Thermal Infrared Emission Spectroscopy of Natural Surfaces: Application to Desert Varnish Coatings on Rocks

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Thermal infrared spectroscopy has become an increasingly important tool for remote compositional analysis and geologic mapping. Most published laboratory measurements have been obtained in bidirectional reflection or transmission, whereas remotely sensed thermal infrared data are obtained by measuring the emitted energy. Section 2 of this paper describes a laboratory technique for determining calibrated emissivities of natural surfaces. Equations are developed to account for the energy reflected from the environment and to determine directly the sample temperature from measurements of hot and cold blackbody targets. Two methods for determining emissivity are developed: one in which only a hot sample measurement is made and the reflected background energy is removed by modeling, and a second in which the sample is cooled and the reflected energy is measured directly. Relative emissivity can be obtained to approximately 1% and absolute emissivities can be obtained to 2–15%, depending on the validity of the assumption that the emissivity of the sample is unity at some wavelength. The emission data agree well with the hemispherically integrated reflection data but point out problems associated with bidirectional reflectance measurements. Section 3 applies emissivity measurements to the study of layered surfaces consisting of desert varnish coatings on granite and granodiorite rock suites. 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. Regardless of whether the varnish is or is not relatively transparent and strongly absorptive, the spectral effect of varnish increases linearly with varnish thickness, indicating that thick patches of varnish dominate the spectral properties. As a result, median varnish thickness can be determined from spectral measurements. In addition, the composition of a substrate can be estimated through varnish layers up to 40–50 μm in median thickness, and the composition of the varnish material can be determined if the substrate material is known. The varnishes studied are composed primarily of clay materials, consistent with previous studies of varnish composition.

1. Introduction

Thermal infrared (IR) vibrational spectroscopy has long been used as an analytical tool for determining the composition of organic and inorganic materials. Major rock-forming minerals have fundamental molecular vibrational modes that produce spectral features in the range from ~6 to ~50 μm, which is the spectral range considered for this work. Recently, vibrational spectroscopy has been used to study the composition of geologic materials, with particular emphasis on remotely obtained emission spectra of natural surfaces [Kahle and Goetz, 1983; Gillespie et al., 1984; Kahle et al., 1988; Crisp et al., 1990; Weitz and Farr, 1992]. Part of this renewed interest in the thermal IR wavelength region stems from the deployment of airborne multispectral scanners, such as the thermal infrared multispectral scanner [Palluconi and Meeks, 1985], the Mars Observer thermal emission spectrometer [Christensen et al., 1992], and the advanced spaceborne thermal emission and reflectance radiometer under development for the Earth Observing System.

A wealth of excellent laboratory spectra that provide a basic understanding of thermal IR spectral features has been obtained [Lyon, 1965; Farmer, 1974; Salisbury and Walter, 1989; Walter and Salisbury, 1989; Salisbury, 1993; Crisp et al., 1990; Hoover and Kahle, 1987; Bartholomew et al., 1989; Salisbury et al., 1991b]. These data have demonstrated the systematic variations in thermal IR spectral features produced by the vibrational motions of atoms within crystalline materials. The frequencies (or wavelengths) of these absorption features vary with mineral composition and crystal structure and provide an excellent means for determining composition. These earlier studies form the foundation for modeling the complicating effects found on natural surfaces, including (1) particle size variations, (2) intimate mixtures with various compositions and particle size distributions, (3) coatings and varnishes, and (4) geometry.

To date, virtually all laboratory spectra have been obtained using reflection or transmission methods [Salisbury and Walter, 1989; Walter and Salisbury, 1989; Salisbury et al., 1991b], with only a limited number of measurements taken in emission [Brown and Young, 1975; Conel, 1969]. In contrast, remotely sensed thermal IR 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 Kirchhoff's law, ε = 1 – R, where ε is the emissivity of the material and R is its hemispherically integrated reflectivity. These conditions are not always met in nature or in a laboratory. For example, bidirectional or biconical reflection measurements are not appropriate for a quantitative assessment of emissivity [Salisbury et al., 1991b]. In addition, spectral measurements collected in a vacuum showed that steep thermal gradients result in an apparent violation of Kirchhoff's law owing to the lack of isothermal conditions [Logan et al., 1973]. Radiative transfer modeling to account for potential nonideal condi-
tions is complex, as scattering by particles close to the wavelength in size may be significant [Conel, 1969; Hapke, 1981; Clark et al., 1990; Salisbury and Wald, 1992; Moersch, 1991]. As a result, not all of the effects of environment are well understood. For example, in reflection measurements through complex, coated surfaces, the incident beam must traverse the coating material twice before the reflectance is measured. Thus any complicating factors, such as geometric effects or temperature gradients induced in the laboratory environment, may affect the final spectrum. 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.

This paper is organized into two distinct parts. In section 2 we describe a laboratory technique for determining emissivity. In section 3 we discuss a particular application of laboratory emissivity measurements to the study of desert varnish coatings on natural surfaces. The objective of the study in section 3 is twofold. First, we discuss the spectral effects of desert varnish on the spectrum of an underlying rock for various thicknesses of varnish. Second, we consider how these spectral measurements can be inverted to determine the composition and thickness of varnish coatings. Those readers not concerned with the intricacies of emission measurements are encouraged to skip directly to section 3 of this paper.

2. LABORATORY THERMAL IR EMISSION MEASUREMENTS

The collection of emission data is complicated by several factors, including (1) instrument calibration over a wide range of energy, (2) removal of atmospheric contributions, (3) difficulty in separating the energy of interest emitted by the sample from that emitted by the instrument and surroundings and reflected off the sample, and (4) determination of the sample temperature. The first two of these factors are common to all spectral measurements; the last two are unique to emission measurements. Each of these problems must be addressed through a quantitative calibration approach that is described below.

