Quantitative thermal emission spectroscopy of minerals: 
A laboratory technique for measurement and calibration

Steven W. Ruff, Philip R. Christensen, Paul W. Barbera, and Donald L. Anderson

Department of Geology, Arizona State University, Tempe

Abstract. Previous descriptions of thermal emission spectroscopy have presented techniques that vary in accuracy and reproducibility. Contributions of thermal energy from the instrument and environment are major calibration factors that limit accuracy in emissivity determination. Reproducibility is related to the stability of these quantities. Sample temperature determination is also a significant factor in arriving at accurate emissivity. All of the factors which impact the measurement of emissivity using an interferometric spectrometer with an uncooled detector are isolated and examined here. An experimental apparatus is presented along with a description of a simplified measurement and calibration scheme used to arrive at quantitative emissivity of minerals. A detailed error analysis examines the effect of errors in each of the calibration parameters in isolation and as part of multiple error propagation. Sample temperature determination from radiance can create emissivity error, but 95% of published minerals have an emissivity maximum of 0.98 or higher, resulting in emissivity error of 2% or less. With worst-case systematic and random errors included, emissivity can be determined with an uncertainty of ~4%. In most cases it is less than 2%. Reproducibility with this technique is better than 1%.

Introduction

Vibrational spectroscopy provides a means for studying geologic materials both in the laboratory and in remote sensing applications. The physical processes which give rise to vibrational spectra and the relationship to mineralogy have been well documented [e.g., Kieffer, 1985; McMillan, 1985; Hawthorne, 1988]. Several techniques are available for performing vibrational spectroscopy including transmission, reflection, emission, and Raman methods. The focus of this paper concerns the acquisition and calibration of thermal infrared emission spectra in the range of ~6~25 μm using Fourier transform infrared (FTIR) spectroscopy. Because emission measurements do not require an active heat source, this method is ideally suited to remote sensing and field applications. A thermal emission spectrometer is being flown on the Mars Global Surveyor orbiter and will provide high spectral resolution data of that planet. The need for a library of thermal emission spectra for comparison with Mars spectra as well as for use in terrestrial applications has driven our investigation of emission spectroscopy.

Emissivity is an intrinsic property of a material, independent of sample temperature, spectrometer characteristics, and environmental conditions. It is defined as the ratio of the emittance of a sample relative to that of a blackbody at the same temperature. Many authors have described techniques for measuring emissivity and the difficulties associated with it [e.g., McMahon, 1950; Lyon, 1965; Low and Coleman, 1966; Conel, 1969, Griffiths, 1972, Hanel et al., 1972, Kember et al., 1979, Chase, 1981; Christensen and Harrison, 1993; Salisbury et al., 1994]. The goal of the evolution of our technique has been to improve both the accuracy and reproducibility of emission spectra. A related objective has been to develop a measurement technique that streamlines the spectral acquisition process and improves the primary goal.

The most often described measurement and calibration technique is the two-temperature method [e.g., Brown and Young, 1975; Kember et al., 1979; Chase, 1981; Conroy et al., 1987; Christensen and Harrison, 1993]:

\[
\varepsilon = \frac{E_{\text{comp}}(T_2) - E_{\text{comp}}(T_1)}{E_{\text{obs}}(T_2) - E_{\text{obs}}(T_1)}
\]

Here energy from the sample \(E_{\text{comp}}\) and blackbody \(E_{\text{obs}}\) targets is measured at two different temperatures. This technique will cancel contributions from reflected and instrument energy as well as from the instrument response function to arrive at an emissivity spectrum of the sample. Though this method is computationally elegant, it has several experimental flaws. Problems arise when trying to match precisely the temperature of the sample and blackbody target. Errors here lead directly to accuracy and reproducibility problems [e.g., McGuire et al., 1992]. Surface thermometry of rocks and minerals is challenging because of the need to measure the temperature of the emitting layer, which is the top few tens of microns of the sample [Nerry et al., 1990]. The two-temperature method also requires that background energetic remain constant during measurement of the four targets. Unless carefully controlled, temperatures within the instrument and environment can vary between measurements because of the presence of targets at different temperatures. Finally, the need to measure four targets to derive a single emissivity spectrum can be experimentally cumbersome.

The technique advocated in the current work is a variation
Figure 1. Schematic diagram of the optical layout of the spectrometer and sample apparatus.

Theory

Background

As was indicated in the abstract, this paper is concerned with emission measurements made with an interferometric spectrometer. This distinction is important because some factors in the calibration of data acquired from an interferometer combined with an uncooled detector are unique. The following discussion highlights these issues. For a more thorough introduction to this subject, see Mertz [1965].

The majority of infrared spectrometers use a Michelson interferometer as the spectral analyzer. This type of interferometer is composed of two mirrors oriented 90° from each other with a beam splitter dividing them at an angle of 45° (Figure 1). The source (a sample or blackbody target) and detector are each located at the end of one of the two arms of the interferometer. The detector, like the source, radiates energy toward the interferometer. This energy gets modulated by the interferometer in the same way as the source energy. Approximately half travels on to the source; the other portion returns to the detector. The detector beam undergoes one less reflection than the source beam and so arrives at the detector 180° out of phase. The result is that during the “dark” fringes from the source beam, the detector beam is “bright,” registering a signal at the detector [Mertz, 1965]. Calibration must address this situation.

Another interferometer-related calibration issue concerns the fact that the detector beam and the reflected source beam return to the source with the same amount of energy as that which reaches the detector. This energy can reflect off the sample and back into the interferometer, producing multiple-order spectral effects as a consequence of retroreflection [Hirschfeld, 1979]. Retroreflection has a trivial effect when the sample surface is not polished but should be considered for polished samples.

A final source of energy is that which reaches the detector directly without having passed through the interferometer. Objects within the spectrometer can radiate energy toward the detector. However, this energy is not modulated by the interferometer and so produces a voltage offset rather than the time dependent voltage associated with an interferogram and thus yields no spectral effects.

