
MEASUREMENT OF TRANSMISSION, ABSORPTION, EMISSION, AND REFLECTION

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35.1 GLOSSARY

A	Area
a	absorption
bb	blackbody
c_2	second radiation constant
E	irradiance
f	bidirectional scattering distribution function
i	internal
L	radiance
P	electrical power
R	reflectance factor
r	reflection
T	temperature
t	transmission
α	absorptance
α'	absorption coefficient
ε	emittance (emissivity)
θ, ϕ	angles
ρ	reflectance
σ	Stefan Boltzmann constant
τ	transmittance
Φ	power (flux)
Ω	projected solid angle

*Deceased.

35.2 INTRODUCTION AND TERMINOLOGY

When radiant flux is incident upon a surface or medium, three processes occur: transmission, absorption, and reflection. Figure 1 shows the ideal case, where the transmitted and reflected components are either specular or perfectly diffuse. Figure 2 shows the transmission and reflection for actual surfaces.

The symbols, units, and nomenclature employed in this chapter follow the established usage as defined in *ISO Standards Handbook 2*,¹ Cohen and Giacomo,² and Taylor.³ Additional general terminology applicable to this chapter is from ASTM,⁴ IES,⁵ IES,⁶ Drazil,⁷ and CIE.⁸ The prefix *spectral* is used

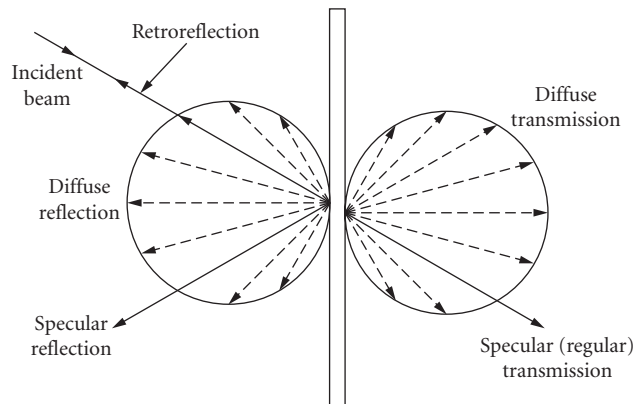


FIGURE 1 Idealized reflection and transmission.

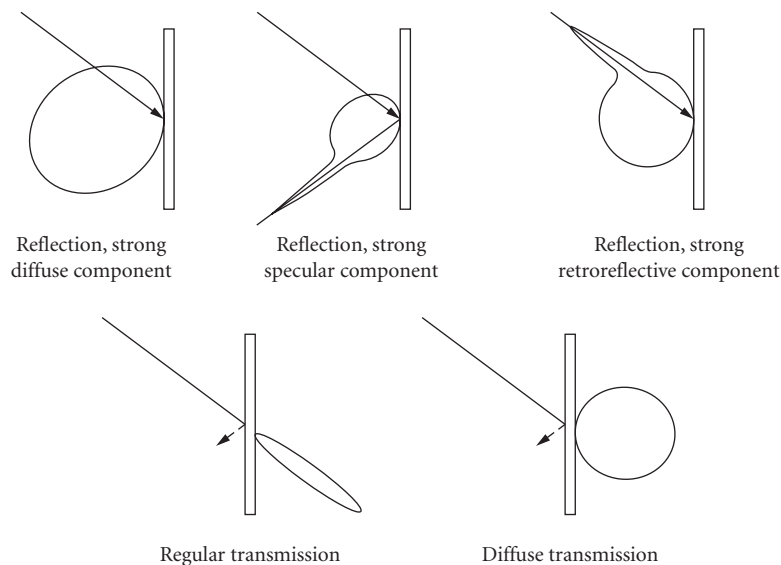


FIGURE 2 Actual reflection and transmission.

to denote a characteristic at a particular wavelength and is indicated by the symbol λ . The absence of the *spectral* prefix implies integration over all wavelengths with a source function included (omission of the source function is meaningless except where the characteristic is constant with wavelength).

There has been a continuing dialog over terminology, particularly between the suffixes *-ance* and *-ivity*.⁹⁻¹³ The suggested usage reserves terms ending with *-ivity* (such as transmissivity, absorptivity, and reflectivity) for properties of a pure material and employs the suffix *-ance* for the characteristics of a specimen or sample. For example, one can distinguish between the *reflectivity* of pure aluminum and the *reflectance* of a particular sample of 6061-T6 aluminum with a natural oxide layer. This distinction can be extended to differentiate between emissivity (of a pure substance) and emittance (of a sample). This usage of *emittance* should not be confused with the older term *radiant emittance*, now properly called *radiant exitance*. In this chapter, the suffix *-ance* will be used exclusively inasmuch as the measurement of radiometric properties of materials is under discussion.

35.3 TRANSMITTANCE

Transmission is the term used to describe the process by which incident radiant flux leaves a surface or medium from a side other than the incident side, usually the opposite side. The spectral transmittance $\tau(\lambda)$ of a medium is the ratio of the transmitted spectral flux $\Phi_{\lambda t}$ to the incident spectral flux $\Phi_{\lambda i}$, or

$$\tau(\lambda) = \frac{\Phi_{\lambda t}}{\Phi_{\lambda i}} \quad (1)$$

The transmittance τ is the ratio of the transmitted flux Φ_t , to the incident flux Φ_i , or

$$\tau = \frac{\int_0^\infty \tau(\lambda) \Phi_{\lambda i} d\lambda}{\int_0^\infty \Phi_{\lambda i} d\lambda} \neq \int_\lambda \tau(\lambda) d\lambda \quad (2)$$

Note that the integrated transmittance is *not* the integral over wavelength of the spectral transmittance, but must be weighted by a source function Φ_λ as shown.

The transmittance may also be described in terms of radiance as follows:

$$\tau = \frac{\int_0^\infty \int_\Omega L_{\lambda i} d\Omega_i d\lambda}{\int_0^\infty \int_\Omega L_{\lambda t} d\Omega_t d\lambda} \quad (3)$$

where $L_{\lambda i}$ represents the spectral radiance $L_{\lambda i}(\lambda; \theta_i, \phi_i)$ incident from direction (θ_i, ϕ_i) , $L_{\lambda t}$ represents the spectral radiance $L_{\lambda t}(\lambda; \theta_t, \phi_t)$ transmitted in direction (θ_t, ϕ_t) , and $d\Omega$ is the elemental projected solid angle $\sin \theta \cos \theta d\theta d\phi$.

