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ON THE USE OF INTEGRATING SPHERE REFLECTOMETERS FOR MEASURING THE SOLAR ABSORPTANCE OF SELECTIVE SURFACES

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Résumé.— Les absorptivités solaires sont souvent dérivées des valeurs de réflectivité mesurées au moyen de dispositifs employant des sphères intégrantes. Les instruments de ce genre ont deux manières de fonctionnement, selon qu'on mesure les réflectivités spectrales ou intégrées. Bien que les absorptivités solaires dérivées des données spectrales soient intrinsèquement plus précises, on trouve en commerce des réflectomètres conçus de façon à mesurer les réflectivités intégrées plutôt que spectrales. Ces instruments sont souvent pourvus de sources de radiation qui ne s'accordent pas avec le spectre solaire, et/ou de détecteurs montrant une réponse caractérisée par la sélectivité spectrale : en ligne de principe ils peuvent par conséquent être sujets d'erreurs lorsqu'ils sont destinés aux surfaces sélectives. Dans le but de fournir une évaluation de l'erreur, on a analysé la théorie de la mesure par rapport à quelques échantillons sélectifs bien caractérisés par leurs propriétés réflectives. La validité des résultats a été confirmée expérimentalement avec l'emploi d'une sphère intégrante équipée de sources et détecteurs différents.

Abstract.— Solar absorptances are often derived from the reflectance values measured with devices which make use of integrating spheres. Instruments of this type can be operated in two different ways, according to whether spectral or integrated reflectances are measured. Though solar absorptances derived from spectral data are inherently more accurate, some commercially available reflectometers are found which are conceived for measuring integrated rather than spectral reflectances. Since these instruments are often provided with radiation sources which do not match the solar spectrum and/or detectors showing a spectrally selective response, they could in principle be affected by errors when dealing with selective surfaces. With the aim of giving an error estimate, the theory of the measurement was analyzed with reference to some selective samples well characterized for their reflectance properties. The results were then given an experimental validation by using an integrating sphere equipped with different sources and detectors.

1. **Introduction.**— The most popular technique for measuring solar absorptance is that of the integrating sphere reflectometer used in the comparison mode. This allows the reflectance of a sample under test to be derived in terms of the known reflectance of a reference sample. Solar absorptance is then obtained according to Kirchhoff's law. Instruments of this type can be operated in two different ways, according to whether spectral or integrated reflectance values are measured. While in the first case a relatively large number of measurements are taken to

provide data for numerical integration over the solar spectrum, in the second case the same integrated reflectance is directly obtained with a single measurement. Thus, a noticeable reduction of the measuring time is achieved, which may be particularly appreciated when dealing with a large number of samples. In addition, also the cost of the apparatus is drastically reduced, being no need for high sensitivity detectors and light dispersing devices, such as monochromators. For these reasons, some commercially available reflectometers are conceived for measuring integrated reflectances directly. Though these instruments are sufficiently accurate for many purposes, nevertheless they could in principle be affected by non negligible errors when investigating selective surfaces, that is materials having a wavelength dependent reflectance. In fact, they are often provided with radiation sources which do not match the solar spectrum and/or detectors which show a selective response. Furthermore, errors may be due also to a slight selectivity of the sphere coating itself, as suggested by Dunkle et al./1/, who first measured directly integrated reflectances.

With the aim of finding how the combined action of source, detector and sphere coating can influence the results, the general theory of the measurement was first established and applied to some particular situations. An experimental validation was then achieved by means of an integrating sphere equipped with interchangeable sources and detectors.

2. Theory.- A schematic view of an integrating sphere reflectometer of the comparison type is shown in figure 1.

Fig.1.- Schematic of an integrating sphere reflectometer of the comparison type.

A radiation beam from an external source is alternatively focused on the sample under test T and on the reference sample R. If S_T and S_R are the detector outputs, the following relation holds :

$$\rho_T = \frac{S_T}{S_R} \rho_R \quad (1)$$

in which ρ_T and ρ_R are the reflectances of the samples, being the latter a known quantity.

The measured reflectance ρ_T is spectrally characterized by the nature of the incoming radiation. When this is a monochromatic light beam, the spectral reflectance $\rho_T(\lambda)$ is measured. The solar absorptance $\alpha_T(S)$ is then derived from the equation :

$$\alpha_T(S) = 1 - \rho_T(S) = 1 - \frac{\int_0^\infty I_S(\lambda) \rho_T(\lambda) d\lambda}{\int_0^\infty I_S(\lambda) d\lambda} \quad (2)$$

where $\rho_T(S)$ is the sample reflectance weighted on the spectral distribution $I_S(\lambda)$ of the solar radiation. When, instead, a radiation beam matching the solar spectral distribution is used, the solar absorptance is readily obtained as :

$$\alpha_T(S) = 1 - \rho_T(S) = 1 - \frac{S_T}{S_R} \rho_R(S) \quad (3)$$

By comparing equations (2) and (3) it is evident that, from an operative point of view, there is much to gain in using the latter, since it requires only one reflectance measurement.

