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Temporal variations in the apparent emissivity of various materials

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1.0 ABSTRACT

Spectral emissivity measurements gathered in the longwave infrared region of the spectrum during a recent airborne hyperspectral data collection experiment indicated that the spectral emissivity of certain organic polymers changed by as much as 10% throughout the day. Inorganic and many other organic materials that were measured at the same time during this experiment showed no change. As this was an unexpected event, a subsequent experiment was designed to make emissivity measurements of several organic and inorganic materials over a 24-hour period/diurnal cycle. The results from this experiment confirmed that certain materials showed a significant spectral emissivity variation over this period. This paper will discuss some possible explanations for this variation and emphasize the significance and implications of this fact on the integrity of spectral emissivity measurements and spectral libraries being constructed in this wavelength region.

Keywords: infrared spectroscopy, emissivity, library spectra

2.0 INTRODUCTION

Emissivity is a fundamental optical property of a surface. This implies that field and laboratory measurements of a material's spectral emissivity, collected under the same geometric conditions and within instrument noise considerations, should be equal.

Spectral emissivity measurements in the longwave infrared portion of the spectrum were collected for several ground control panels deployed at Ellington Field in Houston, TX, USA during an aircraft collection campaign carried out using the SEBASS High-Altitude Research Project (SHARP) developed by the Aerospace Corporation. The collection plan called for the sensor to be flown both during the daytime and nighttime hours. The ground truth team was tasked to make measurements at coincident times to the aircraft overflight. Upon analysis of this data, unexpected differences in the measured spectral emissivity were identified. These differences, in some cases, exceeded 10% at certain spectral positions. In response to this unexpected finding, numerous additional spectral emissivity measurements were made of the materials in question around the clock over a several day period. A comparison of the results obtained from these varying conditions is discussed in the remainder of this paper along with possible explanations of the discrepancies. Some implications of these finding will be discussed as they relate to spectral emissivity libraries and the exploitation of remotely sensed imagery using data from these ground-based instruments.
3.0 EXPERIMENTAL OBSERVATIONS

The longwave infrared spectral emissivity measurements were taken using a Designs & Prototypes Model 102 Field Portable Spectrometer. This instrument employs a microFTIR developed by Korb et al. (1996) and was operated at 4 cm⁻¹ resolution over the bandpass from 1.5 to 25 microns. Measurements were made in accordance with the published field measurement protocols for this instrument established by the Spectral Information Technology Application Center (SITAC) protocols (Salvaggio and Miller, 2001). The spectrometer was calibrated before each measurement using the instrument’s integrated blackbody source. The source was presented to the instrument at both above- and below-sample temperatures. The sample and downwelling radiance measurements immediately followed the instrument calibration runs. Downwelling radiance was measured as the reflected energy from a “crinkled” aluminum foil panel, correcting for both the non-unit reflectance and self-emitted energy from the material itself. The Designs & Prototypes Model 102 was allowed to warm up for two hours before any measurements were made to minimize the effects of instrument drift during the measurement sequence. The entrance aperture of the spectrometer was positioned one meter above the sample surface and downwelling radiance reflectance source.

3.1 Houston Measurements

Spectral emissivity measurements were made of ground control panels placed on a grass field at Ellington Field in Houston, TX, USA on 2003 May 20 and 21. The measurements made on the 2003 May 20 date were started at approximately 1100 local time and continued until approximately 1500 local time. The temperature on this day cycled from 35 to 38 to 35 degrees Celsius during the measurement period. There were scattered clouds building up during the day preceding a thunderstorm that occurred that evening. The relative humidity at the airfield was reported to be 52%. All targets had been protected from dew formation during the overnight period and had been uncovered and exposed to the environment and solar loading for over 5 hours prior to the commencement of measurements. Some of the “darker” targets had very high surface temperatures at the time of measurement. There was no visible trace of surface water on any of the materials measured. The measurements made on 2003 May 21 commenced at approximately 1830 local time and continued through 2030 local time. During this period, the sun set behind some distant clouds. Many measurements were made in total darkness. Recorded air temperatures during this period of time slowly declined from a high of 30 degrees Celsius to 27 degrees Celsius.

