1 NOMENCLATURE

General

ρ	Reflectance	Ratio between reflected and incident radiative flux;
α	Absorptivity	Ratio between absorbed and incident radiative flux;
ε	Emissivity	
I	Radiation intensity	
E	Emissive power	

Subscripts

λ	Spectral or monochromatic, i.e. wavelength dependent
h	Hemispherical (referred to the half-space in front of the specimen plane)
θ	Directional
n	Normal or quasi-normal
e	Emitted
b	Blackbody

2 THEORY AND DEFINITIONS

A detailed analysis of thermal radiation can be found in classical books like the ones by Incropera et al. [1] and especially Howell et al. [2]. We summarize here the concepts that are useful for the purpose of this work.

2.1 Emissivity and Kirchhoff law

The emissivity ε is an adimensional number that gives the measure of how well a body can radiate energy as compared with a blackbody. The emitting ability can depend on factors such as body temperature, the wavelength range being considered for the emitted energy, and the angle at which the energy is being emitted. The spectral, directional emissivity is defined as:

$$\varepsilon_{\lambda,\vartheta} = \frac{I_{\lambda,e}(\lambda,\theta,\varphi,T)}{I_{\lambda,b}(\lambda,T)} \quad (1)$$

where I is the radiation intensity, measured in [$W \cdot m^{-2} \cdot sr^{-1} \cdot \mu m^{-1}$], T the surface temperature and θ,φ an arbitrary direction in spherical coordinates. The radiation intensity emitted by the blackbody does not show a directional behavior since, by definition, its emitted radiation is perfectly diffuse. Kirchhoff law states that, without restriction, holds equation 3:

$$\varepsilon_{\lambda,\vartheta} = \alpha_{\lambda,\vartheta} \quad (3)$$

Where α is the surface absorptivity. For the energy balance, equation (4) must be true for any direction of incident radiation

$$\alpha_{\lambda,\vartheta} + \rho_{\lambda,\vartheta} + \tau_{\lambda,\vartheta} = 1 \quad (4)$$

Where ρ and τ are the hemispherical reflectance and transmission. Since the materials considered in this work are opaque, τ is zero, then

$$\alpha_{\lambda,\vartheta} = 1 - \rho_{\lambda,\vartheta} \quad (5)$$

Integrating spheres can measure the normal, or quasi-normal, hemispherical spectral reflectance, then from equations (3) and (5) we can obtain the normal spectral emissivity, given by equation (6)

$$\varepsilon_{n,\lambda} = 1 - \rho_{n,\lambda} \tag{6}$$

2.2 Planck distribution

The spectral emissive power of a blackbody has been determined by Planck. It is:

$$E_{\lambda,b}(\lambda,T) = \frac{C1}{\lambda^5\left[\exp\left(\frac{C2}{\lambda T}\right) - 1\right]} \tag{7}$$

where the first and second radiation constants are C1 = 3.478E+08 [W · μm^4 · m^{-2}] and C2 = 1,439E+04 [μm · K]. Equation (7) allows us to calculate the total emissivity, with the definition given in equation (8), for a given temperature T:

$$\varepsilon_n = \frac{\int_{\lambda_1}^{\lambda_2}(1 - \rho_{n,\lambda})E_{\lambda,b}(\lambda,T)d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\lambda,b}(\lambda,T)d\lambda} \tag{8}$$

where the interval $\lambda_1 - \lambda_2$ is the available wavelength range. It should be noticed that the emissivity is a temperature-dependent properties in two ways: first, the spectral region of emission changes according to equation (7), as it can be seen in figure 1

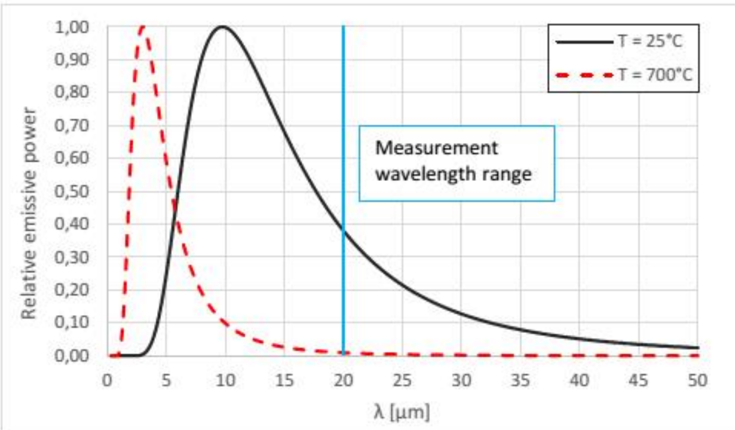


Figure 1: Relative emissive power for different temperatures

second, the spectral properties of the material can change with the temperature.
In this work, measurements are made at ambient temperature, T=25°C, and total emissivities are calculated in the available measured wavelength interval, from 0.3 μm to 20 μm, that covers 73% of the emitted radiation at ambient temperature and 98% at 700°C. An estimate of the total emissivity at 700°C can be given, based on spectral measurements at ambient temperature, and, although this approach is documented in open literature [3], it should be pointed out that the evaluation of the temperature dependency of the optical properties is beyond the purpose of this work. Therefore, the validity of the estimate remains to be proven.

