Introduction

Clean, efficient and reliable energy generation is still one of the most important challenges mankind has to meet. In this context besides further regenerative approaches in particular the interaction of sunlight with matter plays a central role.

While photovoltaic technology is increasingly employed for the generation of electricity, it is less appropriate for hot water generation which is required for purposes such as e.g. heating installations. In this case the direct conversion of sunlight into heat is much more efficient and e.g. realized by rooftop installed solar thermal collectors. Here a solar absorber coating heats a closed liquid cycle making the generated heat accessible inside the building via a heat exchanger. A similar approach is used in solar thermal power plants where heat is finally converted into electricity. For solar thermal applications it is essential that the optical properties of the solar absorber surface meet the requirements and FTIR spectroscopy is the ideal tool to analyze these properties. Also to related questions such as sunlight induced heat transfer through window glass, paintings or varnishes FTIR spectroscopy gives valuable answers.

Room Temperature Emissivity Analysis via FTIR

The requirements for an adequate solar absorber can basically be reduced to two properties. Firstly, in the near infrared (NIR) and visible (VIS) spectral range where the main part of the sun’s emission takes place absorbance should
be preferably high. This ensures maximum energy transfer to the solar absorber and it is the reason why most of such coatings are dark or black to the human eye. Secondly the absorber shall not emit the absorbed energy via mid infrared (MIR) heat radiation to the outer environment but transfer the heat to the closed liquid cycle instead.

It is common practice to describe the above discussed properties via the so-called emissivity $e$ of a material, which is the spectrally dependent ability of its surface to emit radiation. Using Kirchhoff’s law of radiation it can be shown that the emissivity $e$ is related to the reflectance $R$:

$$e(\tilde{\nu}) = 1 - R(\tilde{\nu})$$  (1)

where $\tilde{\nu}$ is the wavenumber given in cm$^{-1}$. The typical operation temperature of rooftop installed solar thermal collectors is approx. 60°C which is as close to room temperature that corresponding solar absorber coatings can be analyzed via room temperature FTIR reflectance spectroscopy. Since most solar absorbers have a rough surface this typically requires an integration sphere for the hemispherical measurement of diffuse reflectance (figure 1).

**Diffuse Reflectance**

The Bruker Optics A562 gold coated integration sphere offers several options such as 2 alternative openings used as sample position or specular light trap (bottom and top) and different internal mirror positions for the background measurement. The angle of incidence is less than 15°, fulfilling the typical emissivity analysis requirement that incidence should be close to perpendicular. The sphere can be easily inserted into or removed from the sample compartment of all VERTEX, INVENIO or TENSOR II series FT-IR spectrometers. With standard mid infrared (MIR) spectrometer components (globar source, KBr beamsplitter and room temperature DTGS detector) it covers the range from approx. 400-7000 cm$^{-1}$. Using a spectrometer with additional optical components this range can be increased towards the far and near infrared. Furthermore an additional PTFE integration sphere is available covering the NIR, VIS and near UV spectral range.

Figure 2 shows the reflectance of a solar absorber measured with integration sphere A562 and a VERTEX using standard optical components. The high reflectivity towards the MIR corresponds to low emissivity values while the low reflectivity towards the NIR is caused by strong absorbance and corresponds to high emissivity. Calculation of emissivity from reflectance data according to equation (1) can easily be carried out with the OPUS software included with each spectrometer. Further evaluation such as calculation of spectrally integrated emissivity in compliance with corresponding standard methods can be realized via the powerful OPUS macro engine and starter macros are available.

**Specular Reflectance**

Besides solar absorbers emissivity is also an important measure for the heat management of other sunlight exposed surfaces such as windows, paintings or varnishes. E.g. in hot climate regions windows should transfer as less heat as possible to the interior of the building in order to save costs for air conditioning. Hence the emissivity requirements may even be inverted compared to solar absorbers, but still FTIR reflectance spectroscopy is the analysis method of choice.

In case of smooth surfaces (e.g. many window glasses) a specular reflectance accessory is more suitable than an integration sphere. Most specular reflectance accessories determine reflectance as the ratio of infrared light reflected by the sample and the light reflected by a gold mirror, assuming a mirror reflectance of 100% (1 respectively). While for the vast majority of applications this is reasonable, it implies some limitations if absolute reflectance values are of particular interest. Even the reflectance of a

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Fig. 2: Typical solar absorber measured with integration sphere A562, large element DTGS detector and VERTEX spectrometer. Note: reflectance normalized such that a value of 1 corresponds to 100% reflectance.