The bidirectional transmittance distribution function (BTDF, symbol f_t) relates the transmitted radiance to the radiant incidence as

$$f_t(\lambda; \theta_i, \phi_i) \equiv \frac{dL_{\lambda t}}{dL_{\lambda i} d\Omega_i} = \frac{dL_{\lambda t}}{dE_{\lambda i}} (\text{sr}^{-1}) \quad (4)$$

Geometrically, transmittance can be classified as specular, diffuse, or total, depending upon whether the specular (regular) direction, all directions other than the specular, or all directions are considered.

35.4 ABSORPTANCE

Absorption is the process by which incident radiant flux is converted to another form of energy, usually heat. Absorptance is the fraction of incident flux that is absorbed. The absorptance α of an element is defined by $\alpha = \Phi_a / \Phi_i$. Similarly, the spectral absorptance $\alpha(\lambda)$ is the ratio of spectral power absorbed $\Phi_{\lambda a}$ to the incident spectral power $\Phi_{\lambda i}$,

$$\alpha = \frac{\int_0^\infty \alpha(\lambda) \Phi_{\lambda i} d\lambda}{\int_0^\infty \Phi_{\lambda i} d\lambda} \neq \int_\lambda \alpha(\lambda) d\lambda \quad (5)$$

An absorption coefficient α' (cm^{-1} or km^{-1}) is often used in the expression $\tau_i = e^{-\alpha' t}$, where τ_i is internal transmittance and t is pathlength (cm or km).

35.5 REFLECTANCE

Reflection is the process where a fraction of the radiant flux incident on a surface is returned into the same hemisphere whose base is the surface and which contains the incident radiation. The reflection can be specular (in the mirror direction), diffuse (scattered into the entire hemisphere), or a combination of both. Table 1¹⁴ shows a wide range of materials that have different goniometric (directional) reflectance characteristics.

TABLE 1 Goniometric Classification of Materials¹⁴

Material Classification	Scatter*	σ^\dagger	γ^\ddagger	Structure§	Example
Exclusively reflecting materials $\tau = 0$	None	0	$\equiv 0$	None	Mirror
	Weak	≤ 0.4	$\leq 27^\circ$	Micro	Matte aluminum
				Macro	Retroreflectors
	Strong	> 0.4	$> 27^\circ$	None	Laquer & enamel coatings
Weakly transmitting, strongly reflecting Materials $\tau \leq 0.35$				Micro	Paint films, BaSO ₄ , Halon
				Macro	Rough tapestries, road surfaces
	None	0	$\equiv 0$	None	Sunglasses, color filters cold mirrors
	Weak	≤ 0.4	$\leq 27^\circ$	Micro	Matte-surface color filters
				Macro	Glossy textiles
Strongly transmitting materials $\tau > 0.35$	Strong	> 0.4	$> 27^\circ$	None	Highly turbid glass
				Micro	Paper
				Macro	Textiles
	None	0	$\equiv 0$	None	Window glass
	Weak	≤ 0.4	$\leq 27^\circ$	None	Plastic film
				Micro	Ground glass
				Macro	Ornamental glass
					prismatic glass
	Strong	> 0.4	$> 27^\circ$	None	Opal glass
				Micro	Ground opal glass
				Macro	Translucent acrylic plastic with patterned surface

*It is suggested that the diffusion factor is appropriate for strongly diffusing materials and that the half-angle is better for weakly diffusing materials.

[†] γ is a half-value angle, the angle from the normal where the radiance has dropped to one-half the value at normal.

[‡] σ is a diffusion factor, the ratio of the mean of radiance measured at 20° and 70° to the radiance measured at 5° from the normal, when the incoming radiation is normal. $\sigma = [L(20) + L(70)]/[2L(5)]$. It gives an indication of the spatial distribution of the radiance, and is unity for a perfect (Lambertian) diffuser.

[§]Structure refers to the nature of the surface. In a microscattering structure, the scatterers cannot be resolved with the unaided eye. The macrostructure scatterers can be readily seen.

The most general definition for reflectance ρ is the ratio of the radiant flux reflected Φ_r to the incident radiant flux Φ_i , or

$$\rho = \frac{\Phi_r}{\Phi_i} \quad (6)$$

Spectral reflectance is similarly defined at a specified wavelength λ as

$$\rho(\lambda) = \frac{\Phi_{\lambda r}}{\Phi_{\lambda i}} \quad (7)$$

(Spectral) reflectance factor (symbol R) is the ratio of (spectral) flux reflected from a sample to the (spectral) flux which would be reflected by a perfect diffuse (lambertian) reflector.

No single descriptor of reflectance will suffice for the wide range of possible geometries. The fundamental geometric descriptor of reflectance is the bidirectional reflectance distribution function (BRDF, symbol f_r). It is defined as the differential element of reflected radiance dL_r in a specified direction per unit differential element of radiant incidence dE_i , also in a specified direction,¹⁵ and carries unit of sr^{-1} :

$$f_r(\theta_i, \phi_i, \theta_r, \phi_r) = \frac{dL_r(\theta_i, \phi_i; \theta_r, \phi_r; E_i)}{dE_i(\theta_i, \phi_i)} \quad [\text{sr}^{-1}] \quad (8)$$

The polar angle θ is measured from the surface normal and the azimuth angle ϕ is measured from an arbitrary reference in the surface plane, most often the plane containing the incident beam. The subscripts i and r refer to the incident and reflected beams, respectively.

By integrating over varying solid angles, Nicodemus et al.,¹⁵ based upon earlier work by Judd,¹⁶ defined nine goniometric reflectances, and by extension, nine goniometric reflectance factors. These are shown in Tables 2 and 3 and Fig. 3. In these tables, the term *directional* refers to a differential solid angle $d\omega$ in the direction specified by (θ, ϕ) . *Conical* refers to a cone of finite extent centered in direction (θ, ϕ) ; the solid angle ω of the cone must also be specified.