The emissivity values at high temperatures can be measured more accurately with a dedicated experimental setup that heats the sample at the desired temperature. The emitted radiation can be measured with the same FT-IR spectrometer equipped with the external input beam accessory. A reference blackbody operating at the same temperature is also needed. An alternative in-situ and high temperature emissivity analysis can be made by means of a IR camera.

3 Experimental Setup and procedures

3.1 FT-IR spectrometer

The total reflectance in the MIR spectral region has been measured with the Perkin Elmer Frontier FT-IR spectrometer. In detail, the Frontier available at the **ThermA***Lab* laboratory of the Politecnico di Milano is equipped with a CsI beamsplitter, which allows a wavelength range up to 40 μm, and its main features are:

- Spectral resolution: 0.4 - 64 cm^{-1}
- Wavelength Accuracy: ±0.1 cm^{-1} at 1600 cm^{-1} ±0.02 cm^{-1} achievable
- Wavelength Repeatability: ±0.02 cm^{-1} at 1600 cm^{-1} ±0.008 cm^{-1} achievable

The spectrometer is equipped with the PIKE Upward IntegratIR 3" gold sphere, schematized in figure 1, for hemispherical reflectance measurements. The incident radiation is deflected towards the sample by a gold mirror, with an angle of incidence of 12°, and the reflected radiation is measured by a liquid nitrogen cooled MCT detector. The wavelength range available with this accessory is from 2 μm to 20 μm.

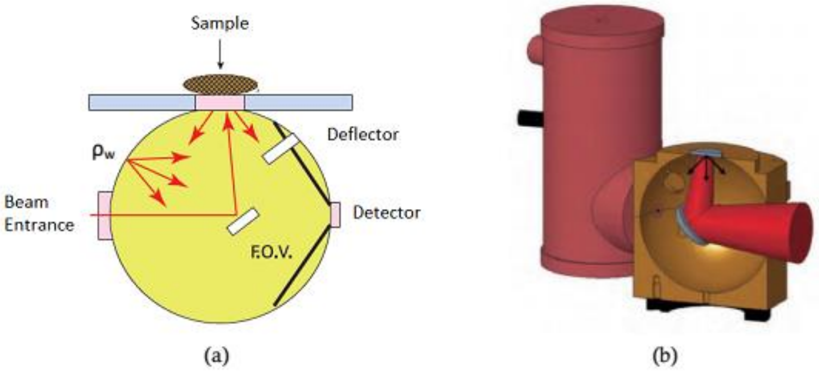


Figure 2: PIKE Upward IntegratIR gold integrating sphere, scheme [5] (a) and 3D drawing (b)

3.2 UV-Vis-NIR spectrophotometer

The spectrophotometer used in this work is a Perkin Elmer Lambda 950, which is a double-beam, double-monochromator spectrophotometer that allows measurements with a high accuracy and spectral resolution. The instrument, just like the Fontier, has a modular design, which allows an easy change of the measurement accessory. Its main features are:

- Spectral resolution UV-VIS: <0.05 nm
- Spectral resolution NIR: <0.20 nm
- Wavelength Accuracy UV-VIS: ±0.008 nm
- Wavelength Accuracy NIR: ±0.300 nm

In this work, the 150 mm Spectralon® integrating sphere is used for hemispherical reflectance measurements. This accessory is equipped with a PMT detector for the UV-Vis spectral region, from 200 nm to 860 nm, and a InGaAs detector for the NIR region, up to 2500 nm. The sample beam hits the sample with a 8° angle of incidence, according to the scheme of figure 3.

