists that can make them.

Notes and references

\textsuperscript{a} Geosciences, University of Aberdeen, Aberdeen, AB24 3UE, Scotland. 
\textsuperscript{b} Dept. of Conservation and Scientific Research, the British Museum, Great Russell Street, London WC1B 3DG, UK. 
\textsuperscript{† Method:} A SERS-substrate was produced by sputter coating sodalime glass slides with gold using an ES 5000 sputter coater. Gold sputter coating was performed for 5 minutes and created a layer less than 1 \textmu m thick. Prior to sputter coating the sodalime glass slide was prepared by drilling pits to serve as sample wells ~ 5 mm deep and 5 mm in diameter with a conical cross-section. Slides were cleaned by sequentially sonication in distilled water, acetone, methanol and dichloromethane (DCM) in an ultrasonic bath. A known volume (4 \textmu l) of DCM containing the dissolved asphaltene or dissolved oil was introduced in small increments into the gold-coated sample-wells. Introducing samples as small increments allowed the solvent to evaporate under ambient conditions until the entire volume had been loaded. When the solvent had evaporated 4 \textmu l of dilute nitric acid (1 M concentration) was dispensed
into the pit and allowed to stand for ~ 2-3 minutes. The aqueous phase remaining within the pit was then removed to aid focusing the microscope on the base of the pit.

Raman Spectroscopic measurements were performed on a Renishaw inVia reflex Raman spectrometer at the University of Aberdeen. Using a 50× objective a Leica DMLM reflected light microscope was used to focus the Ar+ green laser (wavelength 514.5 nm) on the solid samples and the lowest points of the gold-coated pits. Spectra were collected by accumulating 20 spectra over 20 seconds and spectral acquisition was in the range 200-2000cm⁻¹. Laser spot size was approximately 1-2 µm and laser power was 50% (<13 mW delivered to the sample). This laser power was chosen based on its ability to yield reproducible results. However, there is the potential for high laser powers to thermally alter samples, by combusting or pyrolysising involatile hydrocarbons. Cyclisation and desaturation could create aromatised products with grapheme-like structures. In the worst case this would form graphic materials (with D and G-bands) from non-aromaticised precursor materials such as saturated hydrocarbons. Overall the lack of strong D and G bands in the surface enhanced Raman spectra of the Maltene fraction (Fig. 1. and S1) suggests this has not occurred. An awareness of this issue makes it harder to definitively interpret increasing band-broadening as a function of ring number. For example the broad D and G bands of peyrene, with their riding-doublets could reflect the surface enhanced Raman spectra of a small PAH with a proto-graphitic lattice, a chrysene-like spectra thermally altered to produce D and G bands or a standard with low concentrations of SERS-amenable impurities.

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<td>Table 1 Samples used during study</td>
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<td>Sample</td>
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<td>Petroleum</td>
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<tr>
<td>On-shore Niger delta</td>
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<td>Alwyn, North Sea</td>
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<td>Wytch Farm (Sherwood Producer)</td>
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<td>Pyrolysates</td>
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<td>Kiln Pine Tar</td>
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Coal and petroleum samples were obtained from reference collections at the University of Aberdeen. Samples of tar Sand and peat were extracted by sonication in dichloromethane (DCM) and afterwards processed as samples of oil. Oil samples were deasphalted using ASTM D2414 and the proportion of asphaltene determined gravimetrically and the asphaltene precipitate used for SERS. Samples of wood-tar and Kerogen pyrolysate were from personal collections held by SAB and RS (Table 1). Three standards; coronene, chrysene, and pyrene were obtained from Acros Organics while peyrone was obtained from Merck.

Electronic Supplementary Information (ESI) available: [S1 Unprocessed Surface enhanced Raman spectra illustrating the effects of background fluorescence; S2 Surface enhanced Raman spectra of materials structurally related to asphaltene; pyrolysates and peat extracts; S3 Calibration data for SERS analysis of Asphaltene precipitated from Silijan Oil] See DOI: 10.1039/c000000x/