Instrument Calibration

The instrument used to obtain the laboratory data is a Mattson Cygnus interferometric spectrometer. The Fourier transform technique used with an interferometer typically assumes that the detector response is linear with incident energy, and no correction is made for nonlinearity in the instrument response with signal level in the interferogram. Thus, any correction made for nonlinearity in the transformed spectrum is inherently limited by this initial assumption. It is possible, however, to verify linearity in the response.

In an interferometer the energy measured at the detector $E_{\text{measured}}$ as a function of wavelength is the difference between the total energy leaving the target $E_{\text{target}}$ and the energy emitted by the instrument itself $E_{\text{instrument}}$:

$$E_{\text{measured}} = E_{\text{target}} - E_{\text{instrument}}$$  (1)

The voltage generated by the spectrometer $V_{\text{measured}}$ is given by

$$V_{\text{measured}} = (E_{\text{target}} - E_{\text{instrument}})*f$$  (2a)

where $f$ is the instrument response function. Measurement of two blackbodies, one hot and one cold, gives

$$V_{\text{hot}} = (B_{\text{hot}} - B_{\text{instrument}})*f$$  (2b)

$$V_{\text{cold}} = (B_{\text{cold}} - B_{\text{instrument}})*f$$  (2c)

where the energy of each component can be given by the Planck function $B$ at each wavelength. From these equations, $f$ can be determined by

$$f = \frac{(V_{\text{hot}} - V_{\text{cold}})}{(B_{\text{hot}} - B_{\text{cold}})}$$  (3)

If this response function is linear over a wide range of target temperatures, then a plot of $(V_{\text{hot}} - V_{\text{cold}})$ versus $(B_{\text{hot}} - B_{\text{cold}})$ should be linear and go through the origin.

The linearity of the Mattson instrument was determined by measuring spectra of hot blackbodies at temperatures ranging from 60° to 80°C and a cold blackbody at −150°C. These temperatures covered the range of sample temperatures used in this study. A linear fit to these data, constrained to pass through the origin, provides a quantitative estimate of the deviation from linear instrument performance. Deviations between the resulting fit and the measurements were less than 0.4% of flux at all wavelengths, indicating that the initial assumption of linearity was valid. This result is consistent with our expectations because the uncooled thermal detectors used have a linear response over the frequency range of this interferometer.

Atmospheric Contributions

Atmospheric contributions by water vapor and CO₂ were minimized by placing the samples in a closed, N₂-purged chamber during data acquisition and by collecting all samples and calibration targets under similar conditions. The calibration techniques described below should eliminate or minimize atmospheric effects. However, this process was not ideal for the data presented here, and some high-frequency spectral artifacts due to CO₂, H₂O, and instruments remain, most noticeably near 667, 1121, 1220, and >1300 cm⁻¹. These spectral features are well understood, however, and do not affect the results presented in this paper.

Emissivity Determination

Derivation of equations. The determination of emissivity requires that the energy of interest from the sample be separated from the energy emitted by the background, including energy that reaches the detector directly from the instrument as well as background energy reflected from the sample onto the detector. There are three basic approaches to this problem: (1) calculate the background energy reflected from the sample, assuming that the reflectivity of the sample is given by Kirchhoff’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.

Variations on these techniques have been described by
several authors [Buettner and Kern, 1965; Nerry et al., 1990; Brown and Young, 1975; Anderson et al., 1991]. Nerry et al. [1990] have described an approach that utilizes a large box enclosure that is set over the sample to control and determine the background emitted and reflected energy. The advantages of their approach lie primarily in the ability to observe large, undisturbed surfaces, with particular emphasis on field observations. Because of the sample size and the use of reflectance measurements, however, their method includes several complicating steps to determine the nonideal integrating factor and spectral emissivity of the box, the “form factor” of the sample, which is related to the bidirectional reflectance of the sample, and the bidirectional reflectivity of the reflectance standard [Nerry et al., 1990; Becker et al., 1985].

The methods we have developed here use the first two approaches described above (the third approach of cooling the chamber walls was described by Brown and Young [1975], but we were unable to overcome numerous problems with its routine application and will not discuss it further). An important advantage of the work described here is the use of high-emissivity blackbodies for calibration, including one at liquid nitrogen temperature, to determine the instrument response function and background radiation directly, thus eliminating the need for additional measurements.

Beginning with (1), the energy from the target can be separated into two components:

\[ E_{\text{target}} = E_{\text{emitted}} + E_{\text{background}} \]  

(4)

where \( E_{\text{emitted}} \) is the energy emitted by the sample under study and \( E_{\text{background}} \) is the total background energy that reaches the interferometer. This latter term includes energy emitted from the environment directly to the detector \( E_{\text{environment}} \) and energy emitted from the environment and reflected off of the sample \( E_{\text{reflected}} \). In practice, \( E_{\text{environment}} \) cannot be separated from \( E_{\text{instrument}} \) and can be included with this term for the purpose of discussion and calibration. Thus

\[ E_{\text{measured}} = (E_{\text{emitted}} + E_{\text{reflected}}) - E_{\text{instrument}} \]  

(5)

These energies are modulated by the instrument response function \( f \) during measurement to produce the voltage measured by the detector \( V_{\text{measured}} \). The resulting equation gives

\[ V_{\text{measured}} = [(E_{\text{emitted}} + E_{\text{reflected}}) - E_{\text{instrument}}] \cdot f \]  

(6)

Of these, only \( E_{\text{emitted}} \) is of interest; the remaining parameters must be identified and removed by calibration.

