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Quantitative evaluation of vitrinite reflectance and atomic O/C in coal using Raman spectroscopy and multivariate analysis

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ABSTRACT

Vitrinite reflectance (VRo) is a standard petrographic method for assessing thermal maturity (rank) of coal. The vitrinite reflectance technique, however, requires significant petrographic experience, can be time-consuming, and may be biased by analyst subjectivity. Correlations between coal rank and Raman spectral properties are a promising alternative that can supplant some of the limitations inherent in the VRo protocol. The traditional peak-fitting methodologies for quantifying metrics from Raman spectra, however, also suffer from analyst subjectivity that can affect correlations between analyte and spectral properties.

This research combines high-throughput Raman spectroscopy with multivariate analysis (MVA) to create calibration models for the prediction of coal rank though VRo and atomic O/C ratio. MVA techniques eliminate the ambiguous subjectivity prevalent in peak-fitting methods by evaluating the full Raman spectrum, then identifying the integral vibrational modes for constructing accurate models. Partial least squares (PLS) regression models were developed using Raman spectra and VRo values (0.23–5.23%) for 68 geographically diverse coal samples. The calibration set was validated using one-half of the samples to rigorously assess the model's predictive accuracy. The root mean standard error of prediction was 0.19 for the VRo model and 0.014 for the atomic O/C model. Both models exhibited linear correlations, with coefficients of determination (R^2) for the validation set of 0.99 (VRo) and 0.93 (atomic O/C), despite the geographic and rank diversity of the samples. This study demonstrates the applicability and power of using PLS models for the prediction of both the VRo and atomic O/C ratio from Raman spectra. The quantitative MVA protocol contained herein provides a Raman alternative to the VRo industry benchmark for coal rank that is not subject to the limitations and subjectivity of peak-fitting methods.

1. Introduction

Organic petrography utilizes reflected light microscopy to characterize organic macerals present in coal [1,2]. Different types of organic macerals, analogous to inorganic minerals, comprise coal. Vitrinite, part of the humic sub-classification of macerals, comprises the dominant part of coal and is also found dispersed into other sedimentary rocks such as shale and mudrock [3,4]. Vitrinite reflectance (VRo) is a physical property that increases with coal thermal maturity (rank) due to aromatization and condensation of the vitrinite structure [5]. This process is a precursor to the formation of graphite in metamorphic rocks and is a function of temperature, pressure, and time [6,7]. Vitrinite reflectance information is critical to coal utilization, e.g., coke-making for metallurgy [8], and the relationship between VRo and temperature is used to infer thermal maturity in hydrocarbon exploration. Highly experienced petrographers are vital to properly identifying vitrinite macerals. Variability in the measurements can arise from different inter- and intra-lab interpretations, and samples must be prepared with a high-quality polish to eliminate scratches and relief, requiring time and further expertise.

Because of the limitations of the VRo method, Raman spectroscopy has been explored as an attractive alternative for correlating spectral properties to intrinsic sample attributes [9–25]. Raman spectroscopy is an instrumental method that furnishes rapid, non-destructive analyses, requires little to no sample preparation, and can deliver quantitative sample information. Lasers, ranging from ultraviolet to near-infrared wavelengths, are used to excite sample molecules, while the instrumentation collects scattered photons generated from interactions

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between the laser light and sample molecular bonds. Roughly one in one million photons is inelastically scattered with a shift in energy from the excitation wavelength that depends on the specific sample molecular bonds or vibrational modes [26]. Scattering diffuses isotropically and can be collected using sophisticated optics, such that chemical markers of molecular vibrations can be assessed. Selection rules dictate that molecular vibrations are considered to be Raman "active" when there are changes in polarizability, as opposed to infrared spectroscopy, which requires changes in dipole [26,27]. The shared electrons in covalently bonded carbon compounds are highly polarizable, which makes Raman spectroscopy ideal for evaluating the C–C and C=C bonds comprising carbonaceous samples like coal, since there are changes in polarizability.

Raman spectra of coal reveal two distinctive peaks: the disordered, D- or D1-band, and the graphitic, or G-band [28]. These modes occur near ~1350 and ~1580 cm^{-1}, respectively, although the precise frequency depends on the analyte and the instrumental parameters used for data acquisition [15,28–31]. Ancillary D-vibrational modes have been identified and are termed D2 (1620 cm^{-1}), D3 (1500 cm^{-1}), and D4 (1250 cm^{-1}). Studies of simpler molecules like graphite and graphene have proved instructive when attempting to elucidate the origins of the D-band. [28–30,32–34]. While defect-free graphite does not reveal this vibrational mode, graphite possessing defects does exhibit the ~1350 cm^{-1} peak. The D-peak, therefore, requires a defect for it to be Raman active. The G-band originates from aromatic ring C=C bonds (ring-breathing modes), and represents the E_{2g} mode [34–38].

