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Quantification of kerogen content in organic-rich shales from optical photographs

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HIGHLIGHTS

• Kerogen content in oil shale samples is quantifiable from optical photographs.

- Novel method developed and validated for thermally immature Green River Formation.
- Maximum error bounds are ±4 wt% TOC or ±10 GPT.

• Predictions may deteriorate in the presence of "interfering minerals" e.g., clay.

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1. Introduction

Quantification of organic matter content in unconventional resources is of high importance both in their evaluation and development. Over the past few decades a multitude of approaches have been developed, which can be broadly categorized into: chemical analysis (via acidification/oxidation), pyrolysis, well logging, and spectroscopic methods. Details regarding the various approaches within each category are discussed e.g., in Peters et al. [1]. While each class has its own advantages, spectroscopic methods, used for core/outcrop samples, are preferred for their relative rapidity, resolution, and non-destructive nature. This class is the subject of the present paper.

Since Athabasca oil sands have been the subject of extensive spectroscopic studies, we shall first review some of the most

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ABSTRACT

A novel method for quantifying kerogen content from optical photographs of oil shale is presented. It is applied and extensively validated for the thermally immature Mahogany zone of the Green River Formation. The method produces estimates covering scales of a few hundred microns to several hundred feet. It is simple, cheap, non-invasive, and requires no complex instrumentation other than an ordinary optical camera. Images of dry and water wetted samples are equally applicable, with the latter providing better overall predictions for oil yields less than 60 gallons/ton and bitumen-impregnated volcanic tuff beds. Maximum error bounds are ±4 wt% total organic carbon or ±10 gallons/ton oil yield. Applicability of the method is likely limited in the presence of strong optically absorbing minerals with high spatial variability.

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relevant literature therein. Thompson [2] seems to have been the first to utilize the near-infrared (NIR; 1000–2500 nm wavelengths) spectral signatures of bitumen and clay minerals to quantify total bitumen content (TBC) in oil sands. Specifically, he showed that the ratio of a bitumen-specific absorption band, 2180-2260 nm, to the nearby non-bitumen-specific band, 2270-2350 nm, correlates positively with TBC. His experimental setup consisted of two optical filters (one for each spectral band) mounted on a filter wheel, a Tungsten-halogen light source, a receiver lens, and a photo detector. The accuracy of his method was later reported by Lyder et al. [3] to be within ±3 wt%.

Shaw and Kratochvil [4] ascribed the NIR bitumen-specific absorption bands (2285 nm, 2330 nm, 1725 nm, 1760 nm) to overtones and combinations of fundamental vibrations of the constituent methyl and methylene groups. They found that absorbance (presumably the logarithm of reflectance) of crushed samples at these bands obtained from FTIR (Fourier-transform infrared) diffuse reflectance correlated linearly with TBC from Soxhlet extraction. Calibrations were subsequently used to obtain







point measurements of TBC, with a 1 cm^2 sampling window and spaced 1 cm apart, along a 4 m intact core. They reported good positive correlations of *all* wavelengths between 1500 and 2400 nm with TBC (correlation coefficients > 0.75). Measurements were reported to be sensitive to sample distance from the photodetector. Donkor et al. [5] used a similar approach to map TBC profiles along a longer core; 15 m. Predictions were reported to be sensitive to surface roughness.

Lyder et al. [3] and Rivard et al. [6] improved the accuracy and robustness of the two-band model of Thompson [2] by analyzing the NIR spectrum of Athabasca oil sands from 1600 to 30000 nm. Two methods based on Gaussian fitting and wavelet analysis were developed, with accuracies to within 1.1-1.5 wt% TBC. Recently, Speta et al. [7] used hyperspectral imaging via a commercially available instrument, SisuROCK by Spectral Imaging (Specim) Ltd., Finland, to map the spatial distribution of TBC in both fresh and dry cores. The NIR spectrum collected for each pixel was processed and accurately converted to TBC via a modified version of the model developed by Rivard et al. [6]. Their model was based on bitumen features around 1700 and 2300 nm, and clay features around 2200 nm. Predictions for fresh cores seemed generally better (~1.5 wt.% error) than dry cores.

Spectroscopic methods for estimating total kerogen content (TKC) have primarily focused on the mid-infrared (MIR; 1923-22,222 nm), and specifically on the aliphatic absorption band of kerogen (3333–3571 nm). Pomerantz [8] proposed a method whereby organic content and mineral composition of oil shale can be simultaneously estimated from FTIR spectrometry. The method involves the following steps: estimating sample maturity from a spectral decomposition of the aliphatic band, selecting a "kerogen standard" of corresponding thermal maturity out of a number of reference spectra, adding the standard to a spectral library, and un-mixing the entire MIR spectrum into its constituent components. The work takes advantage of the relatively large separation between the spectral features of kerogen in the MIR and most common geological minerals. Herron et al. [9] used essentially the same approach in diffuse reflectance mode on crushed samples and reported a total analysis time of \sim 15 minutes per sample, including sample preparation. Recently, Washburn et al. [10] used FTIR in attenuated total reflectance (ATR) mode to sample MIR spectra over sub-millimeter scale areas of Green River oil shale samples (Mahogany and R-6 zones, Piceance Basin), and subsequently converted them to TKC and mineral composition maps using models calibrated to 96 samples. Automated capabilities were used to facilitate sampling.