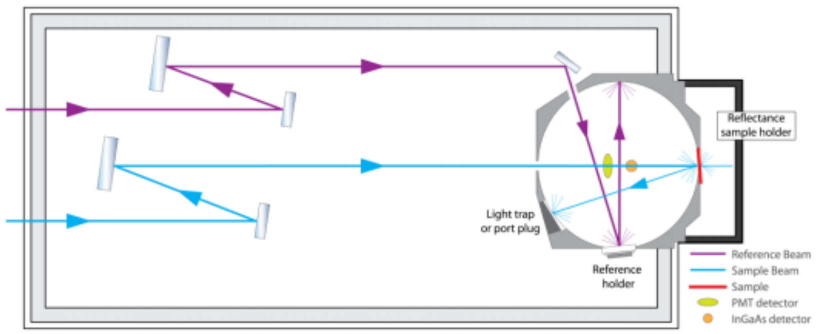


Figure 3: 150 mm Spectralon® integrating sphere optical scheme

3.3 Experimental procedures

3.3.1 Hemispherical reflectance measurements

The two integrating spheres allow the measurement of the normal-hemispherical reflectance, $\rho_{n\text{-}h}$, that is the reflectance for a normal (or quasi-normal) incident radiation and for a sampling region that encompasses the whole half-space in front of the specimen. The samples have been placed with the label side directed towards the sample beam, and have been held in position by a small weight on the gold sphere for MIR measurements, figure 4, and by a dedicated sample holder on the Spectralon® integrating sphere for UV-Vis-NIR measurements, shown in figure 5. No further sample preparation has been carried out. The wavelength range of our analysis goes from 0.3 μm to 2.5 μm for the UV-Vis-NIR region, and from 2 μm to 20 μm for the MIR region, therefore the two ranges overlap from 2 μm to 2.5 μm.

For the IR region, six measurements have been carried out for each sample, three after translating the sample in different positions, and three after a 90° rotation on the same positions.

For the UV-Vis-NIR region, three measurements have been carried out for each sample, because the IR campaign has shown that the sample inhomogeneity has a higher influence on the measurements than its rotation.

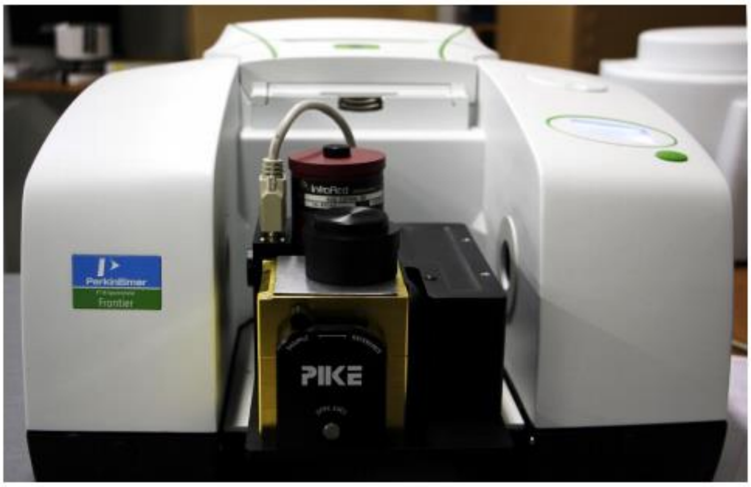
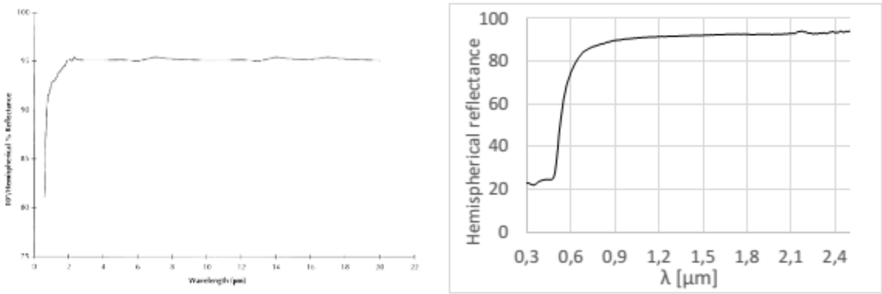


Figure 4: Perkin Elmer Frontier with PIKE IntegratIR gold sphere, sample in test position

Figure 5: Perkin Elmer Lambda 950 with Spectralon® integrating sphere, sample positioning

3.3.2 Infragold correction

Both instruments need to be calibrated with a high diffuse reflectance standard before the test campaign. The Lambda 950 has been calibrated with a NIST certified Spectralon® standard of well-known reflectance. The Frontier have been calibrated with a diffuse gold reference as 100%, then the measurements have been corrected by its measured NIR reflectance, that is assumed constant over the considered wavelength range based on the usual behavior of gold reference materials, as shown in figure 6.



