Assessment of UV-Raman for analysis of petroleum inclusions

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Detection of hydrocarbon components in fluids or solids is useful for investigation of the petroleum potential of a basin. For this purpose, FT-IR or Raman spectrometry techniques are the two most commonly used methods for analysis of fluid inclusions. Raman spectroscopy offers a laser spot size of 1 to 2 micrometers which allows work at the scale of individual phases in a fluid inclusion. However, using visible excitation, fluorescence of aromatic compounds precludes analysis of petroleum-bearing fluids because fluorescence emission is orders of magnitude more intense than Raman scatter. Aromatic compounds present in oil and gas fluoresce in the UV, visible and near-infrared, depending on the excitation wavelength and the number of aromatic rings. Benzene is the smallest aromatic molecule and its fluorescence emission maximum is at the shortest wavelength of the aromatics at about 280 nm. In order to avoid fluorescence, UV-Raman uses short wavelength excitation from a frequency-doubled argon ion laser at 244 nm, below the fluorescence maximum of benzene. A Raman band at 3000 cm^{-1} relative to excitation at 244 nm has an absolute wavelength of 263 nm. UV-Raman scatter can be detected between the excitation wavelength and the wavelength of fluorescence emission. This work examines the potential offered by UV-Raman for analysis of petroleum inclusions. We present spectra acquired on pure paraffinic oils and on petroleum inclusions (oil and condensate).

Pure paraffinic oil contains exclusively *n*-alkanes. Its spectrum (Fig. 1A) shows typical C-H bands with two dominant groups, one between 1550 and 750 cm^{-1} and the other between 2600 and 3150 cm^{-1}. They represent C-C stretching, bending and twisting bands and C-H stretching bands, respectively, with additional features from Fermi resonance. The spectrum of oil in a paraffin-rich natural oil inclusion (Fig. 1B), enclosing a solid

wax phase at 20 ºC (T_m= 66 ºC), shows a main band at around 1610 cm^{-1}, two bands at 1380 and 1435 cm^{-1} and a minor band at 1230 cm^{-1}. Two wide bands with low intensities are located at about 2925 and 3210 cm^{-1}.
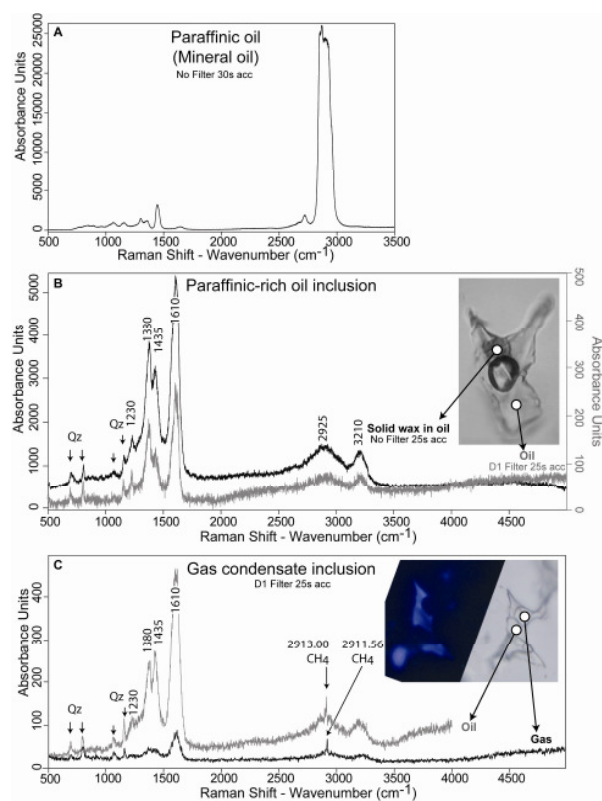

Fig. 1. *(A) UV-Raman spectra of paraffinic oil (mineral oil), (B) of oil and wax in oil inclusions and (C) of oil and gas phase in a gas condensate inclusion.*

The main differences observed between oil and wax in the oil is the ratio between the 1380 and the 1435 cm^{-1} bands and the increasing intensity of the baseline at high wavenumber. None of the C-H vibration Raman bands observed in the pure paraffin oil are present in the oil inclusion spectra. The spectrum of a rim of oil in a gas condensate inclusion (Fig. 1C) is very similar

to that of the paraffin-rich natural oil inclusion (heavier oil). Once again the 1380/1435 ratio is different. The dissolved CH_4 peak is visible at 2913 cm^{-1}. The gas phase (Fig. 1C) has a smooth spectrum with wide peaks at about 1400, 1610, 2925 and 3210 cm^{-1}. The vapour CH_4 peak is also clearly identified, this time at 2911.5 cm^{-1}. All the bands observed in the petroleum inclusion spectra, except methane and quartz, can be attributed to vibration of graphite in ordered and disordered forms. It appears that those vibrations mask all CH or C=C bands produced by hydrocarbon molecules. Since the ordered/disordered carbon bands are not present in the pure paraffinic oil, those are interpreted to be related to the aromatic/resin/asphaltene molecules present in natural oil.

