

THERMAL-INFRARED EMISSION SPECTROSCOPY OF NATURAL SURFACES: APPLICATION TO COATED SURFACES; *Philip R. Christensen, Arizona State University, Tempe, AZ, Stephanie T. Harrison, Goddard Space Flight Center, Greenbelt, MD, Paul Barbera, Steve Ruff, Arizona State University, Tempe, AZ.*

Thermal-infrared vibrational spectroscopy has great potential for remotely determining the composition of planetary surface materials, taking advantage of fundamental molecular vibrational modes that produce spectral features in the range from ~ 3 to >50 μm . Much of the current interest in the thermal infrared wavelength region stems from the deployment of multi-spectral scanners, such as the Thermal Infrared Multispectral Scanner (TIMS) (1) and the Mars Observer Thermal Emission Spectrometer (TES) (2). In order to support these missions, it is necessary to develop an appropriate library of laboratory measurements.

The purpose of this work was to develop a technique which, with a very limited set of assumptions, can be used to determine the emissivity of natural surfaces directly using emitted energy. To date, virtually all laboratory spectra have been obtained using reflection or transmission methods (3-6) with only a limited number of measurements taken in emission (7-9). In contrast, remotely-sensed thermal-infrared data from planetary surfaces are obtained by measuring the emitted energy. For ideal conditions in which the surface is isothermal and all of the reflected and emitted energy can be measured, reflection and emission are intimately related through Kirchoff's law. These conditions are not always met, however, in nature nor in a laboratory. For example, bidirectional or biconical reflection measurements are not appropriate for a quantitative assessment of emissivity (5). Radiative transfer modeling to account for potential non-ideal conditions is complex, as scattering by particles close to the wavelength in size may be significant (8; 10-12). As a result, all of the effects of environment are difficult to fully model. For these reasons we have chosen to obtain data in emission in order to more closely replicate remotely-acquired data and to investigate the range of conditions over which reflectance and emittance can be directly related.

One of the major complications to the collection of emission data is the difficulty in separating energy of interest emitted by the sample from that emitted by the instrument and surroundings and reflected off the sample. There are three basic approaches to this problem: 1) calculate the background energy reflected from the sample, assuming the reflectivity of the sample is given by Kirchoff's law; 2) obtain measurements at several sample temperatures with a fixed background temperature to determine the reflected energy directly; and 3) cool the sample chamber walls to limit background emission. We have developed a laboratory technique for determining calibrated emissivities of natural surfaces using the first two of these techniques. Equations have been developed to account for the energy reflected from the environment and to determine directly the sample temperature using hot and cold blackbody targets. In method one, only a hot sample measurement is made and the reflected background energy is removed by modeling; in method two the sample is cooled and the reflected energy is measured directly. The second major difficulty inherent in emission measurements is the determination of the sample temperature. This problem has been addressed by fitting a blackbody curve over a region where the sample emissivity is assumed to be unity, and then scaling the sample emission back to the temperature of the blackbody (13). A result of this scaling is that the derived emissivities have been normalized to unity at some point and cannot be considered absolute values. However, for most rocks and minerals, there is some wavelength region between 6 and 50 μm in which the initial assumption is very nearly met. Estimates of the error in this technique suggest that relative emissivity can be obtained to approximately 1%, and absolute emissivities to 2-15%, depending on the validity of the assumption that the emissivity of the sample is unity at some wavelength.

The emissivity determined here agrees well with hemispherically integrated reflectance data assuming Kirchoff's law. There are significant differences, however, between emission and

bidirectional or biconical reflectance measurements. These differences arise because these reflectance measurements are not appropriate for conversion to emissivity using Kirchoff's law. Once emissivity has been determined, these data can be used in quantitative studies to model the physics of the interactions between complex surfaces and the outgoing energy. The initial study presented here has investigated the effect of surface coatings, one of many non-ideal effects on the thermal emission from planetary surfaces. These results are directly applicable to emission spectra obtained for varnished terrestrial rocks, and may be relevant to the study of dust-coated surfaces on Mars.

Granite and granodiorite suites were collected with varying degrees of varnish. The distribution of varnish was determined using SEM photographs and spectra were obtained of each varnished sample. To model the effect of varnish, two linear models are developed: the first assumes linear mixing of independent emission from the substrate and varnish (checkerboard model); the second models transmission through an absorbing/emitting medium. For a checkerboard model the resulting emissivity should vary linearly with abundance, whereas for coatings the emissivity should vary linearly with the factor e^{-kx} , and exponentially with coating thickness. It was found that there is a linear relationship between the spectral contribution of the varnish and the median varnish thickness, both in wavelength regions where varnish is relatively transparent and where it is strongly absorbing. These results are consistent with the checkerboard model and indicate that patches of varnish dominate the surface, consistent with the competing processes of varnish growth and spallation on rock surfaces. The SEM observations confirm the wide variation in varnish thickness at small scales. In detail, the spectral properties reflect the combined effect of both the checkerboard and layer models. Although the number of thick varnish patches *decreases* roughly exponentially with increasing thickness, their effect on the spectrum *increases* exponentially with thickness. Thus, the result appears roughly linear with the degree of varnish.

In addition to providing a measure of varnish thickness, the spectral data can be used to estimate the composition of the substrate through varnish layers up to 40-50 μm in median thickness using spectral regions in which the varnish is relatively transparent. Conversely, if the spectrum of substrate material is known, then the composition of the coating can be determined by a linear separation of the substrate and composite spectrum. This approach proved successful and a close match was found between the derived varnish spectrum and that of mixed layer clays, in agreement with earlier work by Potter and Rossman (14). Thus, for rock coatings typical of those found in desert environments on Earth, thermal infrared spectral observations provide an excellent means for penetrating relatively thick (median thickness up to $\sim 40\text{-}50 \mu\text{m}$) layers of this material to probe the composition of the underlying rock. For remote sensing applications on Mars this wavelength region should provide a powerful tool for compositional mapping of coated and dust-covered rocks.

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