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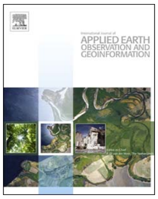

Review article

Near-infrared laboratory spectroscopy of mineral chemistry: A review

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ABSTRACT

Spectroscopy is the science concerned with the investigation and measurement of spectra produced when materials interacts with or emits electromagnetic radiation. Commercial infrared spectrometer were designed from the 1950's onward and found their way into the pharmaceutical and chemical industries. In the 1970's and 1980's also natural sciences notably mineralogy and vegetation science started systematically to measure optical properties of leaves and minerals/rocks with spectrometers. In the last decade spectroscopy has made the step from qualitative observations of mineral classes, soil type and vegetation biomass to quantitative estimates of mineral, soil and vegetation chemistry. This resulted in geothermometers used to characterize metamorphic and hydrothermal systems and to the advent of foliar biochemistry. More research is still needed to bridge the gap between laboratory spectroscopy and field spectroscopy. Empirical studies of minerals either as soil or rock constituents (and vegetation parameters) derived from regression analysis of spectra against chemistry is important in understanding the physics of the interaction of electromagnetic radiation and matter which in turn is important in the design of future satellite missions. Physics based models and retrievals are needed to operationalize these relationships and implement them in future earth observation missions as these are more robust and easy to transfer to other areas and data sets.

1. Introduction

Spectroscopy is the science concerned with the investigation and measurement of spectra produced when materials interacts with or emits electromagnetic radiation. These spectra have been used to chemically characterize earth science materials and to classify them based on diagnostic absorption features that result from molecular vibrational and electronic processes of water molecules, OH groups and other bonds. Over the last decade we have seen many studies that attempt to quantify chemical constituents in water, vegetation, soil, minerals and rocks. Most of these studies use empirical models while some try to develop full inversions based on physical radiative transfer models.

The history of spectrometric measurements dates back to the early 1900's. In 1913, Twyman (part of the Hilger company, UK) designed the first infrared spectrometer. In 1933 and 1944 respectively Kipp and sons in out of the Netherlands and Grubb and Parsons manufactured infrared spectrometers. After world war 2, both US-based Beckman and Perkin-Elmer started the commercial production of infrared spectrometers. However the history of infrared spectrometry dates back to 1823 when Fraunhofer invented the grating which made light dispersion into wavelengths possible (Fraunhofer, 1823). A review of early methods and instrumentation for infrared spectrometry is found in a paper by Bowling Barnes and Bonner (Bowling Barnes and Bonner, 1936).

In the 1950's–1970's researcher were looking at unravelling optical properties of plants (Billings and Morris, 1951; Gates et al., 1965; McClellan et al., 1963). In the 1970's, Graham Hunt and John Salisbury (later joined by Charles Lenhoff) systematically measured spectra of minerals and later rocks and analyzed these spectra linking the diagnostic absorption found to the mineral chemistry and structure. As such their studies resulted in the first spectral libraries of minerals and their interpretation proved to be the 'Rosetta stone' for modern geological remote sensing; allowing scientists to unravel the complex signal of early imaging systems. They started working on silicate minerals (Hunt and Salisbury, 1970) and continued working on carbonates (Hunt and Salisbury, 1971), oxide minerals (Hunt et al., 1971a), sulphide minerals (Hunt et al., 1971b), and salts (Hunt et al., 1972). Next they analyzed rocks starting with igneous rocks (Hunt et al., 1973a,b, 1974), sedimentary rocks (Hunt and Salisbury, 1976a), and metamorphic rocks (Hunt and Salisbury, 1976b).

The United States Department of Agriculture in the 1970's through 1980's (Dixit and Ram, 1985; Norris et al., 1976) performed systematic spectral measurements of dried and ground leaves and related absorption features to foliar chemistry. Probably the first to make the link

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between foliar chemistry and potential for remote sensing were Carol Wessman (Wessman et al., 1988a, 1988b) and Paul Curran (Curran, 1989). These early review papers mark the onset of foliar chemistry using the relationship of particular plant compounds to absorption features. Why do foliar chemistry and try to quantify plant compounds? Chlorophyll is an indicator of plant productivity, nitrogen is a proxy for the availability of nutrients, lignin level is correlated with plant (cellulose) decomposition and the vegetation spectral red-edge is a measure of plant health (stress). These are observations that are relevant for agriculture crop monitoring and yield prediction, for understanding ecosystem functioning, understanding the carbon cycle and the carbon exchange between vegetation and the atmosphere in global change studies. What plant compounds are spectrally active? Biochemical constituents of leaves that can be studied spectroscopically are cellulose, lignin, starch and (nitrogen-based) components such as proteins and chlorophyll. More particularly, in the visible part of the spectrum pigments such as chlorophyll a and b, carotene and xanthophyll determine the reflective properties of leaves. An overview of regression based methods for foliar chemistry is found in (Kokaly and Clark, 1999). There is a wealth of papers showing the potential of quantifying leaf chlorophyll content for various crops and vegetation species (Daughtry et al., 2000; Gitelson and Merzlyak, 1997). The foliar biochemistry community made the step from leaf to canopy estimation thus addressing scale issues and also made the step from empirical to physical models thus allowing transferability and repeatability of retrievals. Hence it serves as a good example for directions the soil and geology communities working on spectroscopy could take.

