Analysis of channel sample in thin section by Raman spectroscopy images

Análisis de muestra de canal en lámina delgada por medio de imágenes de espectroscopía Raman

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This research contributes to the science and technology of materials characterization for the analysis of channel samples from the oil industry, currently using thin films for detailed description with petrographic microscopy, our work is based on using Raman spectroscopy techniques to create images of Raman spectra. Key aspects include understanding the Raman spectroscopy method and the use of thin films in studies of hydrocarbon-bearing rocks. The use of petrographic microscopy and Raman spectroscopy simultaneously allowed detailed spectra of the channel sample to be obtained.

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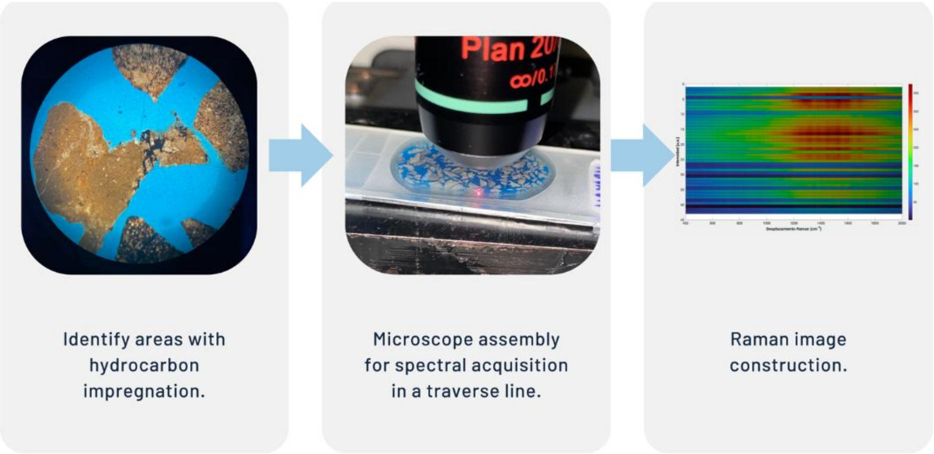
Abstract

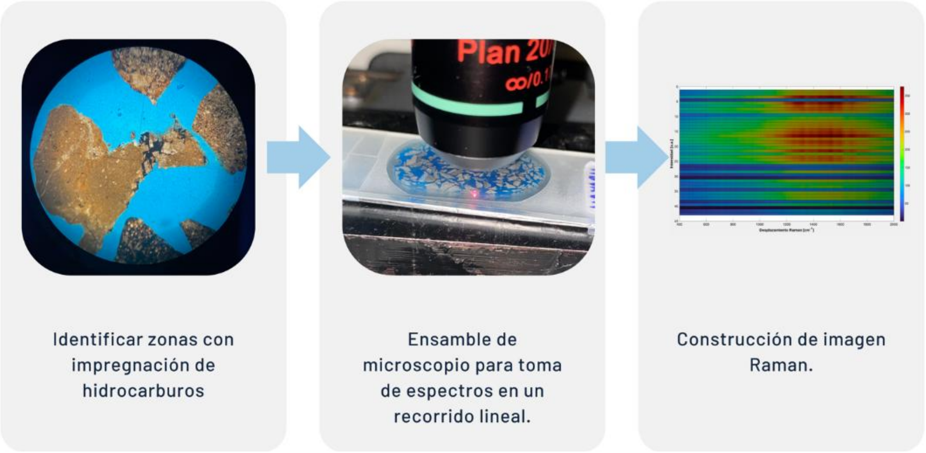
Micro-Raman spectroscopy is an innovative technique for the characterization of hydrocarbon source rocks, specifically in the analysis of core samples in thin sections. This methodology employs an infrared laser that interacts with the molecules of minerals and organic matter, allowing for simultaneous optical imaging with the petrographic microscope and Raman spectrum. In this work, preliminary results of Raman spectra recorded along a line drawn on a thin sheet of a channel sample are presented, using a QE65000-Ocean Optics spectrometer with a spectral resolution of 4 cm^{-1} and a 785 nm laser as the excitation source. To prepare the thin section, the sample is immersed in epoxy resin, cured, and polished in a specialized laboratory until a thickness of 30 µm is reached, where the Raman spectra of the G, D bands, and a carbon double bond, which is related to the organic matter and the resin of the thin section, were analyzed.