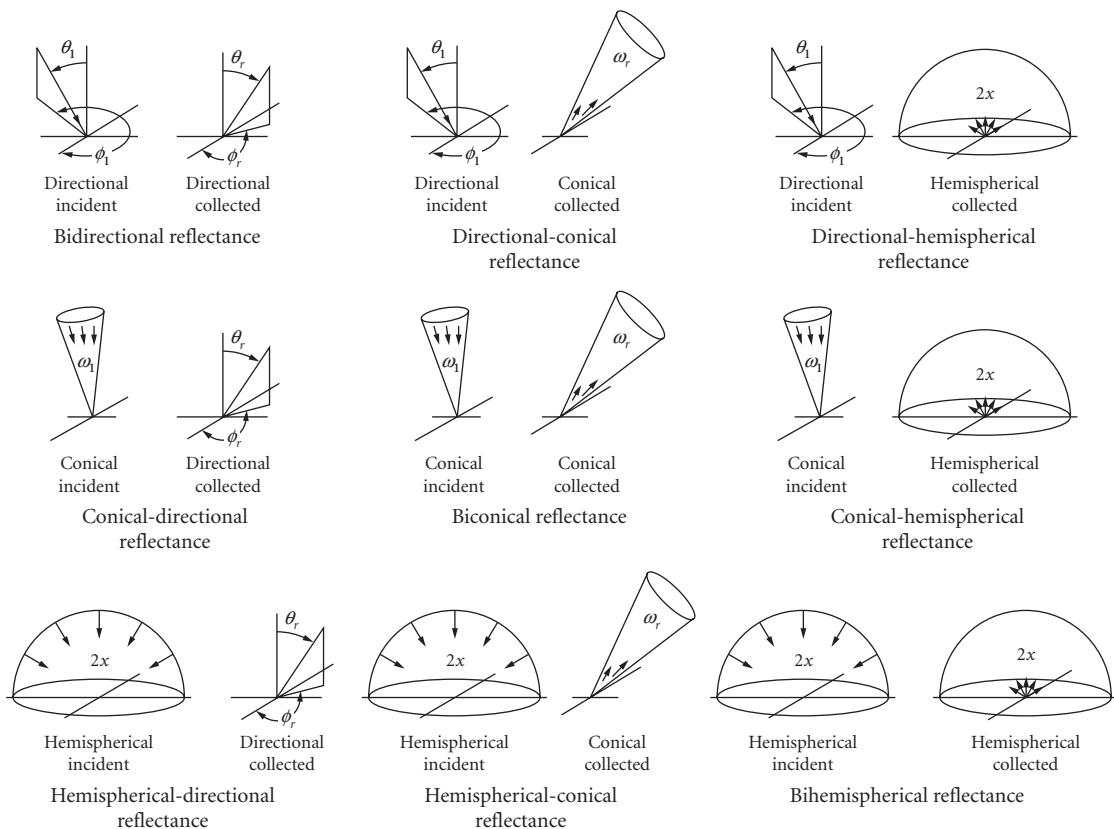
Details on these definitions and further discussion can be found in ASTM STP475,⁴ ASTM E808,¹⁷ Judd,¹⁶ Nicodemus,¹⁸ Nicodemus,¹⁹ and Nicodemus et al.¹⁵

TABLE 2 Nomenclature for Nine Types of Reflectance¹⁵

1. Bidirectional reflectance	$d\rho(\theta_i, \phi_i; \theta_r, \phi_r) = f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r$
2. Directional-conical reflectance	$\rho(\theta_i, \phi_i; \omega_r) = \int_{\omega_r} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r$
3. Directional-hemispherical reflectance	$\rho(\theta_i, \phi_i; 2\pi) = \int_{2\pi} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r$
4. Conical-directional reflectance	$d\rho(\omega_i; \theta_r, \phi_r) = (d\Omega_i / \Omega_i) \int_{\omega_i} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r$
5. Biconical reflectance	$\rho(\omega_i; \omega_r) = (1/\Omega_i) \int_{\omega_i} \int_{\omega_r} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r d\Omega_i$
6. Conical-hemispherical reflectance	$\rho(\omega_i; 2\pi) = (1/\Omega_i) \int_{\omega_i} \int_{2\pi} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r d\Omega_i$
7. Hemispherical-directional reflectance	$d\rho(2\pi; \theta_r, \phi_r) = (d\Omega_r / \pi) \int_{2\pi} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_i$
8. Hemispherical-conical reflectance	$\rho(2\pi; \omega_r) = (1/\pi) \int_{2\pi} \int_{\omega_r} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r d\Omega_i$
9. Bihemispherical reflectance	$\rho(2\pi; 2\pi) = (1/\pi) \int_{2\pi} \int_{2\pi} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r d\Omega_i$

TABLE 3 Nomenclature for Nine Types of Reflectance Factor¹⁵

1. Bidirectional reflectance factor	$R(\theta_i, \phi_i; \theta_r, \phi_r) = \pi f_r(\theta_i, \phi_i; \theta_r, \phi_r)$
2. Directional-conical reflectance factor	$R(\theta_i, \phi_i; \omega_r) = (\pi/\Omega_r) \int_{\omega_r} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r$
3. Directional-hemispherical reflectance factor	$R(\theta_i, \phi_i; 2\pi) = \int_{2\pi} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r$
4. Conical-directional reflectance factor	$R(\omega_i; \theta_r, \phi_r) = (\pi/\Omega_i) \int_{\omega_i} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_i$
5. Biconical reflectance factor	$R(\omega_i; \omega_r) = [\pi/(\Omega_i \Omega_r)] \int_{\omega_i} \int_{\omega_r} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_i d\Omega_r$
6. Conical-hemispherical reflectance factor	$R(\omega_i; 2\pi) = (1/\Omega_i) \int_{\omega_i} \int_{2\pi} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r d\Omega_i$
7. Hemispherical-directional reflectance factor	$R(2\pi; \theta_r, \phi_r) = \int_{2\pi} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_i$
8. Hemispherical-conical reflectance factor	$R(2\pi; \omega_r) = (1/\Omega_r) \int_{2\pi} \int_{\omega_r} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r d\Omega_i$
9. Bihemispherical reflectance factor	$R(2\pi; 2\pi) = (1/\pi) \int_{2\pi} \int_{2\pi} f_r(\theta_i, \phi_i; \theta_r, \phi_r) d\Omega_r d\Omega_i$

**FIGURE 3** Nine geometrical definitions of reflectance.

35.6 EMITTANCE

Emittance (ε) is the ratio of the radiance of an object or surface to the radiance of a blackbody (planckian radiator) at the same temperature. It is therefore dimensionless and can assume values between 0 and 1 for thermal radiators at equilibrium. Spectral emittance $\varepsilon(\lambda)$ is the emittance at a given wavelength. If a radiator is neutral with respect to wavelength, with a constant spectral emittance less than unity, it is called a graybody.

$$\varepsilon = \frac{L}{L^{bb}}, \quad \varepsilon(\lambda) = \frac{L_{\lambda}}{L_{\lambda}^{bb}} \quad (9)$$

Directional emittance $\varepsilon(\theta, \phi)$ is defined by

$$\varepsilon(\theta, \phi) = \frac{L(\theta, \phi)}{L^{bb}} \quad (10)$$

Note that if the body is nongray, its emittance is dependent upon temperature inasmuch as the integral must be weighted by the source (Planck) function.