The last 10 years or so have seen many applications of spectroscopy to quantify the chemical composition of minerals and rocks. In this paper an overview is provided of recent (< 10 year old) studies on quantitative spectroscopy to estimate mineral (soil, rock) chemistry. This paper brings together some of that work (with no intention to provide an all-inclusive overview) closely linking spectroscopy to analytical chemistry with an outlook to the potential for global earth observation and monitoring of earth system variables.

2. Some theoretical considerations

2.1. Background

Electromagnetic radiation is a wave motion which is a stream of particles or a stream of photons. Therefore a common measurement unit of radiation is the wavenumber or the number of waves per cm. The spectroscopic wavenumber is the reciprocal of the wavelength of light in a vacuum. Vice versa many spectrometers use micrometer or nanometer as the unit of measurement. Reflectance is a function of scattered radiance from the surface and the incident irradiance intensity. Usually reflectance is measured by the ratio of the intensity reflected from a sample divided by that of a standard or reference. Commonly used measurement principles are hemispherical-conical (also referred to as hemispherical-directional) reflectance and biconical reflectance (Milton et al., 2009).

2.2. Instrument characteristics

The following are key characteristics for spectrometers from a user perspective: (1) spectral range, (2) spectral bandwidth, (3) spectral sampling interval, and (4) signal-to-noise ratio (SNR).

The spectral ranges (and definitions) that are commonly used in spectrometry include the: visible (VIS: 0.4–0.7 μm), near-infrared (NIR 0.7–1.4 μm), short-wave infrared (SWIR: 1.4–3 μm), mid-infrared (MIR: 3–8 μm), longwave infrared (LWIR) or thermal infrared (TIR: 8–15 μm). It should be noted that this division is dependent on the discipline and application. For example, the International Commission on Illumination, the ISO 20473 scheme and the field of astronomy use slightly different definitions. The manufacturers of spectrometers typically coin the different wavelength regions to the type of detectors and their sensibility. The near-infrared is linked to the sensitivity of silicon (0.7–1.0 μm), the short-wave infrared to InGaAs (1.0–3 μm), the mid-infrared (3–5 μm) to Indium Antimonide and HgCdTe and the Long-wave infrared (7–14 μm) to HgCdTe and microbolometers.

Spectral bandwidth is loosely defined as the width of an individual spectral channel in a spectrometer. This is important as it determines the width of a diagnostic absorption feature that can be resolved by the spectrometer. Spectral sampling interval is the distance in wavelength between adjacent spectral bands (or band passes or channels or spectral response functions of channels) in a spectrometer.

Spectral resolution in remote sensing is a measure of the ability of a sensor to capture fine wavelength intervals and this often is the product of spectral sampling and spectral bandwidth. The International Union of Pure and Applied Chemistry defines spectral resolution in optical spectroscopy as “the minimum wavenumber, wavelength or frequency difference between two lines in a spectrum that can be distinguished”.

The signal-to-noise ratio is more subjective. By definition noise is random variability of the signal and signal is the quantity of light measured by the spectrometer. Two prevailing methods are typically used to quantify the signal-to-noise ratio of a spectrometer: one based on laboratory calibration measures and the second using instrument measures. Signal mean over signal standard deviation is a typical laboratory based measurement. Often reference targets are used for this. Using the instrument dark current (shutter closed) of the spectrometer is an often used instrument method. Manufacturers often also report the so-called Noise Equivalent Spectral Radiance (NESR). This NESR is the spectral radiance required to obtain a SNR of 1.

2.3. Field spectrometers

The reader is also referred to a review paper by Milton et al. who summarized measurement geometries, give an overview of available instruments back in 2009, review principles of multiple view angle acquisitions, and give examples of field spectroscopy for vicarious calibration and atmospheric corrections (Milton et al., 2009).

The Geophysical Environmental Research Corporation (GER) was one of the early manufacturers of near infrared spectrometers. More recently, with the technology developed at GER, SPECTRAL EVOLUTION (http://www.spectralevolution.com/) markets state of the art UV–vis-NIR-SWIR full range spectroradiometers for use in the field and in the laboratory. Likewise since 1990, Analytical Spectral Devices (ASD) built spectrometers and still is manufacturing spectroradiometers (https://www.asdi.com/). One of the early (and now out of production) systems is the so-called portable infrared mineral analyzer (PIMA) developed by the Australian Integrated Spectronics Pty Ltd. With a built in light source this instrument senses the SWIR and is customized for mineralogical studies. Within the LWIR/TIR (typically starting from the SWIR) Fourier transform infrared spectroscopy (FTIR) is used which is a technique to obtain an infrared spectrum of absorption and emission. These FTIR instruments are typically designed for solids (quality control pharmaceutical applications), liquids and gases, but there are several custom designs for studying rocks and (to a lesser extent) vegetation. Companies that manufacture such instruments include Bruker (http://www.bruker.com), Thermofisher (https://www.thermofisher.com/) which markets the nicolet series FTIR systems and the MIDAC corporation (http://midac.com/). Finnish company SPECIM (http://www.specim.fi/) designs hyperspectral imaging camera systems for use in the laboratory and field.

Over the years several spectral libraries have been compiled following the pioneering work of Graham Hunt and John Salisbury who measured and collected spectra of many mineral and rock groups. To highlight a view: the NASA Jet propulsion laboratory of 160 minerals (https://speclib.jpl.nasa.gov/documents/jpl_desc), the USGS spectral library (https://speclab.cr.usgs.gov/spectral-lib.html), the John Hopkins University spectral library (Salisbury et al., 1991) of Salisbury