Calibration Quantities

The factors that affect the measurement of thermal emission have been identified and described previously [e.g., Kember et al., 1979; DeBlase and Compton, 1991; Rewick and Messerschmidt, 1991; Christensen and Harrison, 1993]. It has been recognized that in emission spectroscopy using an interferometric spectrometer, energy related to sample emission, reflection, and background sources is measured. Christensen and Harrison [1993] have defined an equation that accounts for all of these sources:

\[
V_{\text{mean}}(\lambda, T) = \left[ \varepsilon_{\text{sp}}(\lambda) B_{\text{sp}}(\lambda, T) + R_{\text{sp}}(\lambda) \varepsilon_{\text{rb}}(\lambda) \right] \cdot B_{\text{rb}}(\lambda, T) - \varepsilon_{\text{sp}}(\lambda) B_{\text{sp}}(\lambda, T) \]

(2)

The measured voltage, \(V_{\text{mean}}\), varies as a function of wavelength and temperature of the sample (or blackbody) according to (2). The emissivity of the sample as a function of wave-
length, \( e_{\text{samp}} \) is the desired quantity. Sample emissivity must be separated from \( B_{\text{samp}} \), the radiance of the sample which varies with wavelength and temperature according to the Planck equation. \( R_{\text{samp}}B_{\text{env}} \) is the term for energy that is emitted by the environment and reflected off the sample toward the interferometer. The instrument energy is represented by \( e_{\text{inst}}B_{\text{inst}} \), which includes all energy that passes through the interferometer not originating from the sample target. Finally, all of these terms are affected by \( F \), the response function of the spectrometer. The ability to obtain accurate measurements of sample emissivity depends upon the success in accounting for each of these terms.

Excluding the response function, each of the terms in (2) contains a temperature dependent radiance variable \( (B) \), a quantity described by the Planck equation. The relationship between temperature and radiance given by the Planck equation allows radiance to be derived when temperature is known or temperature to be derived when radiance is known. These two situations arise through a combination of experimental technique and algebraic manipulations of (2). When measured spectra of the blackbody and sample are converted to radiance, it becomes possible to manipulate individually all of the terms in (2). The following sections describe the methods for examining these quantities.

**Response function.** The basis for converting spectral measurements to units of calibrated radiance is the removal of the instrument response function [e.g., Hanley et al., 1972]. At its simplest the response function represents the conversion factor between the detector output in volts and the sample output in watts. However, spectrometer components do not respond perfectly at all wavelengths of light. The net result is a departure from ideal spectrometer performance that must be corrected. This correction is accomplished by measuring a blackbody at two different known temperatures. In the case of a perfect blackbody source, \( e_{\text{bb}} = 1 \) and \( R_{\text{bb}} = 0 \). Equation (2) then can be manipulated to produce

\[
F = \frac{V_{\text{bb}}(T_i) - V_{\text{bb}}(T_j)}{R_{\text{bb}}(T_i) - R_{\text{bb}}(T_j)} \tag{3}
\]

The radiance quantities in the denominator are generated by inputting the two known blackbody temperatures into the Planck equation.

**Instrument energy** \( (e_{\text{inst}}B_{\text{inst}}) \). All of the energy that reaches the detector not originating from the sample target combines to produce an inseparable component that will be called “instrument energy.” Using the instrument response function determined from (3) and a blackbody measurement, it is possible to calculate the instrument energy:

\[
e_{\text{inst}}B_{\text{inst}} = B_{\text{bb}} - \frac{V_{\text{bb}}}{F} \tag{4}
\]

This derived quantity represents the sum total radiance of all modulated background energy sources and the detector energy. In this form it is possible to determine whether the emissivity of the instrument \( (e_{\text{inst}}) \) is blackbody in nature. Because the spectrometer is a closed box with only a small opening and operated at ambient temperature, it is expected to behave like an isothermal blackbody. The advantage of blackbody instrument energy is that this quantity can be replaced by a Planck curve at the appropriate temperature thus reducing spectral noise in the final calibration. This analysis is given in the Results and Discussion section.

**Sample temperature.** As stated previously, one of the difficulties in emission spectroscopy is measuring sample temperature. In place of contact measurement, sample temperature can be derived from calibrated sample radiance \( (B_{\text{samp}}) \) to give brightness temperature. This type of noncontact temperature determination, alluded to by Lyon [1962] and expanded upon by Lyon and Green [1975], is simply a form of optical pyrometry.

Calibrated sample radiance is determined by first rearranging (2) to form

\[
e_{\text{samp}}B_{\text{samp}} + R_{\text{samp}}e_{\text{env}}B_{\text{env}} = \frac{V_{\text{samp}}}{F} + e_{\text{inst}}B_{\text{inst}} \tag{5}
\]

Equation (5) yields a quantity that has instrument energy and the response function separated out, resulting in radiance attributable to the sample only, although both emitted and reflected components are included. To isolate the sample radiance variable \( (B_{\text{samp}}) \) in order to determine temperature, it must be assumed that over some portion of its spectrum the sample has an emissivity of one and hence a reflectivity of zero. This assumption is met most closely at the Christiansen frequencies of the spectrum. It is at these frequencies that minerals display an emissivity maximum related to the optical constants \( n \) and \( k \). The Christiansen frequency has been defined by Henry [1948] as the frequency at which the index of refraction \( (n) \) of the sample equals that of the surrounding medium. In some minerals, such as quartz, the primary Christiansen frequency coincides with a low extinction coefficient \( (k) \), producing an emissivity very nearly equal to 1 [Cornet, 1969]. Assuming a value of 1.0, equation (5) can be written directly as

\[
B_{\text{samp(CF)}} = \frac{V_{\text{samp(CF)}}}{F} + e_{\text{inst}}B_{\text{inst(CF)}} \tag{6}
\]

where the subscript CF indicates the unique Christiansen frequency. From this quantity the brightness temperature of the sample can be obtained using the following form of the Planck equation appropriate for units of wavelength:

\[
T = \frac{h \nu}{\ln \left( \frac{2 \pi^2 \hbar^2 \nu^2 (B_{\nu})^{-1}}{h^2 c^3 k} + 1 \right) k} \tag{7}
\]

where \( h \) is Planck’s constant, \( \nu \) is frequency, \( c \) is speed of light, \( \nu \) is wavenumber, \( B_{\nu} \) is radiance, and \( k \) is Boltzmann’s constant. Because the Christiansen frequency is not known a priori, a brightness temperature can be calculated for all wavelengths of the radiance spectrum produced from (5). The highest temperature is then used. For most minerals, use of (6) and (7) results in an error in absolute emissivity that, though small, is nonnegligible. This error will be examined in the Error Analysis section. If the value of the Christiansen frequency emissivity is known a priori from another measurement technique, it can be included in the calibration to provide a true absolute result.

**Reflected energy** \( (R_{\text{samp}}e_{\text{env}}B_{\text{env}}) \). In emission spectroscopy the sample target inevitably is illuminated by thermal energy from the immediate environment and instrument. This energy is reflected off the sample and into the optical path, combining with the emitted energy from the sample. Heating the sample well above room temperature helps to reduce the fraction of reflected to emitted energy, but the reflected component still must be characterized and removed. Difficulty
arises from the need to measure and maintain the temperature of the environment immediately surrounding the sample. Additionally, if the sample has a specular surface, energy from the instrument must be considered a major source of illumination. Finally, if a field stop is used over the top of the sample, care must be taken to keep it from reflecting sample energy or absorbing and then emitting energy back toward the sample.

A technique for quantifying environmental illumination utilizes a gold reflector to directly measure this radiance [e.g., Salisbury et al., 1994]. This technique is practical for routine use only when using a spectrometer with a cooled detector. A detector that operates at ambient temperature produces a very low signal when measuring energy that is close to its own, which is the case with environment energy. The imprecision that results from this low signal-to-noise measurement makes it unsuitable for quantitative work. A second difficulty with this technique is that the measurement is not made at the same time the sample is being measured. Any variability in the instrument or environment will not be accounted for properly. To avoid these problems, the following method is used.

**Sample reflectivity** ($R_{\text{samp}}$): The first variable in the reflected energy term is sample reflectivity. Kirchhoff's law relating reflectivity and emissivity ($R = 1 - \epsilon$) is valid in the current application [Salisbury et al., 1994], allowing a simple substitution to be made for reflectivity. Because emissivity is the desired quantity, replacing $R_{\text{samp}}$ with $1 - \epsilon_{\text{samp}}$ in the algebraic manipulation of (2) eliminates sample reflectivity as an unknown.

**Environment emissivity** ($\epsilon_{\text{env}}$): The energy that illuminates the sample is not necessarily blackbody in nature. Placement of an enclosure with a small aperture over the sample creates an effective blackbody environment. With the proper paint and an opening that is small relative to the field of view of the sample this sort of chamber closely approximates a blackbody cavity.

**Environment energy** ($B_{\text{env}}$): Sources of energy in the laboratory environment, in addition to being nonblackbody, are nonisothermal. The use of a chamber effectively prevents more distant thermal energy sources (e.g., lights and room walls and ceiling) from impinging on the sample. Instead, energy from the chamber is the dominant contribution in the illumination of the sample. If the chamber is temperature controlled, it provides the necessary stability and known temperature of the environment. Because its emissivity is assumed to be 1.0, Planck radiance at the temperature of the chamber can be substituted into (2). The validity of this approach is demonstrated in the Results and Discussion section.

### Emissivity Calculation

Each of the variables in (2) has been accounted for and described. The remaining variable ($\epsilon_{\text{samp}}$) can now be solved for by rearranging (2) to give

$$\epsilon_{\text{samp}} = \frac{V_{\text{meas}} - B_{\text{env}} + B_{\text{init}}}{B_{\text{samp}} - B_{\text{env}}}$$

(8)

This equation is similar to that found in method 1 of Christensen and Harrison [1993] but is written so that the instrument response function $f$ and instrument energy can be determined separately and input into the equation. The variables for the emissivity of the instrument and the environment have been dropped because they are assumed to be unity. Validation of these and other assumptions is given in the Results and Discussion section.

### Experiment

**Apparatus**

Spectra of mineral samples are acquired using a Mattson Cygnus 100 FTIR interferometric spectrometer equipped with an uncooled deuterated triglycerine sulfate (DTGS) detector and KBr beam splitter. Originally designed for transmission work, this spectrometer has been adapted for emission spectroscopy by removing the mirror closest to the external emission port and by disconnecting the internal IR source (Figure 1). The optical path is directed out of the external portal to the sample apparatus so that the sample itself can be used as the infrared source. Energy from the sample is collected by a 7.5-cm-diameter off-axis parabolic mirror with an 11.9-cm focal length and directed toward the interferometer. The mirror geometry produces a 37° cone normal to the sample surface and an elliptical field of view with its major axis variable from 1 to 5 cm. The use of a parabolic mirror increases the signal strength by allowing the collection of energy over a larger solid angle compared to a flat mirror [Handke and Harrick, 1986; Sullivan et al., 1992]. The mirror is mounted coaxially with the sample chamber on an assembly of translation and tilt stages that allows precise alignment through 6 degrees of freedom.

The sample chamber is a 20-cm-diameter double-walled copper cylinder, closed at the top except for a 1.5-cm opening through which the beam passes. Water from a constant temperature circulator is pumped through the volume between the inner and outer walls of the chamber that includes the top as part of this single volume. The interior surfaces have been painted with Krylon Ultra Flat Black. 1602 paint that has an emissivity equal to or greater than the 0.95 average determined by Stierwalt et al. [1963] for Krylon Flat Black. The bottom of the chamber is open to allow samples to be raised into place. A thermocouple placed into an insulated portion of the tubing that carries water out of the chamber is used for the environment temperature measurement.