$$\varepsilon = \frac{\int_0^{\infty} \varepsilon(\lambda) L_{\lambda}^{bb} d\lambda}{\int_0^{\infty} L_{\lambda}^{bb} d\lambda} = \frac{1}{\pi} \frac{\int_0^{\infty} \varepsilon(\lambda) L_{\lambda}^{bb} d\lambda}{\sigma T^4} \quad (11)$$

35.7 KIRCHHOFF'S LAW

In a closed system at thermal equilibrium, conservation of energy necessitates that emitted and absorbed fluxes be equal. Since the radiation field in such a system is isotropic (the same in all directions), the directional spectral emittance and the directional spectral absorptance must be equal, i.e.,

$$\varepsilon(\lambda; \theta, \phi) = \alpha(\lambda; \theta, \phi) \quad (12)$$

This statement was first made by Kirchhoff.²⁰ Strictly, this equation holds for each orthogonal polarization component, and for it to be valid as written, the total radiation must have equal orthogonal polarization components. Kirchhoff's law is often simplified to the declaration $\alpha = \varepsilon$; however, this is not a universal truth; it may only be applied under a limited set of conditions. The geometrical and spectral averaging (integration) is governed by a specific set of rules as demonstrated by Siegel and Howell.²¹ Table 4, adapted from Siegel and Howell²¹ and Grum and Becherer,²² shows the various geometrical and spectral conditions under which the absorptance may be related to the emittance.

35.8 RELATIONSHIP BETWEEN TRANSMITTANCE, REFLECTANCE, AND ABSORPTANCE

Radiant flux incident upon a surface or medium undergoes transmission, reflection, and absorption. Application of conservation of energy leads to the statement that the sum of the transmission, reflection, and absorption of the incident flux is equal to unity, or

$$\alpha + \tau + \rho = 1 \quad (13)$$

TABLE 4 Summary of Absorptance-Emittance Relations²¹

Quantity	Equality	Required Conditions
Directional spectral	$\alpha(\lambda; \theta, \phi, T_a) = \varepsilon(\lambda; \theta, \phi, T_a)$	None other than thermal equilibrium
Directional total	$\alpha(\theta, \phi, T_a) = \varepsilon(\theta, \phi, T_a)$	(1) Spectral distribution of incident energy proportional to blackbody at T_a , or (2) $\alpha(\lambda; \theta, \phi, T_a) = \varepsilon(\lambda; \theta, \phi, T_a)$ independent of wavelength
Hemispherical spectral	$\alpha(\lambda, T_a) = \varepsilon(\lambda, T_a)$	(1) Incident radiation independent of angle, or (2) $\alpha(\lambda; \theta, \phi, T_a) = \varepsilon(\lambda; \theta, \phi, T_a)$ independent of angle
Hemispherical total	$\alpha(T_a) = \varepsilon(T_a)$	(1) Incident energy independent of angle <i>and</i> spectral distribution proportional to blackbody at T_a , or (2) Incident energy independent of angle <i>and</i> $\alpha(\lambda; \theta, \phi, T_a) = \varepsilon(\lambda; \theta, \phi, T_a)$ independent of wavelength, or (3) Incident energy at each angle has spectral distribution proportional to blackbody at T_a <i>and</i> $\alpha(\lambda; \theta, \phi, T_a) = \varepsilon(\lambda; \theta, \phi, T_a)$ independent of angle, or (4) $\alpha(\lambda; \theta, \phi, T_a) = \varepsilon(\lambda; \theta, \phi, T_a)$ independent of angle and wavelength

In the absence of nonlinear effects (i.e., the Raman effect, etc.),

$$\alpha(\lambda) + \tau(\lambda) + \rho(\lambda) = 1 \quad (14)$$

If the situation is such that one of the above Kirchhoff-type relations is applicable, then emittance ε may be substituted for absorptance α in the previous equations, or

$$\varepsilon = 1 - \tau - \rho \quad \varepsilon(\lambda) = 1 - \tau(\lambda) - \rho(\lambda) \quad (15)$$

35.9 MEASUREMENT OF TRANSMITTANCE

A knowledge of the transmission of optical materials and elements, gaseous atmospheres, and various liquids is necessary throughout the realm of optics. Most of these measurements are made with commercial spectrophotometers. It is beyond the scope of this chapter to discuss the design and operation of spectrophotometric equipment except sample-handling practices. For further discussion, see Gram and Becherer,²² ASTM E275,²³ and ASTM E409.²⁴

Conventional spectrophotometers are of the double-beam configuration, where the output is the ratio of the signal in the sample beam to the signal in the reference beam plotted as a function of wavelength. It is incumbent upon the experimenter to ensure that the only difference between the two beams is the unknown. Therefore, if liquid or gas cells are employed, one should be placed in each beam. For gas cells, an equal amount of carrier gas should be injected into each cell, with the unknown to be sample placed in only one cell, destined for the sample beam. For liquids, an equal amount of solute should be placed in each cell. A critical issue with liquid and solid samples is the beam geometry. Most spectrophotometers feature converging beams in the sample space. If the

optical path length (the product of index of refraction and actual distance) for each beam is not identical, a systematic difference is presented to either the entrance slit or the detector. In addition, some specimens (e.g., interference filters) are susceptible to errors when measured in a converging beam. Most instruments also have a single monochromator which is susceptible to stray radiation, the limiting factor when trying to make measurements of samples that are highly absorbing in one spectral region and transmitting in another. Some recent instruments feature linear detector arrays along with single monochromators to allow the acquisition of the entire spectrum in several milliseconds; these are particularly applicable to reaction rate studies.

Conventional double-beam instruments are limited by these factors to uncertainties on the order of 0.1 percent. For lower uncertainties, the performance deficiencies found in double-beam instruments can largely be overcome by the use of a single-beam architecture. The mode of operation is sample-in-sample-out. If the source is sufficiently stable with time, the desired spectral range can be scanned without the sample, then rescanned with the sample in place. Otherwise, the spectrometer can be set at a fixed wavelength and alternate readings with and without the sample in place must be made. Care should be taken to ensure that the beam geometry is not altered between sequential readings.