In practice, things are not so straightforward because the ratio of output signals is dependent on such quantities as the spectral distribution of the radiation beam, the spectral sensitivity of the detector, the spectral reflectance of the sphere coating, other than, of course, of the two samples.

In fact, this ratio may be mathematically expressed as follows :

$$\frac{S_T}{S_R} = \frac{\int_0^\infty I(\lambda) F_T(\lambda) \sigma(\lambda) d\lambda}{\int_0^\infty I(\lambda) F_R(\lambda) \sigma(\lambda) d\lambda} \quad (4)$$

where : $I(\lambda)$ is the spectral distribution of the radiation beam which, in an ideal case, equals $I_S(\lambda)$;

$\sigma(\lambda)$ is the spectral sensitivity of the detector ;

$F_T(\lambda)$ and $F_R(\lambda)$ are the so called "sphere efficiencies", which physically represent the fraction of the entering beam which is collected at the detector port after reflection at T and R, respectively.

The generalized theory of the integrating sphere /2/ applied to the present case provides the following expression for $F_T(\lambda)$ and $F_R(\lambda)$:

$$F_{T,R}(\lambda) = \frac{\frac{a_{T,R}}{A} \rho_{T,R}(\lambda)}{1 - \rho_W(\lambda) \left(1 - \frac{a_E^+ a_D^+ a_T^+ a_R^+}{A} \right) - \frac{a_T}{A} \rho_T(\lambda) - \frac{a_R}{A} \rho_R(\lambda)} \quad (5)$$

in which : a_E , a_D , a_T and a_R are the areas of the four ports (see Fig.1); A is the area of the sphere ;

$\rho_W(\lambda)$ is the spectral reflectance of the sphere wall.

Equations (3), (4) and (5) may be used, starting from known values of $\rho_T(\lambda)$, to foresee the measured values of $\rho_T(S)$ when a sphere is combined with sources and detectors whose characteristics are known. The results, compared with those obtained from equation (2), which is nothing more but a definition, will then disclose the errors which may arise when measuring $\rho_T(S)$ directly.

3. Experiment and calculations.- An experimental validation of the above analysis was achieved by accurately testing for their reflectance properties four samples provided from different sources. A description of the samples is given in table I, where the thermal emittances, which had been previously measured with a heated cavity reflectometer, are also reported.

sample	Nature	Source	Emittance
No.1	Black chrome on brass	Our laboratory	0.04
No.2	Black chrome on aluminum	Commercial	0.18
No.3	Unknown coating on aluminum (°)	Commercial	0.11
No.4	Copper oxide on copper	Commercial	0.11

Table I.- Description of the tested samples.

(°) The nature of the black coating was not disclosed by the supplier

Sample	Solar absorptance				
	From spectral data (AM2)	Xe arc + Si	Xe arc + Pyroelectric	Halogen + Si	Halogen + Pyroelectric
No.1	0.917	0.943	0.931	0.947	0.917
No.2	0.913	0.936	0.916	0.928	0.884
No.3	0.900	0.948	0.916	0.957	0.912
No.4	0.865	0.868	0.869	0.867	0.862

Table II.- Calculated solar absorptances of the tested samples.

The emittance values, as compared with the solar absorptances reported in table II, show that a common feature to the samples was their fairly good selectivity.

The reflectance measurements were performed with a sphere 300 mm in diameter, internally coated with a BaSO_4 paint (Eastman 6080 white reflec-

tance coating), while pressed BaSO_4 powder (Eastman 6091 white reflectance standard) was used to prepare the reference sample.

To obtain the spectral data, a grating monochromator (Perkin Elmer Mod. 210) with a tungsten strip lamp provided for the source. Three different detectors, namely : a photomultiplier (EMI 9558QB), a Si photodiode and a PbS photoconductor, were required to span the spectral region from 0.35 to 2 μm . This region is generally considered to be sufficiently wide to give an accurate representation of the solar absorptance when averaging the spectral data on the solar distribution for air mass 2 (AM2) as given by Moon /3/.

The measured spectral reflectances have been plotted in figure 2.

Fig.2.- Spectral reflectance curves of the samples listed in table I.