All above mentioned methods, while valuable, are bound by one or more of the following limitations: (a) model calibrations are time consuming and complex (e.g., with spectroscopic methods calibration at times involves special sample preparations for obtaining end member component spectra, and use of multivariate regression and/or principal component analysis techniques), (b) measurements are limited to point values often restricting analysis to small scales, and (c) specialized equipment are required contributing to higher cost. The objective of this work is to introduce a much simpler and therefore cheaper alternative for quantifying kerogen content using ordinary optical photographs. The approach circumvents all said limitations and provides spatial maps of TKC spanning scales of a few hundred microns to hundreds of feet. This is not only of interest for resource evaluation, but also estimation of spatial distributions of thermo-mechanical properties required in modeling in-situ retort operations. In this work, analysis is confined to the immature oil shale of the Green River Formation. The premise of the proposed method is that intervals appearing darker in the visible range are richer in grade. Previous studies have made qualitative observations of a connection between the degree of "darkness" of an oil shale sample and its grade (Table 15 of [11]). The present work aims to put this on a quantitative basis. While our method is likely not universal for other source rocks, applicability and possible extensions of the method are certainly worth exploring and discussed herein.

The Eocene Green River Formation contains the largest known oil shale deposit in the world, with an estimated ~4 trillion barrels of oil in-place [12]; an earlier more conservative estimate of ~ 1.5 trillion barrels was given by Dyni [13]. The formation spans the three states of Colorado, Utah, and Wyoming, in the United States. Deposits are primarily concentrated in the Piceance Creek Basin of western Colorado, the Uinta Basin of eastern Utah and western Colorado, and the Greater Green River Basin of southwestern Wyoming, with 1.53, 1.32, and 1.44 trillion barrels of oil in-place respectively [14–16]. Due to the larger areal expanse of the Greater Green River Basin, oil shale therefrom is on average of lowest grade [16]. The lacustrine deposits of the Uinta and Piceance Creek Basins were deposited by Eocene Lake Uinta. These basins at times were connected across the Douglas Creek Arch [17]. In this work, we study samples extracted from both the Piceance and Uinta basins, and focus on the most-studied Mahogany zone. The geologic interval defined by the Mahogany zone contains the largest proportion of high-grade oil shale (defined as higher than 14 wt% organic matter content) in both Uinta and Piceance Basins, and is thus of greatest economic interest [18,12].

The paper is outlined as follows: Section 2 describes a novel method for quantifying TKC from optical photographs. Section 3 focuses on validating the method via core samples covering the entire depth of the Mahogany zone. In Section 4, the method is further validated via smaller laboratory-scale samples. Various calibration approaches are also discussed. In Section 5, we discuss applications, implications, limitations, and possible extensions of the method. Section 6 concludes with a summary of major results.

2. Method

When taking an image of a scene, light reflected from the objects in the scene enters the camera lens in units of radiance: energy per unit time, surface area of captured object, wavelength, and solid angle (W/m² nm sr). In a digital camera, light subsequently projected onto the photosensitive detector is in units of irradiance: energy per unit time, surface area of sensor, and wavelength (W/m² nm). The two are linearly related through the camera equation [19]. Sensors within cameras, CMOS (complementary metal-oxide semiconductor) and CCD (chargecoupled device), release electrons in proportion to the number of photons incident upon them; a phenomenon known as the photoelectric effect. Within the dynamic range of a camera (i.e., the detectable difference between the brightest and darkest objects in a scene) the proportionality is linear. The sensor surface is divided into small regions, corresponding to pixels in the image. Each region is covered with an optical filter (typically one of red, green, or blue) spatially arranged in a certain pattern (most commonly the Bayer pattern). Unless an image is stored in RAW format, the recorded RGB (red-green-blue) values per pixel are often non-linearly transformed via a process called gamma correction and compressed into a lossy JPEG format; both executed internally within the camera. For convenience, we shall use JPEG and RAW as subscripts to denote parameters associated with JPEG and RAW images, respectively.

Reflectance (*R*) is defined as the ratio of the light intensity reflected from an object (*I*) to the light intensity incident upon it (I_0) for a given value or interval of wavelength (Eq. (1)). *R* can be estimated from an image by dividing its RGB_{raw} by the RGB value of a white reference imaged under the same conditions and normalized to the same exposure; denoted by RGBW_{raw} (Eq. (1)).

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