The energy terms can be expanded as the product of blackbody emission, given by the Planck function as a function of temperature \( B(T) \) and the emissivity of the material \( e \). The energy emitted from the environment and reflected from the sample \( E_{\text{reflected}} \) is a function of the emissivity and temperature of the environment \( \varepsilon_{\text{env}} \) and \( T_{\text{env}} \), respectively, as well as the reflectivity of the sample \( R_s \). Thus (6) becomes

\[ V_{\text{measured}} = \left[ \varepsilon_s B(T_s) + R_s \varepsilon_{\text{env}} B(T_{\text{env}}) - \varepsilon_B T_s \right] \cdot f \]  

(7)

where \( \varepsilon_s \) and \( \varepsilon_B \) are the emissivities of the sample and instrument, respectively, and \( B(T_s) \), \( B(T_{\text{env}}) \), and \( B(T_B) \) are energies emitted from the sample, environment, and instrument, respectively (subsequently referred to simply as \( B_s \), \( B_{\text{env}} \), and \( B_B \)). It is generally possible to make the “environment” surrounding the sample sufficiently blackbody in nature through the use of an enclosure to allow \( \varepsilon_{\text{env}} \) to be set to unity.

In a laboratory environment, four independent spectral measurements can be made: (1) hot sample, (2) cold sample, (3) a hot blackbody, and (4) a cold blackbody. These observations give four independent values of \( V_{\text{measured}} \):

\[ V_{\text{sh}} = \left[ \varepsilon_s B_{\text{sh}} + R_s B_{\text{env}} - \varepsilon_B B_B \right] \cdot f \]  

(8a)

\[ V_{\text{sc}} = \left[ \varepsilon_s B_{\text{sc}} + R_s B_{\text{env}} - \varepsilon_B B_B \right] \cdot f \]  

(8b)

\[ V_{\text{bh}} = \left[ \varepsilon_s B_{\text{bh}} + R_s B_{\text{env}} - \varepsilon_B B_B \right] \cdot f \]  

(8c)

\[ V_{\text{bc}} = \left[ \varepsilon_s B_{\text{bc}} + R_s B_{\text{env}} - \varepsilon_B B_B \right] \cdot f \]  

(8d)

where the subscripts sh and sc refer to samples observed hot and cold; bh and bc refer to blackbodies observed hot and cold; \( \varepsilon_s \) and \( \varepsilon_B \) are the emissivities of the sample and blackbody, respectively; and \( R_s \) is the reflectivity of the blackbody. In this set of equations, two variables can be eliminated by assuming that \( R_h = 1.0 \) and \( R_s = 0 \), giving

\[ V_{\text{sh}} = \left[ \varepsilon_s B_{\text{sh}} + R_s B_{\text{env}} - \varepsilon_B B_B \right] \cdot f \]  

(9a)

\[ V_{\text{sc}} = \left[ \varepsilon_s B_{\text{sc}} + R_s B_{\text{env}} - \varepsilon_B B_B \right] \cdot f \]  

(9b)

\[ V_{\text{bh}} = \left[ B_B - \varepsilon_B B_B \right] \cdot f \]  

(9c)

\[ V_{\text{bc}} = \left[ B_B - \varepsilon_B B_B \right] \cdot f \]  

(9d)

In (9), nine variables can be directly measured: \( V_{\text{sh}}, V_{\text{sc}}, V_{\text{bh}}, V_{\text{bc}}, T_{\text{sh}}, T_{\text{sc}}, T_{\text{env}}, T_{\text{sh}}, \) and \( T_{\text{bc}} \), leaving four unknowns \( \varepsilon_s, R_s, \varepsilon_B, \) and \( f \) and four equations.

The instrument response function \( f \) can be determined from measurements of a hot and cold blackbody as in (3). The product \( \varepsilon_s B_B \) can be determined from (9d):

\[ \varepsilon_s B_B = \frac{V_{\text{bc}}}{f} \]  

(10)

The desired quantity \( \varepsilon_s \) can now be determined by either of two methods: one in which \( R_s \) is assumed from Kirchoff’s law and only a single (hot) sample measurement is required and (9a) is used, or one in which no further assumptions are made, both hot and cold samples are observed, and both (9a) and (9b) are used.

Method 1: Emissivity determination assuming Kirchoff’s law. A relatively straightforward means for determining \( \varepsilon_s \) can be developed by assuming that the reflectivity of the sample \( R_s \) is given by Kirchoff’s law:

\[ R_s = 1 - \varepsilon_s \]  

(11)

The sample reflectivity in this case controls only the reflected component of the background energy that reaches the detector and should therefore be of secondary importance for samples heated well above the background temperature. Substituting \( R_s = 1 - \varepsilon_s \) into (9a) and substituting for \( f \) and \( \varepsilon_B B_B \) from (3) and (10), respectively, gives the emissivity of the sample as

\[ \varepsilon_s = \frac{(V_{\text{sh}} - V_{\text{bc}})}{(V_{\text{sh}} - V_{\text{bc}})} \frac{(B_{\text{sh}} - B_{\text{bc}}) + B_{\text{bc}} - B_{\text{env}}}{(B_{\text{sh}} - B_{\text{env}})} \]  