To achieve the ultimate in performance from conventional spectrophotometry, several design characteristics should be included. A double monochromator is essential to minimize stray light. The beam geometry in the sample compartment should be highly collimated to avoid focus shifts with optically thick samples. Some form of beam integration, such as an integrating sphere or other diffuser, should be employed to negate the effects of nonuniform detectors and beam shifts. An exemplary instrument is the high-accuracy spectrophotometer developed by the National Institute for Standards and Technology (NIST), described in Mielenz and Eckerle,²⁵ Mielenz et al.,²⁶ Venable et al.,²⁷ Eckerle,²⁸ and Eckerle et al.²⁹ A particularly useful review is Eckerle et al.³⁰ Similar laboratory instruments have also been built elsewhere by Clarke,³¹ Freeman,³² and Zwinkles and Gignac.³³

Numerous other instruments have been described in the literature; some have been designed for singular or limited purposes while others have a more universal appeal. Use of integrating spheres is common, both for the averaging effects and for the isolation of the specular and diffuse components, as shown in Fig. 4.^{14,34} Several useful instruments are described by Karras,³⁵ Taylor,³⁶ Zerlaut and Anderson,³⁷ Clarke and Larkin,³⁸ and Kessell.³⁹

Conventional instruments lack a wide dynamic range because there are simply not enough photons available in a narrow bandpass in a reasonable time. Solutions include Fourier transform spectrometers with a large multiplex advantage, the use of tunable lasers, and heterodyne spectrometry.⁴⁰

Simple instruments can be purchased or constructed for specific purposes. For example, solar transmittance can be determined using either the natural sun (if available) or simulated solar radiation as the source. A limited degree of spectral isolation can be achieved with an abridged spectrophotometer using narrow bandpass interference or glass absorption filters.

Several publications have suggested methods for making accurate and repeatable measurements including Hughes,⁴¹ Mielenz,⁴² Venable and Hsia,⁴³ Burke and Mavrodineanu,⁴⁴ ASTM F768,⁴⁵ ASTM E971,⁴⁶ ASTM E903,⁴⁷ and ASTM E179.⁴⁸ Calibration and performance assessment of spectrophotometers includes photometric accuracy, linearity, stray light analysis, and wavelength calibration.

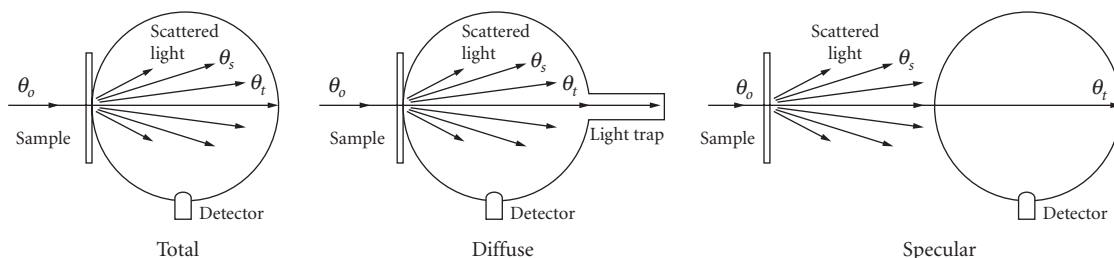


FIGURE 4 Measurement of total, diffuse, and specular transmittance using an integrating sphere.

35.10 RADIOMETRY AND PHOTOMETRY

Particular attention should be paid to luminescent samples that absorb radiant energy in one spectral region and re-emit it at longer wavelengths. Pertinent references include Hawes,⁴⁹ Bennett and Ashley,⁵⁰ ASTM E387,⁵¹ ASTM E275,²³ and ASTM, E409.²⁴

Standards of spectral transmittance are available as Standard Reference Materials from NIST. These take the form of metal-on-glass, metal-on-quartz, and solid glass filters. Most are used for verifying the photometric scale or for checking the wavelength calibration of a recording spectrophotometer. Descriptions of their development and use are given in Mavrodineanu and Baldwin,⁵² Mavrodineanu and Baldwin,⁵³ Eckerle et al.,³⁰ and Hsia.⁵⁴ The standardization laboratories of several countries occasionally conduct international intercomparisons of traveling standards. Recent intercomparisons have been reported in Eckerle et al.⁵⁵ and Fillingner and Andor.⁵⁶

35.10 MEASUREMENT OF ABSORPTANCE

In most cases, absorptance is not directly measured, but is inferred from transmission measurements, with appropriate corrections for reflection losses. These corrections can be calculated from the Fresnel equations if the surfaces are polished and the index of refraction is known. For materials where the absorption is extremely small, this method is unsatisfactory, as the uncertainties are dominated by the reflection contribution. In this case, direct measurements (such as laser calorimetry) must be made as discussed by Lipson et al.⁵⁷ and Hordvik.⁵⁸

35.11 MEASUREMENT OF REFLECTANCE

Instrumentation for the measurement of reflectance takes many forms. Only a few of the definitions for reflectance (Table 2) and reflectance factor (Table 3) have been adopted as standard configurations. The biconical configuration with small solid angles is most suited to a measurement of specular (regular, in the mirror direction) reflection. A simple reflectometer for the absolute measurement of specular reflectance was devised by Strong^{59,60} and is shown schematically in Fig. 5. Numerous detail improvements have been made on this fundamental design, including the use of averaging spheres. Designs range from simple^{61–65} to complex.⁶⁶ Some reflectometers have been built specifically to measure at normal incidence.^{67–69} Measurement methods and data interpretation are also given in ASTM F768,⁴⁵ ASTM D523,⁷⁰ ASTM F1252,⁷¹ Hernicz and DeWitt,⁷² and Snail et al.⁷³

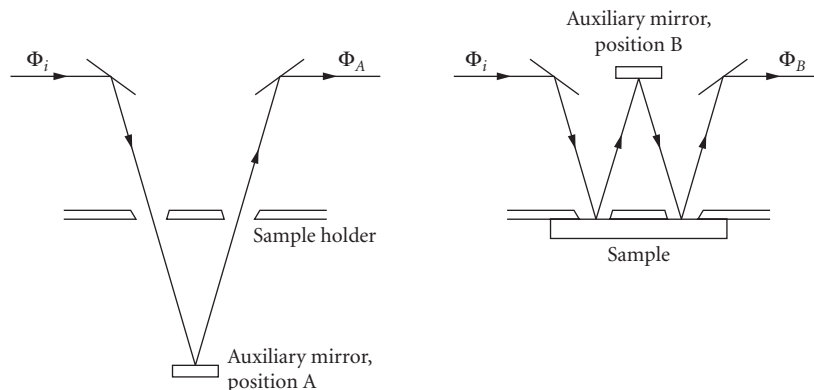


FIGURE 5 The Strong "VW" reflectometer.