They were used to calculate, according to equations (3), (4) and (5), the integrated $\alpha_T(S)$ values that would be obtained with direct measurements. To provide meaningful inputs to these equations, we selected two types of both detectors and sources among those most widely used, thus giving rise to four possible combinations. The sources were an unfiltered Xe compact arc lamp and a tungsten-halogen lamp, whose spectral irradiances have been plotted in figure 3. The detectors were a silicon photodiode, whose spectral responsivity is shown in figure 4, and a pyroelectric sensor, which actually was a neutral detector having a constant responsivity over the spectrum.

The spectral reflectance data for the BaSO_4 paint and powder were derived from the literature /4-5/.

The results of calculations are shown in table II, where the solar absorptances as obtained from spectral data through equation (2) have been reported for sake of comparison in the second column.

Fig.3.- Spectral irradiances of the Xe compact arc and tungsten-halogen lamps. The solar irradiance for air mass 2 has been plotted for sake of comparison.

Fig.4.- Spectral sensitivity of the silicon photodiode.

In order to check the reliability of the data of table II, the integrated $\alpha_T(S)$ were actually measured, equipping the sphere with the sources and detectors previously considered. To make these measurements, the radiation beams from the sources were focused directly onto the samples through a quartz lens, thus by-passing the monochromator. The experiment was highly successful, since none of the measured values differed from the calculated ones by more than 0.005 absorbance units. This result confirmed that both the mathematical approach and the numerical assumptions that had been made on the spectral properties of the sources, the detectors and the BaSO_4 paint and powder were correct. Finally, in order to find whether the data of table II were sufficiently representative to provide information of general interest about the errors that occur when measuring integrated absorbances, the above calculations were extended to a number of selective surfaces described in the literature. Only those surfaces were chosen for which detailed

spectral reflectance curves were available. The data obtained for three of them (e.g. : Al_2O_3 - Mo system /6/, iron oxide film on a steel substrate /7/, Tabor treatment No.110-30 on nickel plated copper /8/), which appeared to be of some significance because of a somewhat irregular behaviour of their spectral reflectances, have been summarized in table III.

sample	solar absorptance				
	From spectral data (AM2)	Xe arc + Si	Xe arc + Pyroelectric	Halogen + Si	Halogen + Pyroelectric
Al_2O_3 - Mo system	0.905	0.952	0.928	0.955	0.902
Iron oxide on steel	0.881	0.921	0.908	0.914	0.873
Tabor 110-30 on Ni plated Cu	0.904	0.971	0.935	0.967	0.900

Table III.- Calculated solar absorptances of the literature samples.

From the data of both tables II and III the following indications may be derived :

- 1- Accurate integrated absorptance measurements can be made, whichever are the source and the detector, provided that the samples are weakly selective below $2\text{ }\mu\text{m}$, as shown by sample No.4.
- 2- The largest errors occur when using the Si photodiode in connection with samples showing an irregular spectral reflectance : this is due to both lack of sensitivity above $1.1\text{ }\mu\text{m}$ and its wavelength dependence below.
- 3- In most cases the $\alpha_T(S)$ values are overestimated. A few exceptions occur when using a neutral detector together with the halogen lamp. They originate from the shift of the irradiance curve of the lamp towards the long wavelength side, where generally the spectral absorptance is decreasing.
- 4- The amount of the errors is likely to be smaller than expected. As a matter of fact, data in the literature /9/ indicate errors even larger when considering the single effect of a poor match of the solar distribution. It may be argued that the total error is to some extent lowered by the algebraic composition of the partial contribution of every single effect. Even so, however, errors of the order of 0.05 absorptance units

may be taken as large when comparing the performances of selective surfaces in view of their efficiency in collecting solar energy. This may be easily understood if one refers, for example, to those applications /10/ for which a 0.01 increase in α_s achieves the same increase in efficiency as decreasing the thermal emittance ϵ_{th} by 0.04. Thus, an error of 0.05 units in α_s gives rise to the same effect as an error of 0.20 units in ϵ_{th} . Since good selective surfaces have an emittance of the order of 0.10 to 0.20, the last consideration clearly suggests the necessity of an accurate measurement of α_s .

4. Conclusions.— Integrating sphere reflectometers for the direct measurement of integrated solar absorptance may be used with confidence when examining materials which show a weak spectral selectivity, at least, below 2 μm . When, instead, strongly selective surfaces are to be investigated, the results thus obtained should be considered with care. This is particularly true when the instrument is equipped with a selective detector such as the silicon photodiode. In any case, when the performances of various absorbers are to be compared on the basis of their solar absorptance and thermal emittance values, the former property should be preferably derived by numerical integration of spectral reflectance data.

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