Fluorescence of inclusion oils was measured using UV-Raman. Heavy oil (1), light oil (2) and two-phase trapping gas condensate inclusions (3 and 4) were used (Fig. 2a, b, c). The spectra were recorded between 250 and 650 nm using low laser power (D1 filter) and a 2400 grooves/mm grating displaying an approximate 10 nm window. Each wavelength window was collected once for 1 second. During acquisition the signal intensity in consecutive windows changed (increase or decrease) in the 300-450 nm area, but the general shape of the spectrum was preserved. All the spectra (Fig. 2) show periodicity in the baseline probably due to filters in the system.

Fluorescence of the heavier oil shows a symmetric low intensity spectrum with a maximum at about 405 nm (1, Fig. 2). The light oil produces a higher intensity spectrum with a maximum at about 385 nm (2, Fig. 2). The liquid in the liquid-rich gas condensate inclusion homogenizes to liquid (vapour volume fraction of 10 % at 20 ºC) and produces a spectrum similar to the light oil from the oil zone but its intensity is less than half and the maximum intensity is at about 375 nm (3, Fig. 2). The oil phase present as a rim in the gas-rich gas condensate inclusion homogenizes to the gas (vapour volume fraction >60 % at 20 ºC) and shows a low intensity left-skewed spectrum with a maximum intensity at 340 nm (4, Fig. 2). The gas-rich and the oil-rich spectra of the two-phase trapping assemblage are similar up to 340 nm. Above this wavelength, the oil-rich signal is more intense. This means that their low-weight aromatic compositions are similar and the oil-rich inclusion is enriched in medium to heavy-weight aromatic molecules. Similarities of the spectra of the oil-rich gas condensate from the gas zone and the light oil from the oil zone indicate a similar overall composition.
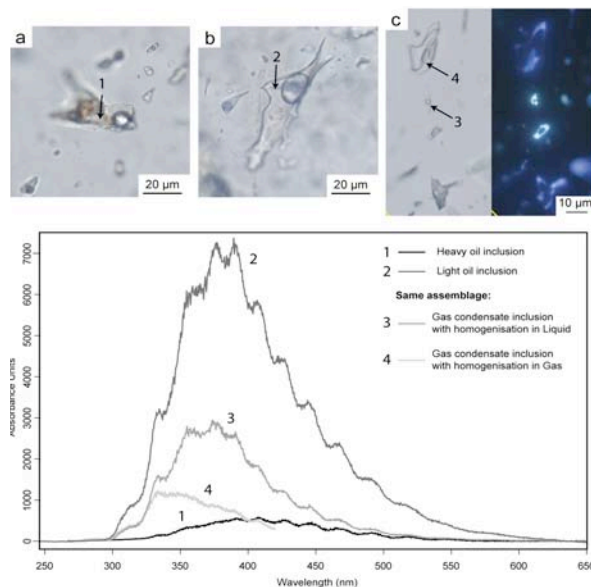

Fig. 2. *Fluorescence spectra of petroleum inclusions using UV-Raman (244 nm). Photomicrographs shows the petroleum inclusions used to measure fluorescence spectra. Oil inclusions in photos a and b are from the oil zone, while oil and gas inclusions on photo c are from the gas-zone in the same reservoir.*

During the Raman scatter spectra acquisition (D1 filter, 25s, 2 acc) a brownish spot formed that fluoresces with an orange colour (observed subsequently with a 365 nm UV lamp). A slight red-shift of the whole inclusion fluorescence colour of the heavier oil inclusions has been noticed following laser irradiation. This suggests that irradiation of petroleum inclusions with focused 244 nm laser light causes some photochemical alteration of the inclusions.

Detection of Raman bands of hydrocarbon molecules in oil inclusions using a 244 nm laser are masked by carbon bands related to molecules containing aromatic rings. Methane has been detected in gas-rich inclusions. The 244 nm laser produces a fluorescence spectrum that can be used to characterise oils.