The mirror/stage assembly and the chamber are enclosed in a plethysmograph glovebox adjacent to the external port of the spectrometer (Figure 1). Both the spectrometer and the glove box are purged continuously with “scrubbed” air from a Balston clean air package that removes particulates, CO2, and water vapor. A purged environment is necessary for two reasons: (1) the KBr beam splitter and the CsI lens in front of the detector will absorb water and degrade over time; and (2) CO2 and water have spectral features in the infrared region. These spectral features would calibrate out if the amount of these gases stayed constant during all measurements. Because this condition is difficult to maintain, an enclosure with sealable access ports (a glove box) is used. Additional N2 gas is pumped into the glove box during acquisition of spectra to enhance the purge. With this purge system the relative humidity inside the glove box/spectrometer system can be maintained to less than 5%.

Particulate samples are poured into Krylon black copper cups with an internal diameter of 3 cm, a thickness of 1.3 cm, and a depth of 0.5 cm. Samples are heated in an oven for several hours at 80°C to eliminate adsorbed water. During measurement the sample is placed in a holder that contains a heater unit. Sample temperature is monitored by an Omega time-proportional temperature controller connected to a ther-
mocouple placed into the sample at its outer edge. The heater unit is regulated by the controller which maintains sample temperature to approximately 0.2°C of the set point.

An integral part of emission spectroscopy is the use of a blackbody reference target with accurately known and controlled temperatures. Two blackbodies have been constructed using designs adapted from those used to build calibration targets for the Photopolarimeter Radiometer on board the Galileo spacecraft and the Thermal Emission Spectrometer on the Mars Global Surveyor. Each blackbody is solid aluminum and cylindrical in shape with a conical cavity 9.5 cm in diameter and a half angle of 15°, giving a depth of 15.75 cm. The inside cone is coated with black epoxy resin paint.

Each blackbody unit contains three electric heaters inserted 5.0 cm into the base of the cylinder and monitored by a 100-ohm platinum resistance thermometer (PRT) placed nearby. One blackbody is powered by three 100 W heaters and is used as the “hot” target (100°C). The second is powered by three 50-W heaters and is used as the “warm” target (70°C). The output of each unit is regulated by separate time-proportional temperature controllers. The temperature of each is monitored by four 1000-ohm PRTs, placed at the tip of the cone and two placed halfway up the cylinder. Each PRT resistance is measured and converted to temperature then averaged to provide a single blackbody temperature. Temperature gradients in the blackbodies, though small, are described in the Error Analysis section.

Procedure

The procedure for acquiring spectra begins by measuring the two blackbody targets. This establishes the instrument response function and initial instrument energy. Next, the sample cup is removed from the oven, inserted into the holder, and allowed to equilibrate to the 80°C heater set point. Multiple interferograms are collected and averaged by the spectrometer where the total number (usually 180) depends on the desired signal-to-noise ratio. The temperature of the water emerging from the chamber is monitored for use in the reflectance calibration. This process, including temperature equilibration, takes about 10 min.

To ensure an accurate determination of instrument energy, which can increase slightly over time, additional blackbody measurements are made about once per hour. Only one blackbody needs to be measured for this purpose following the initial two blackbody measurements.

Nonparticulate samples that do not fit into the cups can also be measured. These samples may be up to 11 cm in the maximum dimension. They are heated in the oven and placed in an insulated cup for measurement. Because active heating during measurement of these samples currently is not available, fewer scans are measured to minimize the problems associated with sample cooling.

Results and Discussion

A theoretical description has been given of the quantities involved in the measurement of emitted energy using a Michelson interferometer with an uncooled detector along with a suggested technique for quantitative calibration. The various quantities have been identified as discreet terms of a larger equation. These terms can now be examined from an experimental vantage point using data from the apparatus described above.

![Figure 2. Twenty-seven response function calculations over a 46-day period. The standard deviation is less than 1%.](image)

Response Function

As defined in this paper, the instrument response function is a quantity independent of instrument energy. Given this fact, small variations in the temperature of the detector, beam splitter, or any other components in the spectrometer should have no effect on the response function. Therefore it should not vary over time. Figure 2 shows 27 different response functions calculated with (3) using blackbody measurements made over a 46 day period. The standard deviation is less than 1%. This variation can be accounted for entirely by small errors in the blackbody temperatures. A 0.1°C error in the measurement of the two blackbody temperatures is sufficient to produce the observed variation. This is strong evidence for the stability of the response function of this spectrometer and its independence from instrument energy.

Much greater variation is evident in the region of water absorption from 1400 to 2000 cm⁻¹ and below 400 cm⁻¹ (Figure 2). This indicates the variability of water vapor content in the beam path from day to day despite the actively purged environment. The variability of water vapor means that a response function must be determined routinely even though the performance of the instrument is stable.

Instrument Energy

Characteristics. The instrument energy (εₘₑₙBₑₙₑ) shown by the solid line in Figure 3a is a radiance quantity derived from (4). To help reduce spectral noise in the final emissivity calculation, this radiance can be replaced with an ideal Planck radiance if it is truly blackbody in nature. A convenient way to demonstrate blackbody character is to convert the derived instrument radiance to brightness temperature using (7). Figure 3b shows the result. Except for noise the temperature plot is flat, as indicated by the superimposed dashed line representing the average brightness temperature. Only blackbody radiance will yield a constant brightness temperature. If, instead, the instrument were behaving like a graybody with an emissivity less than 1.0, for example, 0.99, the brightness temperature of its radiance would vary with wavenumber as demonstrated by the long-dashed line in Figure 3b. Once the average instrument brightness temperature is known, it is used to generate a Planck radiance curve. This is shown in Figure 3a by the dashed line overlaid on the derived instrument radiance. The fit to within 0.1% is further evidence for the “blackness” of the instrument energy. This allows Planck radiance at the derived
instrument brightness temperature to be substituted into the final emissivity solution (8). Because this Planck curve is free of noise, it translates into less noisy spectra.