(a) (b)

Figure 6: Typical infragold® MIR reflectance spectrum [6] (a), measured gold reference UV-Vis-NIR reflectance spectrum

3.4 Uncertainties

Additional test have been carried out to evaluate the measurement accuracy. In particular, repeatability measurements have been carried out on the Frontier with both the gold reference, with ten measurements, and the TA-01 samples, with three measurements on the same spot. The resulting standard deviation is very similar between the two sets of measurements, and is shown in figure 7 for the gold reference

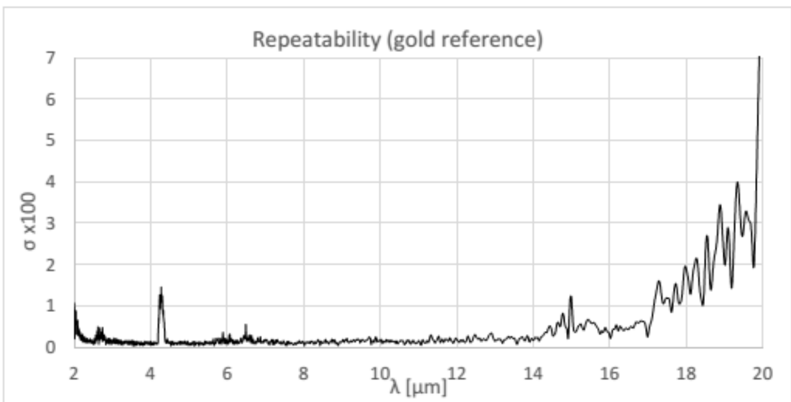


Figure 7: gold reference standard deviation, ten measurements

In particular, a small artifact can be noted around 4.3 μm, and three levels of accuracy can be seen in the whole wavelength range, as summarized in table 1. UV-Vis-NIR measurements are more accurate, although, as it will be shown, the effect of the sample inhomogeneity is one order of magnitude bigger than the accuracy of the instruments.

Table 1: Measurement uncertainties

Spectral range [μm]	**Instrument**	**σ x100**
0.3 – 0.85	Lambda 950	< 0.1
0.85 – 2.5	Lambda 950	< 0.2
2 – 14	Frontier	< 0.3
14 – 17	Frontier	< 0.6
17 – 20	Frontier	< 3

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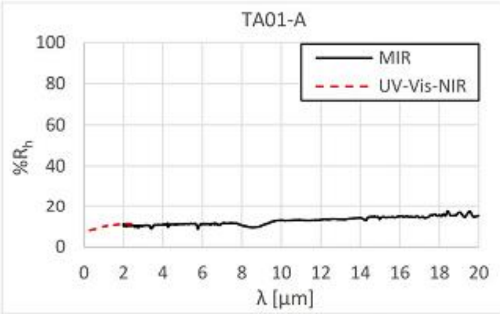
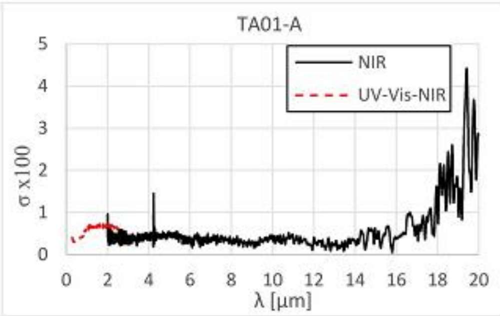


Quasi-normal hemispherical reflectance

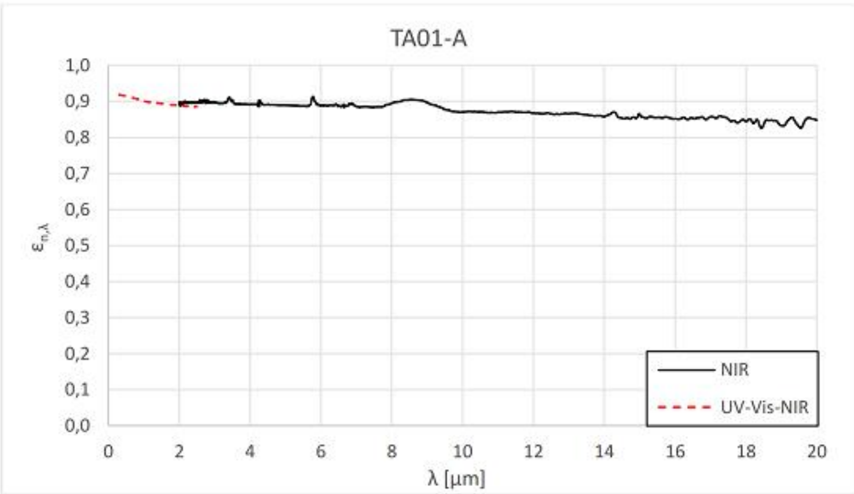
$\varepsilon_n(T_{amb}) = 0.87$

$\varepsilon_n(T_{700}) = 0.89$

Notes:



Standard deviation



Quasi-normal spectral emissivity