Raman Spectroscopy, Petrographic microscope, Thin section

Resumen

La espectroscopía micro-Raman es una técnica innovadora para la caracterización de rocas generadoras de hidrocarburos, específicamente en el análisis de muestras de canal en láminas delgadas. Esta metodología emplea un láser infrarrojo que interactúa con las moléculas de minerales y materia orgánica, permitiendo obtener imagen óptica con el microscopio petrográfico y espectro Raman de manera simultánea. En este trabajo se presentan resultados preliminares de espectros Raman registrados a lo largo de una línea trazada sobre una lámina delgada de una muestra de canal, utilizando un espectrómetro QE65000-Ocean Optics con una resolución espectral de 4 cm^{-1} y un láser de 785 nm como fuente de excitación. Para preparar la lámina delgada, la muestra es inmersa en resina epóxica, fraguada y desbastada en un laboratorio especializado hasta alcanzar un espesor de 30 µm, en donde se analizaron los espectros Raman de las bandas G, D y un doble enlace C=C el cual está relaciona con la materia orgánica y la resina de la lámina delgada.



Espectroscopía Raman, Microscopio Petrográfico, Lámina delgada

Introduction

The characterisation of hydrocarbon-bearing rocks requires advanced techniques to study their composition and structure at micrometric scales. In this context, the use of thin films in petrographic microscopy is a traditional technique used in the oil industry to identify the type of lithology and to analyse the chronostratigraphic age through microfossils. Raman spectroscopy instead provides an alternative to obtain detailed information on the mineral components and organic matter present in these rocks. Channel samples, especially prepared in thin films, allow the textures and mineralogical phases of the rocks to be observed under a petrographic microscope, which is crucial for identifying petrographic features that influence their hydrocarbon generation and retention capacity (Fries, M., & Steele, A., 2010).

Raman spectroscopy complements this characterisation by providing accurate chemical and structural analysis at the micrometre level. Using a laser that interacts with the molecules of the materials present, this technique detects specific vibrations that reveal the composition and internal organisation of minerals and organic matter (Ferrari & Robertson, 2000). Raman spectroscopy is a useful tool for the identification of minerals and the study of carbonaceous material, which is difficult to characterise with optical microscopy and electron beam techniques. For example, it allows differentiation between carbonaceous matter present in primary fluid inclusions, which formed when a rock first cooled from its parent material, and other carbonaceous matter located in late-phase alteration veins within the same rock (Figure 1).

Box 1

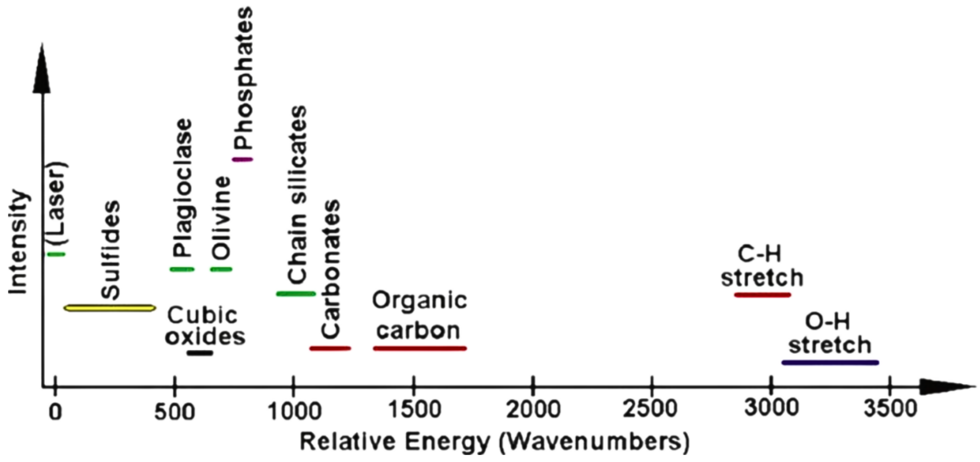


Figure 1

Simplified diagram showing the general positions of prominent Raman peaks for a variety of common rock-forming minerals and compounds