**Stability.** A second issue involving instrument energy is its stability over time. A spectrometer with components that quickly change temperature in response either to exposure to the target or to changes in ambient temperature will require frequent blackbody calibration measurements. A way to examine the first situation is to measure continuously a hot target and look for changes in the raw spectra. Figure 4 shows 12 uncalibrated spectra from a stable, 100°C blackbody acquired during a 2-hour time period. They vary by less than 0.5%. If instrument components were warming (the detector in particular), the spectra would decrease in intensity. This is not the case. Instead, the small variation is the result of the duty cycle of the blackbody heaters.

Changes in ambient temperature will affect instrument temperature stability. A 1° or 2° change in room temperature is significant and will cause a similar change in the instrument temperature. To account for this, a new instrument temperature calculation can be done using the measurement of a single blackbody and (4). Monitoring the temperature of the detector circuit board is a simple way to gauge the point at which this blackbody measurement should be made.

**Sample Temperature**

It is convenient to determine sample temperature radiometrically. Quartz presents an ideal case because its Christiansen
frequency emissivity at 1359 cm\(^{-1}\) is so close to 1.0. Salisbury and D’Aria [1992] indicate a value of 0.998. The brightness temperature of quartz at this point, with this value, is within 0.13°C of the kinetic temperature for an 80°C sample. This allows a Planck curve to be fit at this wavelength (Figure 5) with minimal error (see the Error Analysis section for quantification). For other samples it is necessary to assume that there is a region of the spectrum that has unit emissivity. The mineral spectral reflectance library of Salisbury et al. [1991] shows that Christiansen frequency features of particulate samples vary from nearly zero to several percent reflectivity. Greater than 95% of these minerals have a reflectivity minimum of 2% or less in the region 1800–400 cm\(^{-1}\). This translates to emissivity maxima of 0.98 or greater. The spectra in this library were measured with a bidirectional apparatus, prohibiting direct comparison with emissivity spectra. Of the five hemispherically measured spectra also included, it appears that Christiansen feature reflectance values become even lower. A brightness temperature derived from a 0.98 emissivity maximum would result in an error in calibrated emissivity of approximately 2%.

A more detailed examination of this problem is given in the Error Analysis section. As a general rule, every 1% departure from unity of the Christiansen frequency emissivity results in an equal amount of error in final sample emissivity.

**Reflected Energy**

Energy reflected off the sample results from illumination by the environment. A well-designed, temperature-controlled chamber placed over the sample can serve as a controlled blackbody environment. This allows a Planck radiance quantity to be determined from the chamber temperature and substituted into the reflectance term. A gold diffuse reflector can be used to measure directly the radiance associated with the chamber \(e_{\text{env}}B_{\text{env}}\). This will give an approximate assessment of the blackness of the environment. The chamber must be heated well above its normal room temperature to provide a sufficient delta energy between it and the detector. With the reflector placed in the position of the sample the energy that arrives at the detector originates from the chamber walls. Figure 6a shows the radiance resulting from the reflected energy of the chamber heated to \(\sim 45°C\). When converted to brightness temperature, this radiance yields a nonsloping temperature plot (Figure 6b), indicative of a blackbody. The subtle spectral character in the 550–900 cm\(^{-1}\) region is probably the result of contamination of the reflector.

The precision of this analysis is compromised by the low signal produced by the relatively small difference between the detector temperature (\(\sim 30°C\)) and chamber temperature (\(\sim 45°C\)). Also, the absolute reflectivity of the gold diffuse reflector is not well known. An alternative to direct measurement of environment energy is to use a two-temperature calibration scheme that cancels reflected energy algebraically. If the resulting spectrum compares favorably with a spectrum that uses a calculated environment radiance, the quality of the

![Figure 4](image1.png)

**Figure 4.** Twelve uncalibrated blackbody spectra taken over the course of 2 hours of continuous scanning. The standard deviation is less than 0.5%.

![Figure 5](image2.png)

**Figure 5.** Calibrated radiance of quartz determined from (5). A Planck curve at the temperature determined from the Christiansen feature at 1359 cm\(^{-1}\) is overlaid.
blackbody environment chamber will be established. This analysis is given in the following section.

Calibration Comparison

The calibration technique being advocated in this paper will be referred to as the one temperature method. Method 2 of Christensen and Harrison [1993] is used as a comparison. For this analysis, particulate quartz (250–555 μm grains) is an ideal material. Its spectral character is well known, it has high spectral contrast, and it has a Christiansen feature with ε ≈ 1.0.

Method 2 is a form of the two-temperature technique given by (1). It differs in its use of calculated Planck radiance in the denominator rather than measured blackbodies. This necessitates dividing the sample voltages by the response function so that they are in the same radiance units as the Planck curves. This yields

\[
\varepsilon = \frac{V_{\text{samp}}(T_2)}{F} - \frac{V_{\text{samp}}(T_1)}{B(T_2) - B(T_1)}
\]

The temperatures \( T_1 \) and \( T_2 \) are determined by applying the Planck equation (7) to the Christiansen frequency of the two calibrated radiance curves of quartz that are generated using (5). Emissivity determined using (9) has the advantage of canceling reflected and instrument energy algebraically as in (1) but does not require the precision matching of sample and blackbody temperatures at the time of spectral acquisition. Because \( \varepsilon_{\text{env}}B_{\text{env}} \) and \( \varepsilon_{\text{int}}B_{\text{int}} \) are canceled rather than calculated, a spectrum calibrated with method 2 offers a useful reference to the one-temperature method.