(11)
Method 2: Emissivity determination using two sample temperatures. The four unknowns identified in (9) can be uniquely separated with four spectral measurements consisting of a hot blackbody, a cold blackbody, a hot sample, and a cold sample. Combining (9a), (9b), and (3) gives

$$E_s(\lambda) - E_t(\lambda) = \alpha(\lambda)$$

Assuming that $E_s = E_t = 1$ and selecting a wavelength region where $E_s \sim 1$ gives

$$\frac{B_s(\lambda) - B_t(\lambda)}{B_t(\lambda) - B_r(\lambda)} = \alpha(\lambda)$$

Substituting for $B$ gives

$$\frac{1}{e^{c^2/\lambda T_b} - 1} - \frac{1}{e^{c^2/\lambda T_t} - 1} = \frac{1}{e^{c^2/\lambda T_t} - 1} - \frac{1}{e^{c^2/\lambda T_t} - 1}$$

where $c_2 = c_h/k$, where $c$ is the velocity of light, $h$ is Planck's constant $(6.258 \times 10^{-33} \text{ W s}^{-2})$, and $k$ is Boltzmann's constant $(1.3805 \times 10^{-23} \text{ W s}^{-1} \text{ K}^{-1})$. Solving for $T_s$ gives

$$T_s = \ln \left( \frac{c_2}{\lambda} \right) \left\{ \frac{(e^{c^2/\lambda T_t} - 1)(e^{c^2/\lambda T_b} - 1)\alpha}{(e^{c^2/\lambda T_t} - 1) + (e^{c^2/\lambda T_b} - 1)(\alpha - 1)} \right\} + 1$$

Once $T_s$ has been determined, then $\alpha(\lambda)$ can be determined at all wavelengths by substitution into (15). These values of $\alpha(\lambda)$ are then used to scale the sample spectrum to the known blackbody temperature. If this procedure is used, then the sample temperature is set equal to the blackbody temperature in the emissivity calculations.

This approach was verified by obtaining spectra of a blackbody at temperatures ranging from 61°C to 77°C and correcting them to that of a blackbody at a fixed temperature of 80°C (Figure 1). The initial spectra are shown in Figure 1a, with the corrected spectra shown in Figure 1b. A ratio of the coldest to the hottest blackbodies showed that the
adjusted spectra agreed to better than 0.5%, indicating that a correction for different temperatures can be successfully made. In addition, the “sample” temperature, derived from (16), of each blackbody agreed well with its measured value.

Laboratory Technique

The data were obtained using a Mattson Cygnus spectrometer with uncooled pyroelectric detectors at a spectral resolution of 4 cm⁻¹. Thirty-two individual spectra of each target were collected in 64 s and averaged together to improve the signal-to-noise performance. Two 60° cone blackbodies painted with IR-black paint were used for calibration. In order to provide the maximum sensitivity to ε, the hot sample and the blackbody were heated to ~65°C; the cold sample and the blackbody were cooled to liquid nitrogen temperatures (~196°C). For the spectra presented here, the rocks were heated in an oven for 24 hours in order to achieve isothermality and remove adsorbed water from the sample.

In order to control the emission from the environment, a chamber that places a blackbody cavity over the sample was constructed. The chamber is designed to minimize the energy falling on the sample from outside the chamber and ensure that the energy incident on the sample will be blackbody in nature. A parabolic mirror is placed in the external input port of the spectrometer to focus the beam downward and through a 6-mm aperture in the chamber. The chamber is 14 cm high, and the focused beam diverges and exits through an opening at the base 2 cm in diameter. Solid or powdered samples can be viewed through this opening. The chamber is constructed of insulating material and is kept at room temperature so that temperature variations within a set of measurements are negligible.

Application to Crystalline Quartz

The techniques outlined above were applied to an unweathered, broken sample of massive quartz. Figure 2a gives a comparison of the initial radiance spectra for hot blackbody and hot quartz samples together with the hot quartz spectrum scaled to adjust the sample temperature to match that of the blackbody. The emissivity of quartz was assumed to be unity from 1400 to 1600 cm⁻¹, and this region was selected to determine the sample temperature. Figure 2b shows the spectra for the hot and cold samples and the blackbodies. The difference between the cold sample and cold blackbody spectra is the reflected environment energy, which clearly represents a significant contribution.

The emissivity was calculated using these data and both method 1 (equation (11)), in which the reflected term is calculated, and method 2 (equation (12)), in which the reflected term is directly measured (Figure 3a). For coarse, uncoated materials, such as those illustrated here, the two methods should agree well. As seen in Figure 3a, the two methods agree to within an absolute emissivity of 0.05. Thus for fresh, broken rock surfaces, method 1, which does not require cooling of the sample, should be sufficient for most investigations. However, for more complex samples, such as the coated rocks described below, direct measurement of the reflected energy is preferable.

Figure 3b shows the comparison of the emissivity determined using method 2 with published biconical and hemispherical reflectance spectra of quartz [Salisbury et al., 1991b]. There are major differences between the emissivity measurements and Salisbury et al.’s biconical data. These differences are expected, because the biconical measurements do not satisfy Kirchoff’s law and fail to provide a quantitative determination of emissivity [Salisbury et al.,
Fig. 2b. Hot and cold quartz and blackbody radiance spectra. The upper curves are the hot blackbody and quartz spectra; the lower curves are the cold spectra and are negative because the energy from the cold scene is less than that emitted by the instrument itself.