Source: [*Fries, M., & Steele, A., 2010*]

In this study, both microscopic techniques are combined to analyse channel samples prepared in thin films, assessing both their petrographic characteristics using a petrographic microscope and their molecular composition using a laser Raman microscopy system design. This integrated approach facilitates the analysis of hydrocarbon source rocks, providing essential information for understanding their reservoir potential and key geological properties (Marshall et al., 2007). The results obtained will contribute to a better understanding of the composition and structure of these complex geological systems, enhancing their analysis and evaluation in the context of hydrocarbon exploration and production.

Thin films

Thin sections or thin sections are rock samples used in petrography to study the optical properties of minerals. They are made in such a way that they are polished on both sides to allow light to pass through to observe the optical characteristics of the minerals. The film is fixed to a glass slide. According to Fries, M., & Steele, A., 2010, surface irregularities on thin sections and contamination, such as polymer mounting particles, can interfere with Raman analyses.

Surface imperfections, caused by minerals such as pyroxenes or clays, can scatter the laser excitation beam, and the materials used to create the slices can be confused with materials in the rock or sediment. To avoid this, it is recommended to examine the thin section in reflected light prior to analysis. In addition, the mounting polymer, especially in brittle materials, can be trapped in the cracks, which can make it difficult to interpret the spectra, although it can be differentiated by its spectral signature in the C-H stretching region.

Raman spectroscopy

Raman spectroscopy is a non-destructive analytical technique that provides information about the molecular structure and internal vibrations of the bonds of a material, whether liquid, solid or gas, by inelastic light scattering (Smith & Dent, 2004). When monochromatic radiation of minimum frequency passes through a transparent medium, most of it is transmitted, a fraction is absorbed and a small amount is scattered (less than 10^{-5} of the intensity of the exciting source). Most of the scattered light maintains the same frequency as the incident radiation (known as elastic or Rayleigh scattering), while a very small amount (on the order of 10^{-3} to 10^{-4} of the Rayleigh intensity) is scattered at a frequency slightly higher or lower than the incident radiation. This inelastic scattering is called Raman scattering (Jawhari, 2012).

Optical imaging with microscopy and Raman spectra

Mineralogy and petrography techniques have traditionally relied on thin-sheet optical microscopy to identify minerals and study their arrangement, which allows interpretation of the formation and alteration of these minerals and the source rock. This helps to understand the evolution of geological formations and their relationship to larger units, even inferring events such as the movement of continents. Raman spectroscopy is a useful tool in these analyses, especially for identifying minerals and studying carbonaceous matter, which is difficult to characterise with optical microscopy and electron beam techniques with SEM or EDX (Fries, M., & Steele, A., 2010).

Methodology

The methodology is presented in two parts, the first part covers the creation of the thin film at the Centro Regional de Estudios de Laboratorio Cd del Carmen of Pemex Exploración y Producción KM 4+500. And the second part is the analysis by Raman spectroscopy coupled to a Best Scope BS-5070TTR petrographic microscope adapting the Raman probe to measure the thin film of the channel sample.

Thin film of source rock

The channel sample or drill cuttings are subjected to a cleaning process in the laboratory, as they may contain water, drilling mud and/or plugs. A sample is selected at a stratigraphic level from an exploration well. For channel samples, the following steps are performed (Figure 2):

1. A representative sample of hydrocarbon-bearing rock is selected, washed until any drilling mud and pluggers it may contain are removed, oven dried at a temperature of less than 80ºC.

2. It is then sieved with a 40 and 10 mesh to obtain a homogeneous granulometry.

3. It is agglutinated in an epoxy resin to facilitate its handling. The mixing ratio of the resin and catalyst must comply with the standards to guarantee the preservation of the characteristics of the sample (3:1 ratio), it is left to set until the following day.