In Figure 7a the dashed line represents the one-temperature method calculated using (8), and the solid line is from method...
2. The two match to better than 1% in the absorption features but deviate roughly 1% in the high-emissivity regions. This deviation can be accounted for entirely by the fact that the instrument temperature changed 0.1°C between the first and second measurement of the quartz sample. The absence of any unmatched absorption features indicates that no spectral artifacts exist in the emissivity of the environment (ε_{env}) or the instrument (ε_{inst}). As evidenced by the quality of fit in the absorption bands and the lack of spectral tilt, the radiance values B_{env} and B_{inst} have been quantified properly. The only real difference between these two spectra is the noise (Figure 7b). Because method 2 involves a second sample measurement, there is one more spectrum to contribute noise to the final emissivity result. So, with a better signal-to-noise ratio, the convenience of only one sample measurement, and less sensitivity to temperature changes, the one-temperature method emerges as a favorable technique. The effect of measurement errors and imperfect assumptions is examined below.

**Error Analysis**

**Methodology**

A detailed analysis has been performed to assess the magnitude of random and systematic errors in the one-temperature method. The technique by which these errors were examined was to apply varying input values to the calibration of a raw reference spectrum. In this way, any departure from the known emissivity of the reference spectrum can be quantified and attributed to a given source of error. The effect of single errors is examined first followed by an analysis of the effect of multiple errors propagated through the calibration.

In order to generalize the results to any mineral, a spectrum of constant emissivity is used as a reference rather than a variable emissivity mineral spectrum. This allows the examination of wavelength dependent errors for a fixed value of emissivity. A spectrum of constant emissivity describes both a blackbody and a graybody (ε < 1.0). Both are necessary in order to distinguish emissivity dependent errors. Because a perfect graybody is difficult to create, a synthetic spectrum is substituted. Equation (2) is used to create a raw spectrum that is a synthetic version of that produced by the spectrometer. A 0.5ε graybody at 80°C is used to examine the effect of errors associated with low emissivity at any wavelength. This synthetic graybody and a measured blackbody spectrum at the same temperature are shown in Figure 8.

At this point these raw spectra (V_{ samp}) can be calibrated using (8) to produce emissivity spectra. This calibration would yield spectra with emissivities of exactly 0.5 and 1.0 if the identical input values were used again. However, when the inputs are changed, some deviation from the known emissivity will occur. For example, if the instrument temperature is changed by 0.5°C, the result is a shift in emissivity (the dashed lines in Figure 9) relative to the known values (solid lines). To demonstrate the effect on a mineral sample, a quartz spectrum has been recalibrated using the same 0.5°C instrument temperature error, resulting in the offset seen in Figure 9. By systematically testing each of the input variables of (2) in this manner, the effect on emissivity can be examined.

In order to compare directly changes in emissivity between the graybody and the blackbody references, a simple normalization is employed. The difference between the modified and known emissivity is divided by the known to produce percent delta emissivity plots according to

\[
\Delta \varepsilon(\%) = \frac{(\varepsilon_{\text{mod}} - \varepsilon_{\text{known}})}{\varepsilon_{\text{known}}} \times 100 \tag{10}
\]

Without normalization the errors produced in the blackbody spectrum would appear to dominate those of the graybody.
Single Errors

Five different temperature inputs are required to produce the radiance quantities necessary for calibrated emissivity. These temperatures are either measured or derived from (1) a hot blackbody, (2) a warm blackbody, (3) the instrument, (4) the sample, and (5) the environment. Errors arising from the two blackbody temperatures cannot be treated as single point errors because of the way in which they propagate through the calibration. They are instead included in the subsequent section concerning multiple errors. Each of the graphs in Figure 10 isolates one of the remaining temperature variables and displays the percent delta emissivity resulting from three different possible temperature errors. Figure 10a demonstrates the effect of temperature errors applied to the graybody reference, while Figure 10b applies to the blackbody reference.

Instrument temperature error. The top graphs in Figures 10a and 10b display the effect of the instrument temperature variable. Instrument temperature error arises from changes that occur over the time period between the initial two blackbody measurements and the subsequent single blackbody measurement. When the instrument warms, the initially calculated temperature will be too low. For example, a 0.25°C warming will mean an instrument temperature error of −0.25°C, and the effect on the emissivity of the graybody reference is a change of ∼0.5–0.9% depending on wavenumber (solid line). Figure 10b shows that the change is smaller for a blackbody reference. These two graphs thus demonstrate the emissivity dependence of the instrument temperature variable as well as its wavelength dependence.

Sample temperature error. Sample temperature is derived from the radiance of the sample at its principal Christiansen frequency, yielding a brightness temperature. For minerals that have an emissivity less than 1.0 at this frequency the derived brightness temperature will be lower than the kinetic temperature of the sample. To determine the effect of a nonunit Christiansen frequency emissivity, three different values have been investigated, \( e_{\text{CF}} = 0.99, 0.98, \) and 0.97 at 1359 cm\(^{-1}\) (the Christiansen wavenumber of quartz). These values represent maxima that are commonly encountered in mineral spectra according to the spectral library of Salisbury et al. [1991]. For an 80°C sample the 0.99\( e_{\text{CF}} \) value gives a derived temperature of 79.59°C, and the 0.98 and 0.97\( e_{\text{CF}} \) values yield 79.18°C and 78.77°C, respectively. When these temperatures are used to calibrate the 0.5ε graybody and blackbody references, errors of the magnitude shown by the middle graphs of Figures 10a and 10b result. Note that the effect of these errors is identical for the graybody and blackbody reference, thus establishing sample temperature error as an emissivity independent effect.

Given the potential for different sample temperatures in the laboratory and also in field applications, an evaluation of the temperature dependence of sample temperature error is useful. The same \( e_{\text{CF}} \) values of 0.99, 0.98, and 0.97 are used but with kinetic temperatures of 25°C, 50°C, 75°C, and 100°C. When calibrated assuming \( e = 1.0 \), temperature and emissivity errors arise as shown in Table 1 and Figure 11. Figure 11 demonstrates that with decreasing sample temperature the emissivity error becomes nearly constant at all wavelengths. Also shown is the general trend that for each percentage point departure from unity, emissivity is affected by a similar amount of error.