Raman analysis of organic matter in sedimentary rocks including coal has shown promise in correlating spectral attributes to thermal maturity as determined through VRo, solid bitumen reflectance, and temperature estimates from mineral equilibria [9,10,13–17,19,23–25,39,40]. These studies, however, have predominantly used peak-fitting to reconstruct experimental data. The peak-fitting approach is hindered by subjective analyst data processing and interpretation that can alter, create, or remove presumed trends [15,41]. Therefore, alternative methods for reduction of Raman spectra and correlation to coal rank are required. Applying multivariate analysis (MVA) to Raman spectra eliminates the limitations of peak-fitting, as the analyst does not need to subjectively assess how many peaks are suitable for an accurate reconstruction of the original data, appropriate peak shapes, widths, etc.

Utilization of MVA strategies to develop high-throughput, non-subjective, robust models that can diminish the use of laborious standard methods and reduce experimental costs and time has been widely demonstrated. MVA applications are not limited to Raman spectroscopy, but have been applied to other instrumental techniques including infrared spectroscopy, near-infrared spectroscopy, pyrolysis mass spectrometry, and laser-induced breakdown spectroscopy [42–61]. Raman spectroscopy-MVA models have been shown to facilitate the quantification of chemical constituents in botanical plants used in energy applications [44,54–56,62–65]. These methods provided rapid screening tools to assess downstream applications of feedstocks, a rationale that parallels the quest for an enhanced understanding of the evolution from source rock to fuel production.

The limitations of peak-fitting for using Raman spectroscopy quantitatively have been well illustrated in previous work [15–17,41]. Therefore, MVA calibration models for the quantification of coal properties-VRo and atomic oxygen/carbon (O/C) ratio-were constructed and rigorously assessed herein. Since Raman spectroscopy has been a common alternative for assessing coal properties, coupling spectral data and MVA is an enticing prospect for rapid quantitation of thermal maturity. To the authors' knowledge, this is the first study to evaluate correlations between coal Raman spectra and thermal maturity using MVA.

Table 1
Coal sample characteristics.

Sample Set	Number of Samples	Ultimate Analysis Dry Carbon (%)	VRo Mean-Maximum (%)	Atomic O/C
Argonne	8	65.65–86.71	0.25–1.68	Not provided
CoalTech	10	Not provided	1.38–1.87	Not provided
PA-DCNR[a]	9	Not provided	2.38–5.23	Not provided
DiRenzo Coal	1	Not provided	5.07	Not provided
PA Anthracite Council	1	Not provided	5.22	Not provided
PSU-DECS	39	62.53–85.74	0.23–5.19	0.027–0.206

[a] Pennsylvania Department of Conservation and Natural Resources.

2. Materials and methods

2.1. Samples

Sixty-eight coal samples (Table 1) from across the United States were obtained to provide a widespread representation of different seams, thereby producing more comprehensive models. Samples from the Penn State Coal Database, 2017, EMS Energy Institute, Pennsylvania State University (State College, PA, USA), Argonne National Laboratory (ANL, Lemont, IL, USA), CoalTech Petrographic Associates – Coal Petrography Interlab Program (Murrysville, PA, USA), the Pennsylvania Department of Conservation and Natural Resources (Harrisburg, PA, USA), the Pennsylvania Anthracite Council (Camp Hill, PA, USA), and DiRenzo Coal Company (Pottsville, PA, USA), were used in this study. The samples from the Penn State Coal Database were selected due to their extensive characterization using standard ASTM methods [66–68] and their diverse range of VRo values, spanning from 0.23 to 5.19% (mean maximum) [69,70].

2.2. Sample preparation

The sample preparation employed in this research has been described in a previous study, and was used with a few modifications [41]. All samples were dried in an oven at 110 °C overnight to reduce moisture, since moisture has been shown to increase the fluorescence background caused by oxidation of the sample [17]. The samples from the Penn State Coal Database, Argonne National Laboratory, CoalTech Petrographic, and the Pennsylvania Department of Conservation and Natural Resources were received processed to ~60 mesh top size. A ball mill was used for the comminution of the other samples evaluated in this study. The samples were applied by spatula to aluminum-coated borosilicate glass microscope slides to facilitate the analysis of different coal particles [41]. The presence of predominantly one layer of coal particles was determined optically using bright-field microscope images. Loosely bound coal was removed using canned air, such that the remaining physisorbed particles were strongly adhered to the slide via electrostatic interactions. This preparation facilitated sample mapping and selection of individual coal fragments for collection of spectral data (as described below).

2.3. Organic petrography

VRo values were measured using ASTM method D2798 [66]. The atomic O/C ratios were determined using ASTM D3176 [67]. Results for these parameters were provided by the institutions from which the samples were obtained. (Penn State Coal Database, 2017, EMS Energy Institute, PSU; CoalTech Petrographic Associates – Coal Petrography Interlab Program).

Samples that did not have a prior vitrinite reflectance characterization (Pennsylvania Department of Conservation and Natural Resources, Pennsylvania Anthracite Council, and DiRenzo Coal