4. Once the resin has set, the sample is cut into a rectangular shape with a diamond saw to obtain a preliminary sheet, ensuring that the surface is flat and suitable for polishing.

5. The roughened sample is adhered to a glass slide using an adhesive that reacts with UV light. This ensures that it is firmly adhered (Solis Correa, 2023).

6. To reduce the thickness of the sample and approach the final thickness (30 µm), different grains of silicon carbide paper, usually 120, 220 and 400, are used, wetting the surface to avoid excessive heat and maintain the integrity of the sample (Casique et al., 2018).

7. For final polishing, a 600 grit aluminium oxide or silicon carbide powder is used to obtain a thickness of 30µm, ensuring optimal light transmission through the thin film during petrographic observation.

8. Finally, the thickness of the foil is checked with the BestScope BS -5070TTR petrographic microscope to ensure that it meets the 30 µm standard required for petrographic analysis (Casique et al., 2018).

Box 2

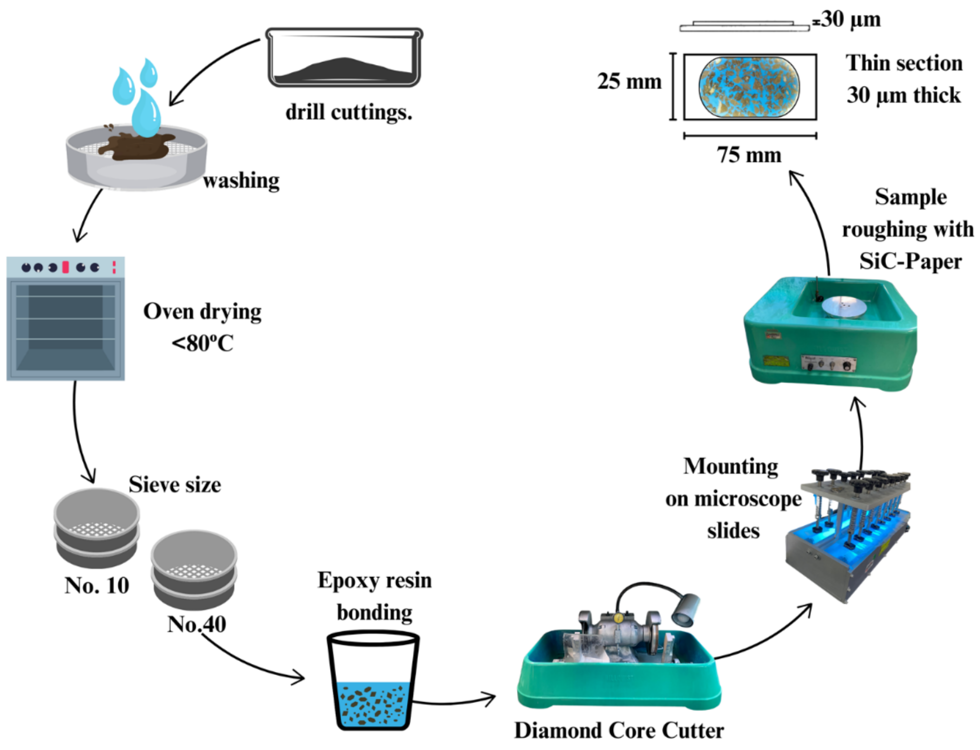


Figure 2

Methodology for the creation of a 30µm thick, thin film: Washing and drying of the sample. Sieved and impregnated in epoxy resin. Cut and mounted on slides. Deburring with SiC (Silicon Carbide) paper 120, 220 and 400 grit; final polishing with 600 grit Silicon Carbide powder

Source: [*Own elaboration*]

Design of the laser Raman microscopy system

The Raman equipment was mounted on the BestScope BS petrographic microscope of the UNACAR Optics Laboratory, as shown in Figure 3. The optical system consists of a 785 nm infrared laser module, connected to a bifurcated optical fibre, coupled to the laser and the spectrograph.