Environment temperature error. In the experimental setup described above, the source of illumination of the sample is a water-cooled chamber placed over the sample. The environment temperature used to quantify this illumination is measured from the tube carrying the water exiting the chamber. Because the interior wall of the chamber is made of thin copper (0.064 inch) and painted with high emissivity paint, the temperature of the water should be the temperature of the radiating surface of the chamber. The temperature of the water leaving the chamber tends to be about 0.2°C higher than that of the water going in. Using this value as the systematic error and with a thermocouple accuracy of ±0.1°C, the environment temperature error is estimated at ±0.3°C.

The bottom two graphs in Figures 10a and 10b demonstrate the effect of a +0.3°C error along with values that are 2 and 3 times this value. Because a blackbody produces no reflected energy, it is unaffected by environment energy as shown in Figure 10b. The graybody is affected by environment energy, and a temperature error of +0.3°C produces an emissivity error of about 0.5%.

Multiple Errors

The previous analysis has shown the effect on emissivity of individual temperature errors. The effect of multiple errors that propagate through the calibration is the subject of the final set of graphs (Figures 12a and 12b). This multiple-error analysis, given below, provides a more complete assessment of the accuracy of the one-temperature method.

Blackbody temperature error. Blackbody measurements are the most crucial element of an accurate emissivity calibration. In addition to the need for unit emissivity, the temperatures of the blackbodies must be known with good accuracy. The instrument response function, calculated with the two blackbody measurements, is used in the derivation of the instrument and sample temperatures. This means that errors in the blackbody temperatures lead to errors in these derived temperatures, ultimately affecting the emissivity result.

Blackbody temperature is acquired through measurements from four platinum resistance thermometers (PRTs) implanted within the aluminum cone of each blackbody. The manufacturer-supplied accuracy value of these PRTs is ±0.041°C at 100°C, and the accuracy of our ohm meter gives temperature errors of ±0.03°C. This yields a random error of ±0.071°C. Systematic errors will arise from any temperature gradient between the heaters and PRTs and also between each...
embedded PRT and the emitting surface of the cone. The average standard deviation in temperature of the four PRTs is 0.26°C for the hot blackbody and 0.18°C for the warm one. These values give a good indication of the efficient heat conduction of the aluminum over the several centimeters between the lower PRTs near the heaters and the upper PRTs at the midpoint of the cone. This apparent efficiency suggests that the temperature gradient over the ∼1 cm distance between each PRT and the radiating surface can be neglected. An additional systematic error results from the duty cycle of the blackbody heaters. To minimize this error, the blackbodies are scanned for several times the period of the duty cycle, and the average PRT resistance is recorded. With these efforts, duty cycle error can be neglected. The net blackbody temperature error then is the standard deviation of the PRT temperatures plus random error, resulting in ±0.33°C for the hot blackbody and ±0.25°C for the warm one.

**Error propagation.** To evaluate the effects of propagated error, the following technique has been used. An instrument response function is generated using actual blackbody measurements but modified by including the estimated blackbody temperature errors. All combinations of blackbody temperature errors have been input into the calculation of the response function using (4): (1) hot blackbody (bbh) + 0.33°C and warm blackbody (bbw) + 0.25°C; (2) bbh + 0.33°C and bbw − 0.25°C, (3) bbh − 0.33°C and bbw − 0.25°C, and (4) bbh − 0.33°C and bbw + 0.25°C. Once the four modified response functions have been generated, they can be used in the calculations of instrument and sample temperature. The resulting incorrect temperatures are given in Table 2. At this point, the emissivity of the gray-
Table 1. Effect of Christiansen Feature Emissivity and Kinetic Temperature on Brightness Temperature

<table>
<thead>
<tr>
<th>Kinetic Temperature, °C</th>
<th>εCF Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td>25.00</td>
<td>24.99</td>
</tr>
<tr>
<td>50.00</td>
<td>49.78</td>
</tr>
<tr>
<td>75.00</td>
<td>74.62</td>
</tr>
<tr>
<td>100.00</td>
<td>99.48</td>
</tr>
</tbody>
</table>

The radiance from three different emissivities at four different temperatures was used to calculate the brightness temperatures shown in the table.

body and blackbody references can be calculated with (8) using the modified response functions and the derived instrument and sample temperatures of Table 2. Because a graybody is affected by environment energy, a +0.3°C environment temperature error is included. The departure from the known emissivity is calculated as before and shown in Figure 12a.

To complete the analysis of multiple error effects, the error associated with deriving sample temperature from a nonunit emissivity Christiansen feature must be included. For this analysis the value of 0.98ε is used because greater than 95% of the particulate minerals measured by Salisbury et al. [1991] have a calculated emissivity > 0.98. Table 2 gives the sample brightness temperatures (T samp) calculated using the modified response functions. Using the modified instrument and sample brightness temperatures, the graybody and blackbody references are calibrated according to (8). The resulting departure from their known emissivity is shown in Figure 12b.

Summary of Error Analysis

The effect on emissivity of all known sources of error in the one-temperature method have been modeled according to the techniques described in the previous sections. The resulting error plots (Figures 10–12) are intended to be used as an indication of the accuracy of the method and for addressing issues related to reproducibility. The following is a generalized description of the results of the error analysis.

Accuracy. Figure 12a gives a baseline indication of the accuracy that represents the impact of blackbody temperature errors as they propagate through the calibration. If the two blackbodies have errors with the same sign, as is the likely case with systematic error, the effect on emissivity is small. In fact, only low-emissivity features will be affected, the result of the strong emissivity dependence of instrument and environment temperature errors. The magnitude of error increases when blackbody temperatures have errors of opposite sign, but this is a less likely case. Figure 12b includes a sample temperature error that arises from a nonunit emissivity Christiansen feature using a typical value of 0.98ε. If it is assumed that blackbody temperature errors have the same sign, the net emissivity error is roughly 2%, with only a small emissivity and wavelength dependence.