1991b]. The maximum emissivity at the Christiansen frequencies and the emissivity at wavenumbers greater than 1350 cm$^{-1}$ are low, and the major band between 1050 and 1250 cm$^{-1}$ is much broader in the reflectance data. There is a much better agreement with the hemispheric reflection data, as expected, since Kirchoff's law is not violated [Salisbury et al., 1991b]. However, the reflectance data were taken of particulate quartz (75–250 µm), so a quantitative comparison of the bands depths is not possible. Despite this difference, there is a very good agreement in the

Fig. 3a. Emissivity determinations of quartz. Emissivity derived using the data from Figure 2b and the methods described in the text. The dashed curve was calculated from method 1 (equation (11)), in which the reflected term is calculated. The solid curve was calculated from method 2 (equation (12)), in which the reflected term is directly measured.
emissivity over the wavelength range for which reflectance data exist. In particular, emissivities at the Christiansen frequencies of 1350 and 820 cm\(^{-1}\) agree well, as does the shape of the major band between 1050 and 1250 cm\(^{-1}\). Thus in the case where it is appropriate to compare the emissivity and reflectance data, there is very good agreement between the two techniques.

**Error Analysis**

The primary systematic errors in determining absolute emissivity are (1) error in determining the effective radiative temperature of the sample for reference to the blackbody, (2) uncertainties and nonlinearities in the instrument function, (3) variations in temperature of the instrument and chamber during a complete set of measurements, (4) error in knowledge of the reflected component of the observed sample energy, (5) temperature gradients in the sample, and (6) nonunit emissivity of the calibration blackbodies.

As shown in Figure 1, errors in correcting the temperature of a sample with an assumed emissivity of unity at some wavelength to that of a known blackbody were approximately 0.5% in flux or emissivity, even when the temperature difference was as much as 14°C. In practice, the temperature differences between sample and blackbody were less than 5°C, so the error due to temperature uncertainty should be ≤0.5%.

If the maximum emissivity in the sample is less than unity, then the resulting normalized emissivities will be in error. An estimate of this error can be made using the sample temperature derived from the blackbody fit. For the data presented here, the deviation between the derived sample temperature and the temperature at the beginning of data collection was <5°C. Assuming a worst case, in which this difference was due entirely to the fact that the maximum emissivity was not unity, the deviation would translate to an error in emissivity of ~0.1. Thus in the worst case, emissivities determined in emission can be considered absolute only to this precision. In practice, however, this temperature variation is in large part due to difficulties in measuring sample temperature and cooling during data acquisition. In addition, the analysis performed in the study was done on quartz-rich rocks in which the emissivities between 6 and 7 μm are much closer to unity, so the absolute errors are ~1%.

The instrument response function for method 1 was determined using thermocouple temperature measurements of these blackbodies. Nonlinearities in response result in an error in flux or emissivity of ≤0.5%.

The instrument and sample chamber temperatures were calibrated, and temperature accuracy was determined to <2°C and found to be stable to <1°C. A worst case estimate of these errors was computed assuming a 2°C error in the sample, instrument, and environmental temperatures. The ratio of the resulting emissivities, which represents the error, is shown in Figure 4 for a granite sample. The emissivity error is emissivity dependent but for typical values is less than 1.5%.

Error in knowledge of the reflected component is difficult to assess. However, the use of a cold sample is specifically intended to remove this effect, including the complication of emission and reflection from the instrument itself. The errors should be comparable to the accuracy of the spectral measurements of the cold sample (~1%) times the magnitude of the contribution of the reflected component (~0–25%), resulting in an error significantly less than 1%.

Errors introduced due to temperature gradients in the sample are also difficult to determine directly because there
low-temperature surface processes in arid environments, and its potential for dating of surface exposures [Hunt, 1954; Engel and Sharp, 1958; Hunt and Mabey, 1966; Hooke et al., 1969; Potter and Rossman, 1977, 1979a; Perry and Adams, 1978; Allen, 1978; Dorn and Oberlander, 1981, 1982; Dorn et al., 1986]. Excellent work has been done on the composition of desert varnish, including the use of IR spectral techniques similar to those described here [Potter and Rossman, 1977, 1979a].

Desert varnish consists of a dull to lustrous, bluish-black to black coating of iron and manganese oxides, clays, and trace elements that form coatings on a variety of rock surfaces [Engel and Sharp, 1958; Potter and Rossman, 1977, 1979a; Elvidge, 1979; Allen, 1978]. Typical varnishes are made up of over 70% clay, consisting of montmorillonite, illite, and kaolinite, with minor amounts of chlorite [Potter and Rossman, 1977, 1979a]. The iron-manganese oxides in desert varnish consist of hematite and birennise [Potter and Rossman, 1979b], which occur in both amorphous and crystalline structural forms [Perry and Adams, 1978]. These oxides are responsible for the color of the varnish itself; the black coating exposed on the surface of the rock consists predominantly of manganese oxide, whereas the red-orange color on the underside of the rock is due to the preponderance of iron oxide.

The origin of desert varnish has been widely debated, with the rock substrate believed by some researchers [Engel and Sharp, 1958] to be the oxide source, whereas external derivation (i.e., dust or underlying soil) of varnish constituents is preferred by others [Perry and Adams, 1978; Potter and Rossman, 1977, 1979a; Allen, 1978]. The clay minerals in particular appear to have been transported from external sources [Potter and Rossman, 1977]. Microbial activity has also been proposed as an important component in the development of desert varnish [Dorn and Oberlander, 1981]. For the purposes of our study, however, the origin and rate of formation are of minor importance.