A path was delimited on the Y axis of the sample surface and the Raman spectrum was measured every 1 mm, obtaining a total of 43 spectra, the purpose of adapting the HD camera is to observe that the laser does not hit the epoxy resin. The signal is captured with the Ocean Optics QE 65000 spectrometer. The data is captured with SpectraSuite software for Windows operating systems, then the data is saved in .txt format for graphing in Matlab.

The processing was done by trimming the spectral band selection from 400 to 2000 $^{cm-1}$, for all the spectra obtained. A surface plot was made in Matlab to evaluate the maximum peaks using a colour scale.

Box 3

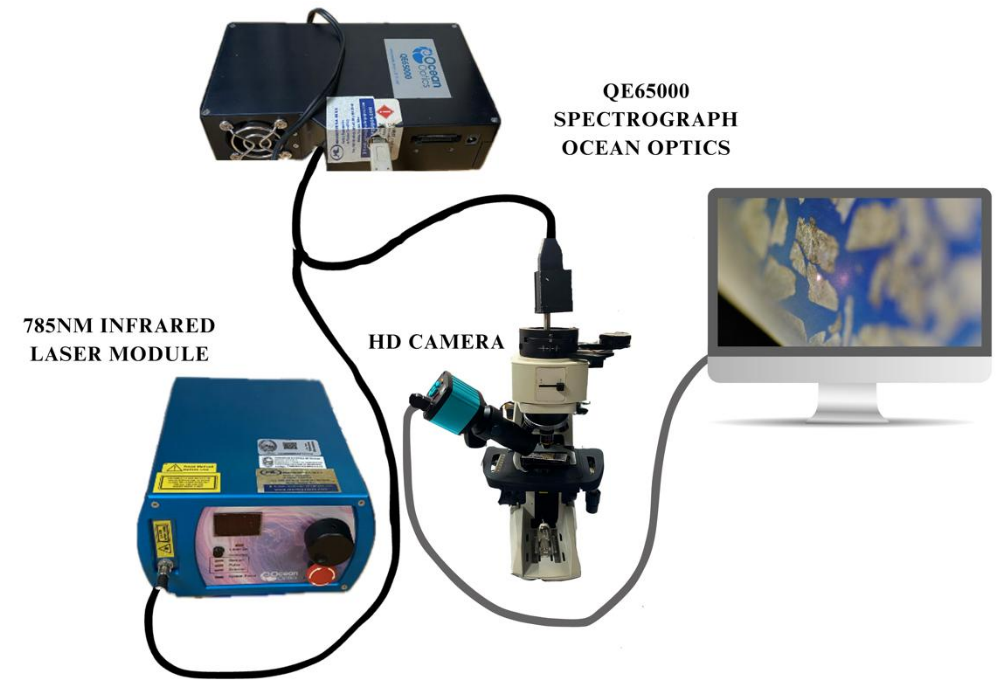


Figure 3

Adaptation of the QE65000 spectrograph to the Best Scope BS-5070TTR petrographic microscope, using a 785 nm infrared laser module with 20x objective as excitation source, and an HD camera with 4x objective to verify the laser path

Source: [*Own elaboration*]

Results

Raman spectra of a thin-film scan of the sample

The optical Raman microscopy system was developed for the simultaneous acquisition of images with the petrographic microscope and the Raman probe, which allows the reading of the data where there is no presence of epoxy resin. The data presented are from a single run of the sample, since, having a heterogeneous sample, the data are shown with high fluorescence. It is known that when analysing low concentration materials (below 1%) and materials that fluoresce or samples with fluorescent impurities, they raise the fluorescence background and interfere considerably with the Raman signal (Jawhari, 2012). This phenomenon commonly occurs in organic materials and certain compounds.

The Raman bands identified were as follows:

Quartz: ~450- $^{462\text{cm}^{-1}}$ (Rutt, H. N., & Nicola, J. H., 1974), (Ostroumov et al., 2002).