In addition to the measurements of the panel materials, the Designs & Prototypes spectrometer was pointed directly up to record the spectral radiance from the sky propagating toward the ground above the sensor. Three of these measurements were made over the course of the two day ground-collection campaign; one deliberately viewing a cloud on 2003 May 20, and a second and third at the end of each measurement day.

Figure 1 illustrates the spectral emissivity measurements made of the water contained in the calibration pools located at Ellington Field for the experiment campaign. These measurements were made at 1400 local time on 2003 May 20 and 2000 local time on 2003 May 21. These spectra exhibit differences on the order of 1% to 2% across the bandpass of interest. Figure 2 illustrates measurements made of the indigenous grass at the airfield. Grass is a water-dominated material. These measurements, made at approximately the same times as the water measurements in Figure 1 exhibit differences smaller than those observed from the water surface. Spectra from a black foam core poster board panel are shown in Figure 3. Again, these spectra exhibit very small differences on a wavelength-by-wavelength basis over the bandpass of
Figure 1  Longwave infrared spectral emissivity for water collected at Ellington Field, Houston, TX, USA using a Designs & Prototypes Model 102 field portable spectrometer.

Figure 2  Longwave infrared spectral emissivity for indigenous grass collected at Ellington Field, Houston, TX, USA using a Designs & Prototypes Model 102 field portable spectrometer.
Figure 3  Longwave infrared spectral emissivity for black foam core poster board collected at Ellington Field, Houston, TX, USA using a Designs & Prototypes Model 102 field portable spectrometer

Figure 4  Longwave infrared spectral emissivity for silicon rubber commercial roofing underlayment collected at Ellington Field, Houston, TX, USA using a Designs & Prototypes Model 102 field portable spectrometer
interest at these two times of day. While the emissivity measured during the daytime hours is 1% to 2% higher than the emissivity measured at night, they do not exhibit a significant variation as a function of time and environmental conditions. The spectral emissivity of these materials appears to remain constant over time as one would expect the inherent optical properties of a material to remain. Figure 4 shows the first exception to this rule of emissivity constancy that was noticed. The material measured for this figure was another high emissivity material, silicon rubber. This material is often used as an underlayment for commercial stone roofs. The silicon rubber material exhibited the highest daytime temperature (95°C) of all materials measured. The material temperature was in line with all the other materials for the evening measurements (32°C). These measurements show a variation of several percent at particular locations across the bandpass and smaller or negligible differences at other locations.

Under good measurement conditions in the field, the Designs & Prototypes spectrometer is capable of measuring radiance and computing emissivity with 0.01-unit repeatability at all wavelengths when compared to laboratory data (Salvaggio and Miller, 2001). As evidenced in Figures 1 through 4, the field measurements made as part of this collection campaign do not meet the repeatability criteria that this instrument is capable of producing. This problem is exemplified in materials exhibiting overall lower emissivity values across the bandpass. Figure 5 shows the spectral emissivity of a 3M Tyvek panel at times very close to those shown for previous samples. The emissivity values for this material are different by approximately 0.1 units, on the order of a 10% difference in magnitude. Many other examples were obtained where the emissivity measured for the same material changed as the day proceeded. These other example data may be obtained from the authors upon request.

Possibly the most unexpected measurements that were made during the Ellington Field collection campaign are the sky measurements shown in Figure 6. These three measurements were made pointing the foreoptic of the spectrometer in a direct-nadir geometry (viewing the sky directly overhead). The three measurements that were made were; 1) 1518 local time, clear sky conditions, 2) 1931 local time, fully cloud covered sky, and 3) 2041 local time, clear, star-filled sky.

![Figure 5](image_url)

**Figure 5** Longwave infrared spectral emissivity for 3M Tyvek collected at Ellington Field, Houston, TX, USA using a Designs & Prototypes Model 102 field portable spectrometer
The measurement made at 1518 local time is far “too bright” in the longwave infrared bandpass. At this time there were no visible clouds within the spectrometer’s field-of-view. The measurement made at 1931 local time was made after the sky had completely clouded over. Another measurement was made at 2041 local time, after the sky had cleared following a thunderstorm. It can be seen that the cloud cover shows an increase in the overall radiance over this later clear sky measurement, however, the increase is not as great in magnitude as the spectral radiance measurement made earlier in the day.

