

The measurement of moisture content in mineral ore samples

Application Note

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Abstract

Near-infrared (NIR) diffuse reflectance measurements of oil shale samples were made using a Cary 500 spectrophotometer equipped with a Praying Mantis diffuse reflectance accessory (DRA). The oil shale samples had been stored at varying humidity in order to measure the absorption of moisture. A linear relationship was found to exist between the amount of water absorbed (g) and the non-bonded -OH band at 1900 nm. Trends were not observed for -OH bands at 1400 and 2200 nm.

Introduction

Based on current levels of consumption, the world's reserves of crude oil are estimated to last approximately 20 years¹. As such, alternative sources of fuel need to be investigated. The world's vast oil shale reserves are one potential alternative for supplying the world's energy needs, although viable methods for extracting, analyzing and processing oil shales need to be developed. The Department of Applied Chemistry at RMIT University is currently investigating the feasibility of using infrared and near-infrared diffuse reflectance spectroscopy to predict the oil yield from oil shale samples. During this investigation, the problem of moisture in samples arose. The primary concern with moisture in shale samples is its potential effect on calibration models for accurately predicting oil yield, and this led to an investigation involving the analysis of moisture content in oil shales. In the near infrared region, both bonded and non-bonded hydroxyl groups are observed. The first overtone of bonded and non-bonded -OH occurs at 1400 nm. The combination band for non-bonded -OH is at 1900 nm and at 2200 nm for bonded -OH.² Diffuse reflectance spectra of oil shale samples with different moisture content were thus collected, and spectral properties correlated with moisture content.



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Theory

Diffuse reflection spectroscopy is particularly useful in the analysis of substances for which traditional methods and techniques fail, for example coal and oil shale. Diffuse reflection occurs when incident light is scattered in all directions (as opposed to specular reflection where the angle of incidence equals the angle of reflection). Diffuse reflectance spectra can exhibit both absorbance and reflectance features due to contributions from transmission, internal reflection and specular components. Spectra are also affected by sample preparation, particle size, packing density and sample concentration.

The Praying Mantis DRA is designed to measure diffuse reflectance. The incorporation of two 90° off-axis ellipsoids forms a highly efficient diffuse reflection collection system. One of the ellipsoids focuses the incident beam on the sample while the second collects the radiation diffusely reflected by the sample and directs this reflected light to the instrument detector (Figure 1). Both ellipsoids are tilted forward, allowing the specular component to be deflected behind the collecting ellipsoid, thus minimizing spectral distortions.

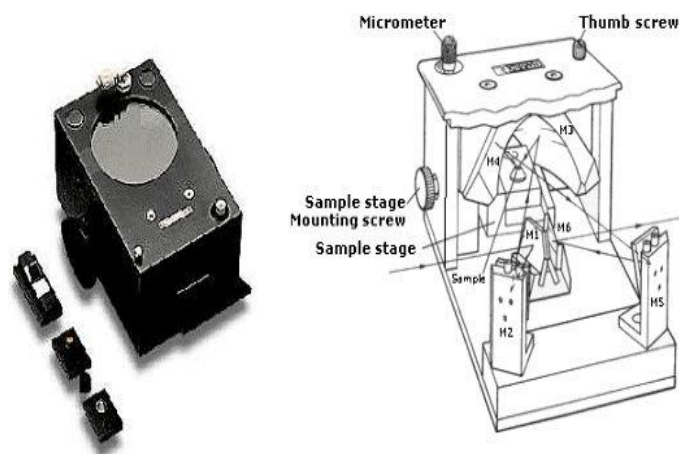


Figure 1. The Praying Mantis diffuse reflectance accessory and optical diagram

Materials and methods

Saturated salt solutions were utilized to obtain a range of relative humidity with which to study the effects of moisture on the NIR diffuse reflectance spectra of oil shale samples. Table 1 summarizes the saturated salt solutions used and the relative humidity achieved with each solution. Zero humidity was achieved with the use of silica beads acting as a desiccant. The temperature of the laboratory ranged from 22 – 24 °C.

To ensure a saturated solution, 50% more than the solubility weight of each salt was added to 100 mL of distilled water and left in the bottom of sealed desiccators for a week to equilibrate. In the meantime shale samples, exhibiting identical mineral and organic components, were thinly spread into Petri dishes and placed in an oven at 105 °C until constant weight was achieved. These samples were then placed into the desiccators (10 in total) and left to equilibrate to constant weight.

Equipment:

(For part numbers please refer to Reference 3)

- Cary 500 UV-Vis-NIR Spectrophotometer
- Praying Mantis DRA
- Cary 400/500 Extended Sample Compartment

Table 1 List of saturated solutions, their relative humidity and the temperature range for which the humidity remains stable.

Saturated solution	Solubility in 100 cc water at 25°C ⁴	Relative humidity (%) ⁵	Temperature range (°C)
LiCl·H ₂ O	86.2 g	11.3	20 – 70
CH ₃ COOK·1.5H ₂ O	253 g	22.2	-10 – 30
MgCl ₂ ·6H ₂ O	167 g	32.7	10 – 50
NaI·2H ₂ O	184 g	39.2	5 – 35
NaBr·2H ₂ O	79.5 g	58.2	-10 – 35
CuCl ₂ ·2H ₂ O	110.4 g	68.4	10 – 30
NaCl	35.7 g	75.1	5 – 60
BaCl ₂ ·2H ₂ O	58.7 g	90.3	5 – 60
K ₂ SO ₄	12 g	97	15 – 60

Protocol

The Praying Mantis DRA was installed into the Cary 500 spectrophotometer (Figure 1) and aligned.⁶ The wavelength range was set to scan from 2300 to 1300 nm. The 'SBW' (spectral bandwidth; nm), 'beam mode', 'average time', and 'slit height' were set to 5, double, 0.3 sec, and reduced respectively. 'Zero/baseline' correction was selected for baseline correction, using powdered KBr as a reference. Diffuse reflectance spectra of the powdered oil shale samples were obtained using the standard sampling cup supplied with the Praying Mantis accessory. The sampling cup was overfilled with oil shale samples and a constant weight (~30 g) placed on top to pack the samples consistently. The sample surface was scraped flat with the straight edge of a spatula. This process was made as reproducible as possible to minimize inter- and intra-sample variation due to surface appearance and packing density.