The characterization of appearance of materials involves measurements of reflectance, both diffuse and specular. Numerous procedures and instruments have been devised for goniophotometry, the measurement of specular gloss with biconical geometry. Measurements are made at several angles from normal (20° , 30° , 45° , 60° , 75° , and 85°) depending upon the material under scrutiny. Further details can be found in ASTM C347,⁷⁴ ASTM E167,⁷⁵ ASTM D523,⁷⁰ ASTM E1349,⁷⁶ ASTM E179,⁷⁷ ASTM E430,⁷⁸ Erb,⁷⁹ and Hunter.⁸⁰

The measurement of diffuse reflectance can be accomplished using any one of the nine definitions from Table 2 and integrating where necessary. One could, for example, choose to measure the bidirectional reflectance distribution function (BRDF) as a function of incident beam parameters and to integrate over the hemisphere, but this would be a tedious process, and the large amount of data generated would be useful only to those involved with detailed materials properties research. Most practical measurements of diffuse reflectance involve the use of an integrating sphere. Several papers have discussed the general theory of the integrating sphere.^{81,82}

In the visible and near-IR spectral regions, the integrating sphere is the instrument of choice for both specular and diffuse specimens. Many papers have been written detailing instruments, methods, and procedures, some of which are shown in Fig. 6. The specular component of the reflected flux can be included to determine the total reflectance (Fig. 6a) or excluded to measure just the diffuse component (Fig. 6b). The angle of incidence can be varied by placing the sample at the center of the sphere (Fig. 6c), Edwards et al.⁸³ Others making contributions include Clarke and Compton,⁸⁴ Clarke and Larkin,⁸⁵ Dunkle,⁸⁶ Egan and Hilgeman,⁸⁷ Goebel et al.,⁸⁸ Hisdal,^{89,90} Karras,³⁵ McNicholas,⁹¹ Richter and Erb,⁹² Sheffer et al.,^{93,94} Taylor,⁹⁵ and Venable et al.²⁷ Some of these methods have been incorporated into standard methods and practices, such as ASTM C523,⁹⁶

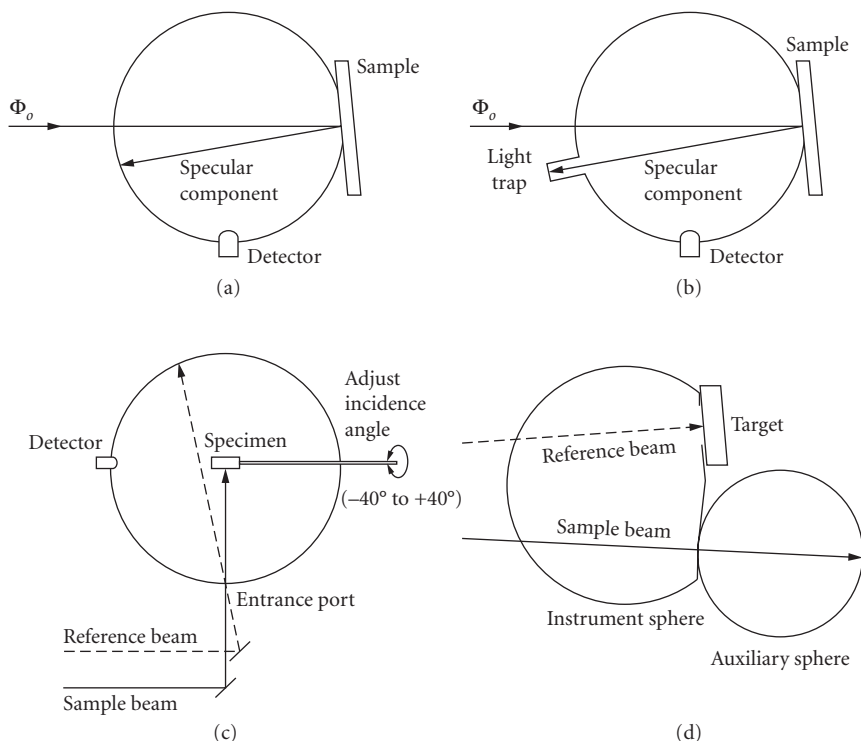


FIGURE 6 Measurement of diffuse reflectance using an integrating sphere.

35.12 RADIOMETRY AND PHOTOMETRY

ASTM E429,⁹⁷ ASTM E903,⁴⁷ CIE,⁹⁸ and IES.⁹⁹ Most integrating sphere measurements require reference to some form of an artifact standard, but the double-sphere method (Fig. 6d) produces absolute diffuse reflectance.^{37,38,100,101} Lindberg¹⁰² has demonstrated a method to scale relative measurements to absolute.

Alternative forms of hemispherical irradiation and/or collection have been described, several of which are shown in Fig. 7. Specular hemispherical (Fig. 7a), paraboloidal (Fig. 7b), and ellipsoidal (Fig. 7c) collectors have been used, particularly in those spectral regions where integrating sphere coatings are difficult to obtain.^{86,103–109} The Helmholtz reciprocity principle has been invoked to demonstrate the reversibility of the source and the collector.¹¹⁰ Hemispherical irradiation has also been employed by placing a cooled sample coplanar with the wall of a furnace and comparing the radiance of the sample with that of the wall of the furnace as shown in Fig. 7d.^{86,111–113}

The procedures and instrumentation for the measurement of reflectance factor are identical with those for diffuse reflectance using the $0^\circ/45^\circ$ or $45^\circ/0^\circ$ geometry with annular, circumferential, or uniplanar illumination or viewing. Reference is made to a white reflectance standard characterized for reflectance factor, which must be compared with a perfect diffuse reflector. Pertinent references are ASTM E1349,⁷⁶ ASTM E97,¹¹⁴ ASTM E1348,¹¹⁵ Hsia and Weidner,¹¹⁶ and Taylor.^{36,117}