The work described here is not intended to expand earlier compositional studies of desert varnish. Instead, we consider varnish merely as a component in a complex “mixture” of materials and attempt to quantify the degree to which a coating masks the spectrum of the underlying rock. Thickness values for desert varnishes range from less than 2 μm to over 200 μm, with typical values between 10 and 30 μm (see review by Dorn and Oberlander [1982]). Thus it provides an excellent starting point for studying the effects of a coating on the infrared spectrum of the underlying rock. This relationship between varnish thickness and the resulting spectrum is important as a potential tool for determining the composition of varnished rocks using remote sensing on the Earth and other planetary surfaces and for quickly estimating varnish thickness. We note, however, that varnish varies widely in composition and that its formation appears to be related to specific environmental conditions. It is therefore not intended to be a direct analog for coatings that may occur on other planetary surfaces. Because of the common incorporation of microcrystalline clay minerals in its structure, it may, however, provide some insight into the effect of dust coatings on Mars.

**Approach**

**Sample selection.** Two suites of varnished granite and granodiorite samples were collected from sites in the Marble
Mountains, California [Thliveris, 1990]. These suites were specifically chosen to provide a wide range of varnish thickness over a range of substrate compositions. Other rock types in this study area disintegrate more rapidly than the varnish develops and did not produce thick varnish samples. In order to ensure proper representation of sample composition and spectral character, only samples with unmarrined varnished surfaces, indicating minimal transport, were used.

Varnish thickness determination. To determine the thickness of varnish surface coatings, each sample was analyzed in cross section under the scanning electron microscope (SEM). Sample preparation involved a four-stage process: (1) embedding the sample in epoxy, (2) cutting the sample to size, (3) grinding and polishing the sample, and (4) carbon coating the sample (see Thliveris [1990] for details).

Preservation of the desert varnish coating was of utmost concern because of the possibility of chipping at the cut edge. To minimize chipping and retain the continuity of the desert varnish coating, each sample was embedded in a resin-hardener mixture, cut to 1/4-inch (~0.64 cm) thickness, and then examined for chipping under a microscope. Any small holes were filled in with resin-hardener before the final cutting, and a final inspection was made to verify that no holes existed.

**Data**

Varnish thickness. Varnish thickness values were directly measured from SEM photographs. Low-magnitude (17×) reference mosaics were constructed for each sample of the varnished rock suites; high-magnification (170×) mosaics were used to obtain varnish thickness measurements, taken each 60 μm along the varnish cross section. The composition of each mineral constituent and of varnish coatings were confirmed by an X ray diffraction instrument attached to the SEM. Elements consistently identified in the varnish coatings include Mn, Fe, Ba, Ti, Al, and Si.

The resulting varnish thickness histograms for each granite sample are shown in Figure 5. The median thickness of the granite suite varied from 4.2 to 27.5 μm; the maximum thicknesses ranged from 127 to 236 μm (Table 1). The median thickness of the granodiorite suite varied from 3.5 to 17.4 μm, with maximum thicknesses from 30 to 107 μm. In general, the varnish is not uniformly distributed over the rock surface but instead occurs in localized accumulations within surface depressions.

Emissivity measurements. Figure 6 gives the emissivity spectra for the suite of varnished granite samples. The data were collected using the techniques described in section 2,
and the emissivities were derived using method 2 (equation (12)) with both hot and cold samples. Each spectrum represents an area approximately 2 cm in diameter taken from the same rock surface used to measure varnish thickness. Figure 7 gives the results for the suite of varnished granodiorite rocks.

Discussion

The effect of increasing varnish thickness on the thermal IR spectral properties is twofold. First, there are wavelength regions in which spectral features decrease in absolute depth with increasing varnish thickness but show little spectral variation (e.g., 1160 to 1300 cm\(^{-1}\); Figure 6). The varnish material is interpreted to be absorbing but spectrally gray in these regions. Second, there are wavelength regions in which new absorption features appear and increase in relative depth with increasing varnish thickness. For example, although the overall absorption in the region from 900 to 1350 cm\(^{-1}\) decreases with varnish thickness, the band from 950 to 1100 cm\(^{-1}\) increases in depth relative to the band between 1160 and 1300 cm\(^{-1}\). The varnish material must therefore have strong absorption features that are contributing to the composite spectrum in these wavelength regions. These two properties suggest that the appropriate use of different wavelength regions will allow a determination of the substrate composition and varnish thickness, using wavelengths where the varnish is spectrally grey, and the varnish composition, using regions where it is strongly absorbing.

**Modeling varnish abundance.** Two approaches to modeling the effect of varnish thickness on the resulting spectra have been considered: (1) "simple" linear mixing of end-member spectra and (2) full radiative transfer treatments incorporating multiple scattering and the particle size and