In order to make sense of the phenomenology that had been observed, blackbody radiance curves were computed to match the sky radiance in regions near 6 and 15 microns. These regions were chosen since the atmosphere is optically thick near the band centers and as such will appear as a pure emitter at the ambient air temperature to the sensor. The resulting curves shown in Figure 7 represent blackbodies at 300K and 306K. The ambient temperature recorded at Ellington Field at 1500 and 2000 local time confirmed these derived values exactly.

Figure 8 illustrates just the longwave infrared region of the measured sky spectra along with blackbody curves that match these regions fairly well. The radianc spectrum collected of the clear night sky (2041 local time) is matched quite well by a 265K blackbody. This is a reasonable estimate for the radiative temperature of a clear, early summer, Houston sky. The cloudy sky spectrum (1931 local time) is matched fairly well by a blackbody radiator at 278K. The cloud layer present at this time was very thick, and it is safe to assume that this cloud was optically thick in the longwave infrared window. A blackbody at 278K produced a reasonable match to this sky spectrum. The derived temperature of 278K is approximately 12K cooler than the ambient air temperature. Using the standard adiabatic lapse rate of the atmosphere, this temperature differential would indicate that the base of the cloud layer was approximately 2 km in altitude, or approximately 7,000 feet AGL. Base on observations made at the airfield, this estimate is quite reasonable.

The 1518 local time measurement was made when there were no visible clouds, yet a window temperature of 293K can be estimated using the blackbody curve shown in Figure 8. The physical phenomenon that is causing the addition of this radiance is a spectrally-flat radiator with a fairly high longwave infrared emissivity; however, it is producing no detectable phenomenon in the visible wavelength regions. The radiance source cannot be cirrus clouds since the estimated temperature of 293K is too high for ice to exist in the atmosphere. The unknown radiator is not likely to be water vapor as the emissivity is too low to totally fill the longwave bandpass, particularly since the relative humidity at the airfield was only reported to be 52%. Water vapor absorption coefficients are 4 orders of magnitude less than liquid water (Hanst, 1998), so a likely candidate is the presence of liquid water.

There are two possible explanations for the differences that are seen, both involve the presence of liquid water. Liquid water has a very high emissivity in the longwave infrared region of the spectrum and is for all intents and purposes transparent in the visible region. Liquid water can be adsorbed (not absorbed) on surfaces or can form very tiny sub-visual droplets in the atmosphere. Based on reported liquid water absorption coefficients (Hanst, 1998), this probably requires too much water to be adsorbed on the surface to not be visually noticeable. In addition, the silicon rubber which showed significant emissivity differences between these two collection times was too hot to have any significant amount of adsorbed water during the daytime measurement. The more probable explanation was that liquid water in the form of nano-droplets was present which were sufficiently small to be Rayleigh scattering particles in the visible region with a small visible absorption coefficient thus producing negligible attenuation to the eye. Mass spectrometer measurements made over the past several decades have shown that water molecules can attach to air molecules in rather significant numbers. Near the earth's surface, there are ample aerosol particles that can serve as nucleation sites. A question arises as to how many water molecules must be attached before the water starts behaving like a liquid versus a vapor?

An estimate can be made of the amount of liquid water in the path. From Figure 7, the radiative air temperature was measured by the field spectrometer to be 306K in the spectral regions where the air is optically thick. This is close to the 308K ambient air temperature measured at the time of the spectral radiance was collected. Making the assumption that most of the water is local and therefore emitting at the effective air temperature of 306K, one can estimate an emissivity for this 306K liquid water emitter that would produce a match to the measured sky radiance. Figure 9 shows the spectral radiance assuming an emissivity of 0.8 translates to about 5-7 microns of water per molecule (Hanst, 1998).
Figure 6  Spectral radiance recorded by making a direct nadir looking measurement of the sky overhead at Ellington Field, Houston, TX, USA using a Designs & Prototypes Model 102 field portable spectrometer (the instantaneous field-of-view of the sensor is approximately 80 milliradians)

Figure 7  Blackbody radiance curves overlaid on the sky radiance measurements shown in Figure 6 – the temperatures of these radiators were chosen to provide a good fit in the optically thick regions outside the 8 to 14 micron transmission window in the atmosphere
Figure 8  Blackbody radiance curves overlaid on the sky radiance measurements shown in Figure 6 – the temperatures of these radiators were chosen to provide a reasonable fit in the longwave infrared bandpass.