Carbonate: $^{\sim 1415\text{-}1437\text{cm}^{-1}}$ (Band C) (Hernando Alonso et al., 1937).

Carbon: ~1350(Band D) and ~1600 $^{\text{cm}^{-1}}$ (Band G) (Myers, G. A., Kehoe, K. K., & Hackley, P., 2017), (Lambrecht et al. 2021).

Silicon: 520.4 $^{\text{cm}^{-1}}$ (S-band) (Myers, G. A., Kehoe, K. K., & Hackley, P., 2017).

Carbon-carbon double bonds: $^{1540\text{cm}^{-1}}$, 1500 $^{\text{cm}^{-1}}$ (La Rosa-Toro Gómez, A., & D'Arrigo, D. V., 2022), (Fries, M., & Steele, A., 2010).

It is important to mention that carbon is a relevant material in the area of materials and energy engineering, for example graphene is also characterised by its D and G bands, since due to its two-dimensional structure and its high thermal and electrical conductivity, they are key in technological innovation (Madrigal Rodríguez, 2024), (Vargas Henao, 2024).

Box 4

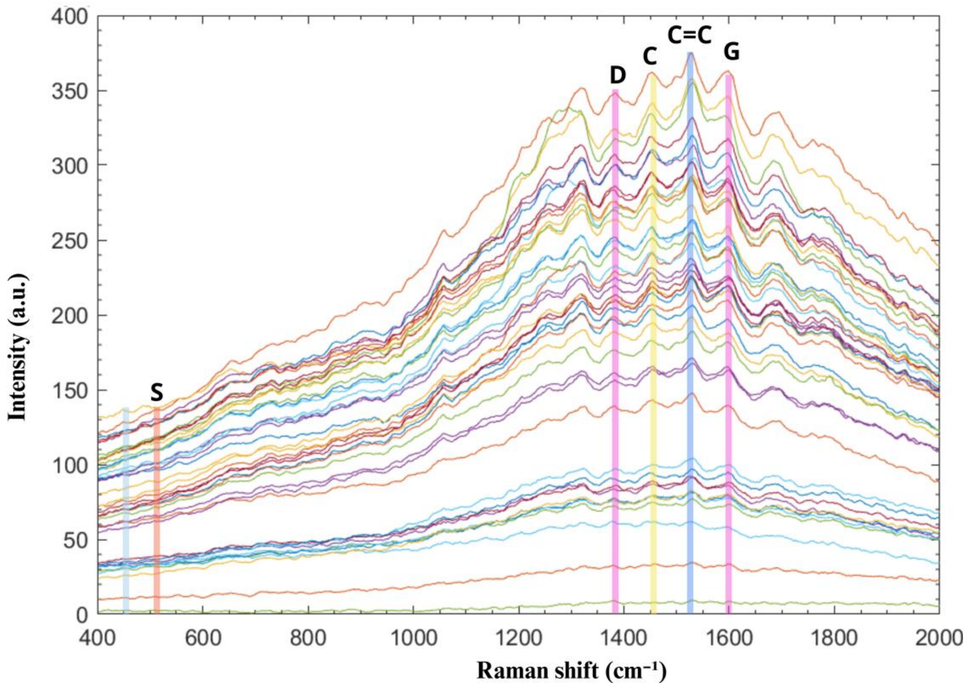


Figure 4

Shown are 43 Raman spectra of a Y-path of a thin film of channel sample, Raman shift from 400 to 2000 cm^{-1}

Source: [*Own elaboration*]

Surface map of Raman spectra

A graph is presented in figure 5, as a start for the creation of a Raman image for a channel sample. For a qualitative analysis it is important to identify the bands of higher intensity (warm colours) with a colour map that allows to delimit the regions with presence of organic matter, or with presence of carbon double bonds.