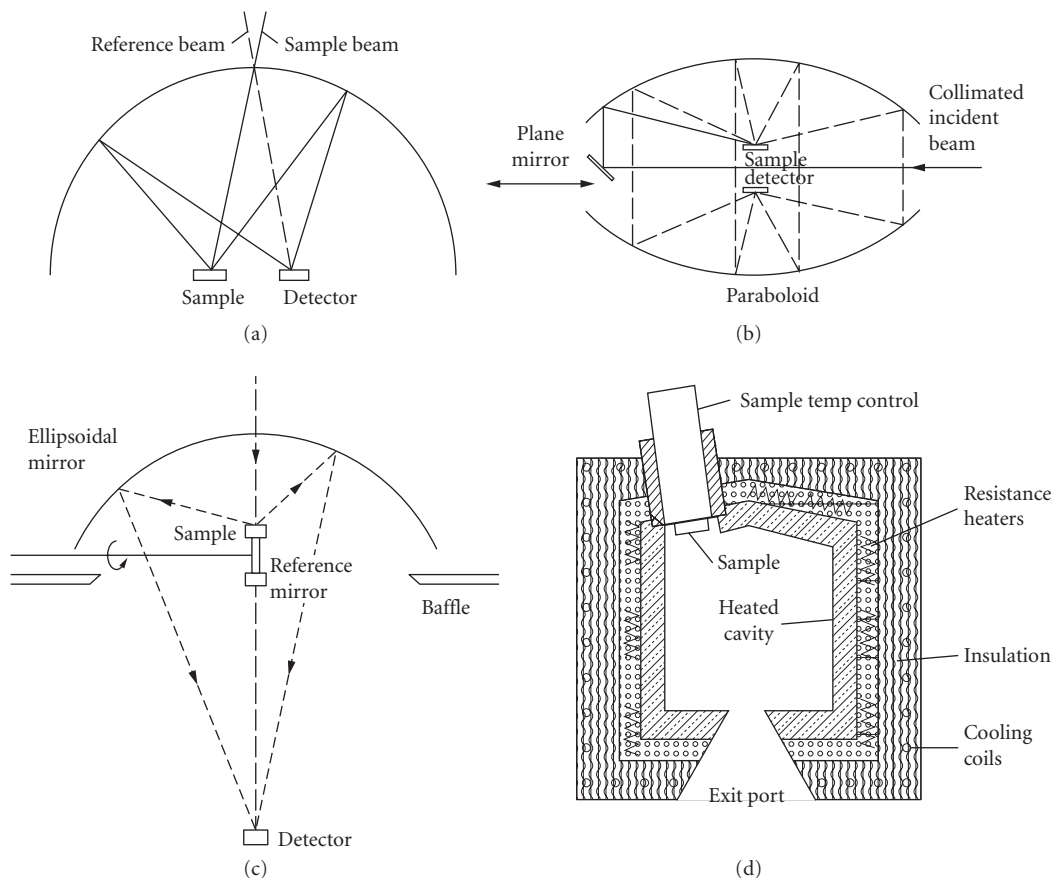


FIGURE 7 Measurement of diffuse reflectance using alternate methods.

Orbiting sensors measure the radiance of the earth-atmosphere system with some known geometry (generally nadir) and in well-defined wavelength bands. The quantity of interest is reflectance, as it is related to factors such as crop assessment, mineralization, etc. Corrections must be made for the atmospheric absorption, emission, and scattering and for the BRDF of the target. BRDF has been characterized in the field using the sun as the source, as described by Duggin.^{118,119}

Laboratory measurements of BRDF are made using goniometers where the sample-source angle and sample-receiver angle are independently adjustable. Coherent sources (lasers) are employed for the characterization of smooth specimens where a large source power is necessary for adequate SNR for off-specular angles and where speckle is not a concern. Incoherent sources (xenon arcs, black-body simulators, or tungsten-halogen) sources are often employed with spectral filters for more diffuse specimens. Similar measurements and techniques are employed to characterize bidirectional transmittance distribution function (BTDF) and bidirectional scattering distribution function (BSDF). For further information, see Asmail,¹²⁰ ASTM E1392,¹²¹ and Bartell et al.¹²²

The measurement of retroreflection poses the situation that the return beam coincides with the incident beam. The usual solution is to employ a beam splitter in the system, allowing the incident beam to pass and the return beam to be reflected. This immediately imposes both a significant loss in flux and the situation where the beam reaching the sample is partially polarized, unless a non-polarizing beamsplitter is employed. In addition, it is imperative that the reflected component of the incident beam be well-trapped, as the radiometer is looking in the same direction. The special vocabulary for retroreflection is given in CIE¹²³ and ASTM E808.¹⁷ Test methods are given in ASTM E810,¹²⁴ ASTM E809,¹²⁵ and Venable and Johnson.¹²⁶ An instrument specifically designed to measure retroreflection is detailed in Eckerle et al.¹²⁷

Most measurements of reflectance are relative and require artifact standards. Specular reflectance measurements are occasionally made using the absolute technique shown in Fig. 5, but are more commonly done using a simple reflectance attachment for a commercial spectrophotometer, requiring a calibrated reference. Freshly deposited metallic films have been used, with the assumption that an individual coating is the same as accepted data as shown in Table 5 for Al and Au.^{128–133} Standards for specular reflectance are also available.^{135–137}

Diffuse reflectance standards exist in several forms. Ideally, a perfect ($\rho = 1$, lambertian) diffuser would be used, particularly for measuring reflectance factor.^{138–140} Certain materials approach the ideal over a limited angular and wavelength range. Historically, MgO was used in the visible spectrum.^{141,111} It was replaced first by BaSO₄¹⁴² and more recently by PTFE^{143,144} and ASTM E259.¹⁴⁵ Table 5 also shows a typical 6°/hemispherical reflectance factor for PTFE.¹⁴⁶ This fine, white powder, when pressed to a density of 1 g/cm³, is close to ideal over a wide spectral range. It is not quite lambertian, showing a falloff of BRDF at angles far removed from the specular direction¹⁴⁷ and exhibiting a slight amount of retroreflection. It may also be slightly luminescent when excited by far-ultraviolet.¹⁴⁸

In the infrared, two materials have proven useful. Flowers of sulfur^{149–151} is suitable over the spectral range 1 to 15 μm . Gold is highly reflective and very stable. To be useful as a diffuse reflectance standard, it must be placed on top of a lambertian surface. Several substrates for gold have been suggested, including sandpaper¹⁵² and flame-sprayed aluminum.

PTFE is a satisfactory laboratory standard but is not well-suited for field use as it is not particularly rugged and is highly adsorbant and therefore subject to contamination. Several solutions have been proposed for working standards, including Eastman integrating sphere paint (BaSO₄), Vitriolite tile, and the Russian MS20 and MS14 opal glasses. These materials are, in general, more rugged, stable, and washable than PTFE. Further details can be found in CIE¹⁵³ and Clarke et al.¹⁵⁴

Discussion on the fabrication, calibration, and properties of various diffuse reflectance standards can be found in ASTM E259,¹⁵⁵ Budde,^{156,157} Egan and Hilgeman,¹⁵⁸ Fairchild and Daoust,¹⁴⁷ Morren et al.,¹⁵⁹ TAPPI,¹⁶⁰ and Weidner.^{161,162} International intercomparisons of laboratory standards of diffuse reflectance have been reported in Budde et al.,¹⁶³ and Weidner and Hsia,¹⁴⁶ and IES.⁹⁹

There are no standards available for retroreflection. However, NIST offers a Measurements Assurance Program (MAP) to enable laboratories to make measurements consistent with other national standards.