Errors associated with temperature changes of the instrument and environment during sample measurements, and incorrect sample temperatures, add to the baseline blackbody temperature errors. To quantitatively assess the effect of these changes, Figure 10 can be added to Figure 12. Perhaps more useful is the ability to assess qualitatively the impact of these temperature changes on the appearance of emissivity spectra. A warming instrument will impart a sloping continuum toward lower wavenumbers that affects both high- and low-emissivity features. This is also true of an incorrect sample temperature, but the sloped appearance will be even more pronounced, serving as an indicator that a low Christiansen feature emissivity may be responsible. Finally, an incorrect environment temperature will create a sloping effect, but because high-emissivity features are much less affected, a reduction in spectral contrast will be the most noticeable effect.

Reproducibility. The reproducibility of multiple measurements of the same sample can be used as an indication of the precision of the one-temperature method. For these measurements a ~3 cm diameter × 2 mm thick slab of vein quartz was used. This type of sample eliminates the possibility of orientation effects that arise from viewing a relatively small number of crystals in a particulate sample. It also eliminates the effects of settling or other changes that result from agitation. The slab can be positioned repeatedly in the same orientation to ensure a consistent view for each measurement. Figure 13a shows the results of eight measurements of the slab from eight different days over a 10-day period. The standard deviation of these spectra is given in Figure 13b. The greatest deviations occur in the region of water absorptions (>1400 cm\(^{-1}\)) demonstrating the variable nature of atmospheric gases. This is also true of the CO\(_2\) spike at 667 cm\(^{-1}\). The remaining narrow spikes are due to spectrometer artifacts.

Over most of the wavelength range the standard deviation averages roughly 0.3%. A notable departure occurs around 500 cm\(^{-1}\) where the deviation jumps to about 1%. Possible expla-

Table 2. Effect of Blackbody Temperature Errors on Derived Instrument and Sample Temperatures

<table>
<thead>
<tr>
<th>T_{inst}</th>
<th>T_{samp}</th>
<th>ε_{CF}</th>
<th>ε_{CF}</th>
<th>T_{samp}</th>
<th>ε_{CF}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bbh+, bbw+</td>
<td>29.55</td>
<td>80.29</td>
<td>79.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bbh+ , bbw-</td>
<td>28.14</td>
<td>80.12</td>
<td>79.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bbh - , bbw</td>
<td>20.20</td>
<td>79.71</td>
<td>78.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bbh , bbw</td>
<td>30.68</td>
<td>79.88</td>
<td>79.08</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All combinations of expected hot and warm blackbody temperature errors were applied to the calibration of an 80°C "sample" with either a 1.0 or 0.98 emissivity Christiansen feature. The initial instrument temperature was 29.42°C. Abbreviations are bbh, hot blackbody; bbw, warm blackbody.
nations for this arc that (1) spectrometer responsivity rolls off sharply at wavelengths <500 cm⁻¹ (see Figure 2), (2) the combination of low emissivity at long wavelengths of the quartz absorption doublet makes it more susceptible to instrument and environment temperature errors, and (3) this quartz doublet is sensitive to orientation effects [see Wenrich and Christiansen, 1996].

Conclusions

The goal of acquiring accurate and reproducible emissivity spectra of minerals has been achieved through understanding, controlling, and quantifying factors that complicate the measurement. The experimental uncertainty of these spectra has been determined from a detailed error analysis. Background contributions associated with instrument and environment energy have been examined and quantified. This is facilitated by the use of radiance rather than relative energy units during calibration. Through experimental technique and algebraic manipulation of the root equation that describes the measurement, each of the quantities it contains has been characterized.

A streamlined method of spectral acquisition has been devised that requires only a single measurement of the sample, a departure from many of the previously described emission techniques. A controlled sample environment of known temperature makes this possible. Blackbody references are measured only once during the course of sample measurement in order to establish the instrument response function.

The error analysis has modeled the effects of various temperature errors on emissivity spectra. Those associated with the two blackbodies have the capacity to propagate errors throughout the calibration. This is minimized when the two temperatures are systematically high or low as opposed to high.
and low. Errors associated with changes in instrument temperature can be minimized by recalibrating a blackbody reference and recalculating instrument temperature. Radiance-derived sample temperature determination is favored over kinetic temperature measurement. The presence of an emissivity maximum (Christiansen feature) \( \approx 0.98 \) in 95% of the mineral spectra surveyed allows sample temperature to be determined from calibrated radiance with accuracy better than 2%. As a general rule, each percentage point deviation from unity of this feature yields approximately the equivalent error in a sample's emissivity spectrum. The stability and measurement of environment temperature are enhanced through the use of a water-cooled chamber placed over the sample. This chamber minimizes the error that arises from an uncontrolled environment.

Temperature errors produce spectral emissivity errors that can be both wavelength and emissivity dependent, prohibiting the assignment of a single error value to our technique. However, even with the worst-case combination of errors, sample emissivity values generated with the one-temperature method are expected to be correct to \( \pm 4\% \) and in most cases to within 2% uncertainty.

**Acknowledgments.** We thank Joshua Bandfield (Arizona State University) for making repeated quartz measurements for the reproducibility analysis. Discussions with Melissa Lane (Arizona State University) provided useful insights into some of the calibration issues. Jack Salisbury and Roger Clark gave detailed critiques of the manuscript that have improved the quality of this paper, for which we thank them. This work was supported by NASA grant NAGW 943.

**References**


D. L. Anderson, P. R. Christensen, and S. W. Ruff, Department of Geology, Arizona State University, Box 1404, Tempe, AZ 85287-1404. (e-mail: dla@email.asu.edu; phil@elex.asu.edu; ruff@esl.ucr.la.asu.edu)

P. W. Barbera, Fiberquant Incorporated, 5025 S. 33rd Street, Phoenix, AZ 85040.

(Received June 14, 1996; revised December 11, 1996; accepted February 18, 1997.)