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate Fraction α</th>
<th>Median Thickness, μm</th>
<th>Emissivity at 526 cm(^{-1})</th>
<th>533 cm(^{-1})</th>
<th>1049 cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB15A</td>
<td>0.96</td>
<td>4.2</td>
<td>1.0</td>
<td>0.96</td>
<td>0.985</td>
</tr>
<tr>
<td>MB15C1</td>
<td>0.90</td>
<td>7.9</td>
<td></td>
<td>0.93</td>
<td>0.970</td>
</tr>
<tr>
<td>MB15D</td>
<td>0.58</td>
<td>16.5</td>
<td></td>
<td>0.90</td>
<td>0.934</td>
</tr>
<tr>
<td>MB15B</td>
<td>0.22</td>
<td>27.5</td>
<td></td>
<td></td>
<td>0.918</td>
</tr>
<tr>
<td><strong>Granite Suite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MB56A</td>
<td>0.84</td>
<td>3.51</td>
<td></td>
<td>0.93</td>
<td>0.919</td>
</tr>
<tr>
<td>MB28</td>
<td>0.47</td>
<td>15.9</td>
<td></td>
<td>0.89</td>
<td>0.903</td>
</tr>
<tr>
<td>MBUN</td>
<td>0.34</td>
<td>17.4</td>
<td></td>
<td>0.82</td>
<td>0.882</td>
</tr>
<tr>
<td><strong>Granodiorite Suite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6. Thermal emissivity spectra of the varnished granite suite. These spectra were measured in emission and derived using method 2 described in the text. Sample MB15A (least varnished) is shown as a dotted line, MB15C1 is shown as a short-dashed curve, MB15D is shown as a long-dashed curve, and MB15B (most varnished) is shown as a dot-dashed curve. The unvarnished granite is shown as a solid curve.
optical constants of each material. Multiple scattering of the outgoing energy is clearly important and should be included for optically thick samples composed of small particles. It has been addressed explicitly using radiative transfer models that make different assumptions about the single scattering albedo and phase function [Conel, 1969; Hapke, 1981; Morsch and Christensen, 1991; Henderson et al., 1992]. In theory, multiple scattering should be less important in the thermal IR than in the visible and near IR given the relatively low reflectivity of the materials and the long wavelength of the energy, both of which tend to minimize multiple scattering. In addition, mixing studies of relatively coarse particles (75–250 μm) show remarkably good agreement between measured and calculated spectra of mixtures (J. L. Thomson and J. W. Salisbury, The mid-infrared reflectance of mineral mixtures (7–14 μm), submitted to Remote Sensing of the Environment, 1992). Thus, we limit ourselves to linear mixing, which appears justified by the ability of this model to successfully reproduce measured spectra as discussed below.

We consider two possible models, both of which are linear in the strict sense. In a “checkerboard” model, the two components are assumed to emit independently so that

$$\varepsilon_{\text{mix}} = \varepsilon_1 \alpha + \varepsilon_2 (1 - \alpha)$$  \hspace{1cm} (17)

where $\varepsilon_{\text{mix}}$ is the observed emissivity of the mixture; $\varepsilon_1$ and $\varepsilon_2$ are the emissivities of the substrate and coating, respectively; and $\alpha$ is the fraction of component 1 in the mixture.

In a “layered” model, component 2 is modeled as a coating over component 1, using the equation of transfer through an absorbing/emitting medium given by [e.g., Schanda, 1986]

$$\varepsilon_{\text{mix}} = \varepsilon_1 e^{-kr} + \varepsilon_2 (1 - e^{-kr})$$  \hspace{1cm} (18)

where $k$ is the absorption coefficient and $x$ is the layer thickness. Equation (18) has the same form as (17), with $\alpha$ replaced by $e^{-kr}$. For a checkerboard model, the resulting emissivity should vary linearly with abundance, whereas for coatings, the emissivity should vary linearly with the factor $e^{-kr}$ and exponentially with coating thickness.

A test of these models was performed by determining the fraction of the two end-members ($\alpha$ or $e^{-kr}$) required to fit the composite spectrum. If this fraction is exponential with measured thickness, then the layered model is more appropriate, whereas a linear relationship suggests that a checkerboard model is best and the varnish is dominated by patches of material covering the surface.

Because the spectrum of the varnish is not known a priori, wavelength regions were selected in which the varnish is spectrally flat, as evidenced by a simple decrease in the spectral contrast of the varnished rocks with increasing varnish thickness (e.g., 1189 cm$^{-1}$ for granite). For these regions the varnish was assumed to have an emissivity of unity. This technique works best if wavelength regions where the varnish is spectrally grey correspond to regions where the substrate has strong absorptions, as is the case here.

Using a blackbody spectrum for the varnish together with the unvarnished granite spectrum, the substrate fraction $\alpha$ of each varnished rock was determined (Table 1) and plotted against the median varnish thickness (Figure 8). It is apparent from Figure 8 that the derived substrate fraction is roughly linear with measured thickness, consistent with a checkerboard model.
This method can be extended by computing a synthetic spectrum over the full wavelength range using unvarnished granite and a blackbody as end-members and the values of $\alpha$ derived above. Here, the assumption that the varnish is spectrally black over the full wavelength range is clearly wrong, and this model will not provide a good fit at most wavelengths. However, the difference between this and the measured spectrum should represent the spectrum of the varnish. In addition, the depths of the absorption features should be a function of varnish thickness. The measured and fit spectra of each varnished granite sample are shown in Figure 9; differences between the synthetic spectrum and the measured spectrum for both the granite and the granodiorite suites are given in Figure 10. The noise level in Figure 10 is relatively high because these curves are the differences between two derived spectra, each of which is derived from four individual spectra. However, a systematic trend in

Fig. 8. Dependence of apparent substrate fraction $\alpha$, derived using a linear mixing model, on median varnish thickness.

Fig. 9. Comparison of varnished granite spectra to fit spectra. Spectra were fit at 1189 cm$^{-1}$ using unvarnished granite and a blackbody as end-members together with the values of substrate fraction $\alpha$ given in Table 1. Observed spectra are shown as solid curve; synthetic spectra are shown as dashed curves. (a) Sample MB15A; (b) sample MB15C1; (c) sample MB15D; (d) sample MB15B.
difference spectra for both rock suites is apparent. This trend is consistent with an increase in the spectral effect of the varnish with increasing thickness.

The trend of increasing spectral effect with varnish thickness was investigated by relating band depths in the derived varnish spectrum to varnish thickness. The depths of bands in the derived varnish spectra corresponding to strong absorptions at 526 and 1049 cm$^{-1}$ (Figure 10) were plotted versus the median thickness for the granite suite (Figure 11). These data show that in the region of strong varnish absorption bands, the relationship between spectral features and thickness is also roughly linear, again consistent with a checkerboard model. A rough extrapolation of these data suggests that useful separation of the varnish and substrate composition can be obtained for varnish thicknesses of up to 40–50 μm.