Box 5

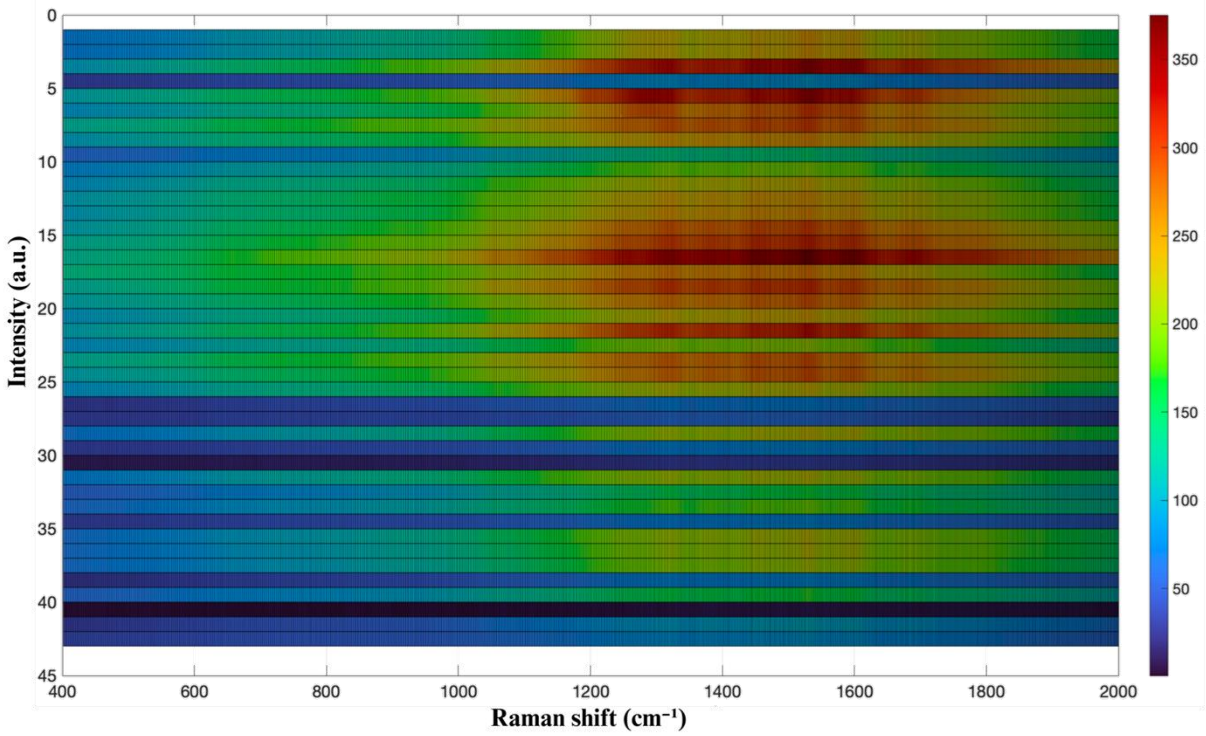


Figure 5

Surface map of 43 spectra on a y-axis path of a thin sheet of channel sample. The warmer colours are seen for high intensities and cooler colours for low intensities

Source: [*Own elaboration*]

Statements

Conflict of Interest

The author declares that he has no conflicts of interest. He has no known competing financial interests or personal relationships that might have appeared to influence the article reported in this chapter.

Authors' contributions

Citli Celeste Castelán Antúnez, Preparation of this document; Flores Gil Aarón, Patiño Carachure, Cristobal and Urrieta Almeida, Edgar, Support in the development of the project and writing of the document.

Availability of data and materials

The information contained in this document is available upon request from the principal author.

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Conclusion

In conclusion, the simultaneous use of petrographic microscopy and Raman spectroscopy allowed us to obtain detailed spectra of the channel sample. The spectra obtained from the thin film channel sample show the presence of minerals such as quartz, carbon and silicon, among others that are yet to be identified; in addition to other bands such as those associated with polymers with the carbon double bond. The bands D 1360 cm-1 and G 1600 cm-1 of carbon structures were identified, as well as the band associated with carbonate 1450 cm-1. The analysis revealed a high fluorescence in the spectra, due to the heterogeneity of the sample and the presence of organic matter associated with rock with high clay content.

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