Figure 9  Graybody radiance curves overlaid on the sky radiance measurements made at 1518 local time of a “clear” sky – the overlaid graybody curve was computed at a temperature of 306K with a broadband emissivity of 0.8.
3.2 Washington, DC Measurements

In an attempt to resolve many of the questions that were generated during the Ellington Field collection campaign, samples taken from the panels used were returned to the Washington, DC area so that more careful measurements could be conducted.

The first set of measurements addressed the question of whether the solar loading had any effect at producing the significant difference in spectral emissivity that was observed earlier. For these measurements, spectral radiance leaving the sample was collected while the material was in full sunlight and again while the material was being shaded. The sun block employed was kept far away from the sample so that the contribution to the downwelling radiance field was negligible. No significant changes were observed in this data beyond the noise expected from the Designs & Prototypes spectrometer.

The second set of measurements was taken over a 24-hour period from 19 through 20 August 2003. The sky was very clear on the 19 August with temperatures ranging from a low of 23°C to a high of 31°C. The morning of 20 August was clear and about 25°C warming to an afternoon high of 36°C with light clouds late. Many materials showed non-significant spectral emissivity variation in both the data collected at Ellington Field and in the time series collected in Washington, DC. Figures 10 and 11 show two materials that did exhibit significant changes over the 24-hour measurement period. The first material was a white foam core poster board. This material is used during many collection campaigns as a ground control panel due to its unique spectral signature as well as its low cost to deploy. The material is hydrophilic and will tend to take on moisture in humid environments. The second material was 3M Tyvek. It was chosen for its hydrophobic nature. The choice of material and the presence of significant changes in spectral emissivity indicate that it is probably not surface absorbed water or surface adsorbed water causing the discrepancies in emissivity. Clearly there was some external factor that was significantly influencing the measurements being made. In the data collected at both locations, there was a significant amount of variation in the downwelling radiance measurements. This suggests, as has been previously mentioned, that some atmospheric component is causing the observed difference measured emissivity.

![Graph showing spectral emissivity for white foam poster board](image)

Figure 10 Longwave infrared spectral emissivity for white foam poster board collected at Fort Belvoir, VA, USA using a Designs & Prototypes Model 102 field portable spectrometer
4.0 FUTURE WORK

Measurements have been started to take the same sample materials used in the previous two studies and examine them in the controlled confines of an environmental chamber. The temperature and relative humidity profile will be chosen to represent a typical Houston, TX, USA summer day. The measurements will be made with both the Designs & Prototypes Model 102 spectrometer and a Surface Optics 400T infrared reflectometer. The difference in collection philosophy between these two instruments will be used to make the same measurement both considering the atmospheric path between the instrument and the material as well as eliminating it. It is hoped that this study will clarify the source of the variation that is being observed, indicating whether it is a material-based phenomenology or to confirm the current suspicion that it is an atmospheric constituent that is not being accounted for in current measurement protocols.

5.0 CONCLUSIONS

The question must be addressed as to what is causing the emissivity variations? These measurements tend to point to particles in the sub-100 nm size range that have essentially no infrared or visible scattering component but have a large infrared absorption component. These findings are concerning as they raise doubt on the integrity of many infrared spectral measurements that have been made and included in spectral libraries over the years. Of particular concern are those materials with average emissivity values across the longwave portion of the spectrum below 0.9. Clearly, the authors of this paper and the measurement community need to continue to search for the cause of these variations and needs to establish acceptable field measurement protocols that can eliminate or minimize these variations.
6.0 ACKNOWLEDGEMENTS

Special thanks need to be given to Herbert J. Mitchell for his contributions to this work. His perseverance and drive to understand physical phenomenology are inspiring and make us all ask the questions that need to be asked when making optical properties measurements. The authors would also like to thank the National Geospatial-Intelligence Agency (NGA), the National Air & Space Intelligence Center (NASIC), and the Rochester Institute of Technology for their support and/or sponsorship for these studies.

7.0 REFERENCES