The linear relationship found between median thickness and spectral properties indicates that the spectral signature
Fig. 11. Dependence of band depth on median varnish thickness (in micrometers) of granite suite. Band depths were determined from Figure 11. The 526-cm\(^{-1}\) band is shown as a solid curve, and the 1049-cm\(^{-1}\) band is shown as a dashed curve. Error bars representing 1.5% of the emissivity are shown.

of varnish on naturally occurring rocks is dominated by patches of thick varnish. This finding is consistent with the competing processes of varnish growth and spallation that affect the distribution of varnish on rock surfaces. The SEM observations confirm the wide variation in varnish thickness at small scales. In reality, the spectral properties reflect the combined effect of both the checkerboard and the layer models, because the patches of varnish vary in thickness. Although thick patches decrease in abundance roughly exponentially, their effect on the spectrum increases exponentially with thickness. Thus the result appears roughly linear with the degree of varnish. To the extent that median varnish thickness is representative of the age of a surface and the development of varnish, the spectral properties of varnished rocks should vary linearly with varnish development.

Varnish composition. In addition to providing a measure of varnish abundance, the data in Figure 10 can be used to estimate the composition of the varnish material. Figure 12 shows an emission spectrum of an optically thick varnish obtained from an intensely varnished granite together with that of a mixed-layer illite/smectite clay. These materials were reported by Potter and Rossman [1977] as a major component of varnish based on an excellent match with the infrared spectrum of varnish. As seen in Figure 12, there is a good agreement between the spectrum of the varnish material, derived here, and that of the mixed-layer clay, in agreement with the results of Potter and Rossman [1977]. The similarity between the derived varnish spectrum and that of mixed-layer clay is particularly remarkable in the 400- to 600-cm\(^{-1}\) region, where the spectrum of the underlying granite also shows considerable variability. The lack of perfect agreement in the location of absorption bands between our laboratory clay and the granite varnish is consistent with the range of spectral features associated with a range in clay composition from 95% illite layers to 35% illite layers in a mixed-layer illite/smectite clay [Salisbury et al., 1991b].

The identification of clay demonstrates that the spectrum of a varnish coating can be separated from that of the underlying rock substrate. This agreement further supports the ability of IR spectroscopy to separate complex, mixed spectra using relatively simple techniques.

Finally, a synthetic spectrum was computed for each of the granitic rocks using the average unvarnished granite spectrum and the spectrum of varnish used in Figure 12 together with the component fractions \(\alpha\) determined previously (Figure 13). These synthetic spectra represent a different approach to those shown in Figure 9, because now the varnish spectrum is assumed to be known. As can be seen, when both end-members are known, then there is reasonable agreement throughout the entire spectrum, again indicating that the varnish and substrate components can be successfully separated. It is also apparent that a linear mixture of the two components provides a good fit to the observations, thus justifying the initial assumptions of linearity in the mixing models.

Conclusions

A technique which, with a very limited set of assumptions, can be used to determine the emissivity of natural surfaces directly by using emitted energy has been developed. The emissivity determined here agrees well with hemispherically integrated reflectance data, assuming Kirchhoff'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 Kirchhoff's law. As a result, the direct emission techniques provide a better quantitative determination of emissivity than the reflectance measurements, with the exception of hemispherically integrated reflectivity.

Estimates of the error in this technique suggest that relative emissivity can be obtained to approximately 1% and absolute emissivities can be obtained to 2–15%, depending on the validity of the assumption that the emissivity of the sample is unity at some wavelength. The resultant emission spectra can then 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 nonideal effects on the thermal emission from planetary
Fig. 13. Synthetic spectra of unvarnished granite and optically thick varnish mixtures. (a) Synthetic spectrum of sample MB15A (dashed curve) produced using value of $a$ given in Table 1 together with the measured spectrum (solid curve) of MB15A; (b) synthetic (dashed line) and measured (solid curve) spectra of sample MB15C; (c) synthetic (dashed line) and measured (solid curve) spectra of sample MB15D; (d) synthetic (dashed line) and measured (solid curve) spectra of sample MB15B.

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 both on the Earth and on Mars. The following conclusions can be drawn from the results presented here.

1. For varnish coatings typical of those found in desert environments on Earth, thermal IR spectral observations provide excellent means for penetrating relatively thick (median thickness up to ~40–50 μm) layers of this material to probe the composition of the underlying rock. For remote sensing applications in arid regions, this wavelength region should provide a powerful tool for compositional mapping of varnished rocks.

2. The spectrum of a varnish material can be successfully separated from that of the underlying substrate by using relatively simple linear mixing models. As a result, the composition and thickness of the varnish can be determined. 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 [1977]. Thus the presence of varnish will be indicated by the presence of clay minerals, a potentially important result for remote sensing applications.

3. The relationship between varnish thickness and spectral properties was investigated using two models: linear abundance mixing and transmission through an absorbing/emitting layer. Both in wavelength regions where varnish is relatively transparent and in those where it is strongly absorbing, there is a linear relationship between the spectral contribution of the varnish and the median varnish thickness. This relationship is consistent with a model in which relatively thick patches of varnish contribute most effectively to the resulting spectral properties. Overall, the spectra of varnished rocks can be reasonably modeled using linear abundance dependent on median varnish thickness. The varnish can therefore be treated as a component of the surface, the spectral effect of which is the same as if it were distributed throughout the sample rather than as a layer on top. These results also suggest that varnish thickness can be mapped using measured emissivities, both in hand samples and remotely over large areas.