Fig. 3: Absolute reflectance of a coated window glass measured with VERTEX spectrometer, A519 (see inset) and DTGS detector. The angle of incidence is ~11° fulfilling the typical requirements for emissivity analysis.
perfect gold mirror is rather ~98-99% and further deviations can be caused by scratches, dirt or other imperfections. One way to account for this is to use a calibrated reference mirror and correct reflectance spectra accordingly. This is feasible but will also cause additional costs and maintenance, since regular recalibration would be required.

A smarter approach is realized by the Bruker Optics absolute VW reflectance accessory A519 where the influence of the reference mirror is already avoided during the measurement. Its 180° rotatable precision measuring head ensures that the reference mirror is part of the beam path during both sample and background measurement. Therefore the ratio of sample and background measurement is independent from the reference mirror since its influence is canceled out (see application note #12). Note that the A519 accessory was also employed to develop the industry standard EN12898 for the emissivity measurement of window glass.

Figure 3 shows the absolute specular reflectance of window glass with rather high MIR reflectance (low emissivity) and low NIR reflectance (high emissivity). Since this is qualitatively similar to solar absorbers this glass type allows for a certain heat transfer and might rather be suitable for cold or moderate climate regions. Since the A519 beam path implies that the infrared beam hits the sample twice, the accessory is primarily suited for high reflectance samples (approx. > 25%) and measures the square of the sample reflectance. In case of low reflectance the limited optical throughput may cause deviations and a relative reflectance accessory (e.g. the Pike 10Spec) is preferable, in particular since for low reflectance samples the influence of the reference mirror is negligible.

High Temperature Emissivity Analysis via thermal Emission

In solar thermal power plants huge arrays of parabolic mirrors focus sunlight on solar absorbers in order to heat up a liquid medium (e.g. synthetic oil or molten salt) which is finally utilized for electricity generation. Depending on the power plant’s design the operation temperature of the applied solar absorbers can reach 400°C or even more. Since optical properties at such elevated temperatures may substantially differ, the validity of room temperature reflectance is limited and FTIR thermal emission spectroscopy of hot samples can be an alternative.

Figure 4 shows the water cooled emission adapter A540 which is available for the VERTEX series and allows for temperatures up to 400°C. In case of thermal emission, emissivity is given by the ratio of sample emission and the emission of a black body radiator at the same temperature:

$$\varepsilon(\tilde{\nu}, T) = \frac{\text{Sample emission } (\tilde{\nu}, T)}{\text{Black body emission } (\tilde{\nu}, T)}$$

This procedure removes the single channel characteristics of the spectrometer and serves as normalization since by definition there is no object which can emit more thermal radiation than a black body. Black body reference samples can either be self-made by deposition of a sufficiently thick soot layer on top of a roughened metal sheet. For lower temperatures (< 200°C) a varnished black body reference is available. In figure 2 the emissivity of two solar absorber samples measured with a VERTEX spectrometer and A540 at T=200°C is depicted and the result identifies sample 1 as defective.

The advantage of the above described emission setup is its simplicity making it a rather economic solution. Nevertheless it should be stated that using black reference samples is an approximation leading to spectra very close but not
identical to an ideal black body as described by Planck’s radiation law. Therefore Bruker Optics also offers the adaptation of a black body cavity source (tunable from 50°C to 1050°C) which is actually coming closest to the ideal black body in the sense of Kirchhoff and Planck.

Furthermore there are cases where sample temperatures higher than 400°C might be required. Also this limitation can be overcome by use of a high temperature cell reaching temperatures up to 800°C. In order to ensure utmost flexibility Bruker Optics developed an external emission platform for the VERTEX itform allowing for different source combinations (see figure 6). Besides the beam path of the cavity source the emission platform includes a beam path for a 2nd source which is software selectable via an automated mirror. Depending on the application either the A540 emission adapter or the high temperature cell can be adapted as the 2nd source.

Nowadays for the determination of emissivity there are also so-called emissiometers commercially available. Although they can be useful for particular applications, the information content of such measurements is very limited compared to FTIR based emissivity analysis. An emissiometer is not able to determine spectrally resolved but only spectrally integrated emissivity values, leading to rather incomplete results. For detailed characterization and deeper understanding of material properties the spectral information given by FTIR spectroscopy is therefore essential.

**Summary**

FTIR spectroscopy is the ideal tool to determine the emissivity of surfaces which is directly related to its heat transfer properties. In case of room temperature applications, depending on surface roughness either diffuse or specular reflectance is the method of choice. For high temperature applications the measurement of infrared thermal emission is a suitable alternative.