Results and discussion

Diffuse reflectance spectra were imported into Matlab (The MathWorks, Inc., Massachusetts, U.S.A) and converted to pseudo-absorbance ($\log_{10} 1/R$). Second derivatives were calculated from these spectra using an 11-point, quadratic Savitsky Golay function. A comparison of the averaged pseudo-absorbance spectrum with the averaged second derivative spectrum is illustrated in Figure 2. The first overtone of bonded and non-bonded -OH occurs at 1400 nm. The two bands appearing at 1728 and 1758 nm are attributable to aromatic -CH and to CH₂ and -CH₃ combination band of bonded -OH.¹ It was observed that the amount (weight) of moisture absorbed by each oil shale sample depended on the relative humidity. Furthermore, an increase in the combination band of non-bonded water (1900 nm) was observed with increasing moisture content. The area under the second derivative curve at ~ 1900 nm was subsequently calculated for each sample and plotted against the amount of moisture absorbed (Figure 3). Figure 3 indicates a linear relationship between the amount of moisture absorbed

by each sample and the intensity of the non-bonded -OH band at 1900 nm, indicating the possibility of using this region for quantitatively predicting moisture content in oil shale and other mineral matter. However similar trends were not observed with the -OH bands at 1400 and 2200 nm.

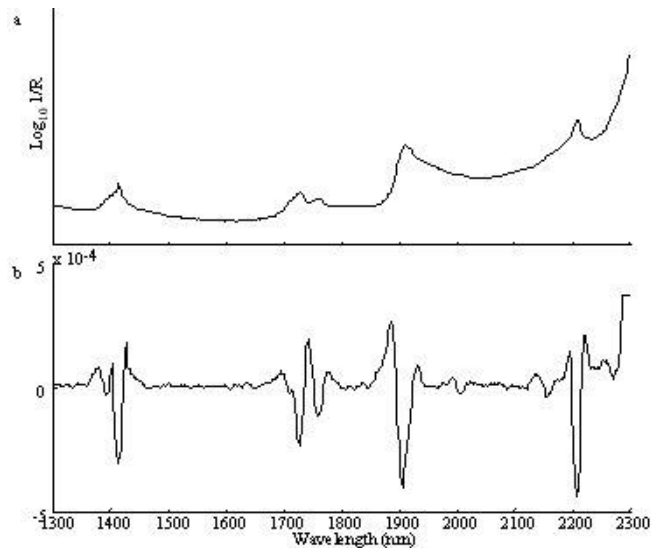


Figure 2. Diffuse reflectance NIR spectra of oil shale were converted to pseudo-absorbance (a) and second derivatives were calculated (b)

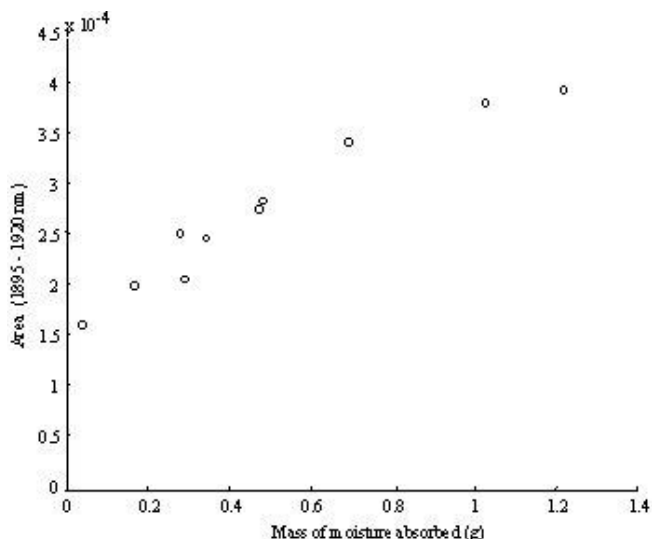


Figure 3. Mass of moisture absorbed (g) versus area under the curve (1900 nm)

Conclusion

Diffuse reflectance NIR spectra of oil shale samples with different moisture content were obtained using a Cary 500 spectrophotometer equipped with a Praying Mantis DRA. Spectroscopic differences between the samples were observed at the 1900 nm non-bonded –OH band. A linear relationship was found to exist between the area under this band and the mass of water absorbed by the sample.

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References

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2. Adams, M.J., B.C. Beadle, and G.F. Kirkbright, *Analytical Chemistry*, 1978. **50**(9): p. 1371-1374.
3. Part Numbers:

Product	Part Number
Cary 500 UV-Vis-NIR Spectrophotometer	00 100710 00
Praying Mantis DRA (Harrick Scientific)	00 100469 00
Cary 400/500 Extended Sample Compartment	00 100466 00
Cary WinUV Scan Software	85 101584 00

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6. Cary WinUV Scan Software, 'Cary Help', Version 2.0

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