TABLE 5 Reflectance Standards

Wavelength (nm)	Aluminum	Gold	PTFE (6°/hemi)
250		0.295	0.973
300	0.921	0.346	0.984
350	0.921	0.330	0.990
400	0.919	0.360	0.993
450	0.918	0.358	0.993
500	0.916	0.453	0.994
550	0.916	0.800	0.994
600	0.912	0.906	0.994
650	0.906	0.947	0.994
700	0.898	0.963	0.994
750	0.886	0.970	0.994
800	0.868	0.973	0.994
850	0.868	0.973	0.994
900	0.891	0.974	0.994
950	0.924	0.974	0.994
1000	0.940	0.974	0.994
1100		0.975	0.994
1200	0.964	0.975	0.993
1300		0.975	0.992
1400		0.975	0.991
1500	0.974	0.975	0.992
1600		0.975	0.992
1700		0.976	0.990
1800		0.976	0.990
1900		0.976	0.985
2000	0.978	0.976	0.981
2100		0.976	0.968
2200		0.976	0.977
2300		0.976	0.972
2400		0.976	0.962
2500	0.979	0.977	0.960

35.12 MEASUREMENT OF EMITTANCE

Measurements of emittance can be done in several ways. The most direct method involves forming a material into the shape of a cavity in such a way that near-blackbody radiation is emitted. A measurement then compares the radiation from a location within the formed cavity to radiation from a flat, outside surface of the material, presumably at the same temperature.¹⁶⁴ The cavity can take the form of a cylinder, cone, or sphere. Similarly, a small-diameter, deep hole can be drilled into a specimen and radiation from the surface compared to radiation from the hole. Care must be taken that the specimen is isothermal and that the reflected radiation is considered. The definitive measurements of several materials, such as tungsten,¹⁶⁵ were determined in this fashion. The significant advantage in this direct method is that it is relative, depending on neither absolute radiometry or thermometry, but only requiring that the radiometer or spectroradiometer be linear over the dynamic range of the measurement. This linearity is also determinable by relative measurements.

If a variable-temperature blackbody simulator and a suitable thermometer are available, the specimen can be heated to the desired temperature T_s and the blackbody simulator temperature T_{bb} can be adjusted such that its (spectral) radiance matches that of the specimen. Then the (spectral)

emittance is calculable using the following equations for spectral emittance $\varepsilon(\lambda)$ and emittance ε (for a graybody only).

$$\varepsilon(\lambda) = \frac{e^{c_2/\lambda T_s} - 1}{e^{c_2/\lambda T_{bb}} - 1}, \quad \varepsilon = \frac{T_{bb}^4}{T_s^4} \quad (16)$$

If an absolutely calibrated radiometer and a satisfactory thermometer are available, a direct measurement can be made, as L_b is calculable if the temperature is known. Again, the reflected radiation must be considered.

Simple “inspection meter” techniques have been developed, and instrumentation is commercially available to determine the hemispherical emittance over a limited range of temperatures surrounding ambient. These instruments provide a single number, as they integrate both spatially and spectrally. A description of the technique can be found in ASTM E408.¹⁶⁶

Measurements of spectral emittance are most often made using spectral reflectance techniques, invoking Kirchhoff's law along with the assumption that the transmittance is zero. A review of early work is found in Dunn et al.,¹⁶⁷ and Millard and Streed.¹⁶⁸ The usual geometry of interest is the directional-hemispherical. This can be achieved by either hemispherical irradiation-directional collection, or, using Helmholtz reciprocity,¹¹⁰ directional irradiation-hemispherical collection. Any standard reflectometry technique is satisfactory.

A direct method for the measurement of total (integrated over all wavelengths) hemispherical emittance is to use a calorimeter as shown in Fig. 8. A heated specimen is suspended in the center of a large, cold, evacuated chamber. The vacuum minimizes gaseous conduction and convection. If the sample suspension is properly designed, the predominant means of heat transfer is radiation. The chamber must be large to minimize the configuration factor between the chamber and the specimen. The chamber is cooled to T_c to reduce radiation from the chamber to the specimen. The equation used to determine emittance ε is

$$\varepsilon = \frac{P}{\sigma A(T_s^4 - T_c^4)} \quad (17)$$

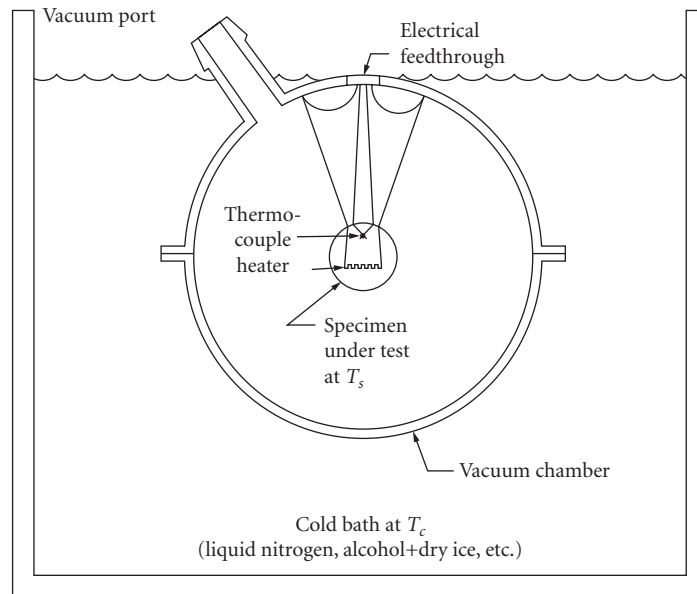


FIGURE 8 Calorimetric measurement of total hemispherical emittance.

where P is the power input to the specimen heater necessary to maintain an equilibrium specimen temperature T_s and A is the specimen area. The equation has been simplified with the aid of the following assumptions: (1) no thermal conduction from the specimen to the chamber, (2) no convective losses, (3) equilibrium has been achieved, and (4) the specimen area is much less than the chamber area. The power can be supplied electrically by means of a known heater or optically via a window in the chamber. In the latter case, a direct measurement of the ratio of solar absorptance α_s to thermal emittance ϵ_T can be directly obtained if the optical source simulates solar radiation. By varying the input power, the emittance can be determined as a function of temperature. There are numerous small corrections to account for geometry, lead conduction, etc. Details can be found in ASTM C835,¹⁶⁹ ASTM E434,¹⁷⁰ Edwards,¹⁷¹ and Richmond and Harrison.¹⁷²

Several attempts have been made to define and characterize artifact standards of spectral emittance for direct measurements.^{10,11} These were specimens of a thermally stable metal (i.e., Inconel) which were calibrated for emittance as a function of wavelength at several temperatures. No such standards are currently available. Interlaboratory comparisons have been made and reported.¹⁷³

Special problems include measurements at cryogenic temperatures¹⁷⁴ and effects of partially transparent materials.¹⁷⁵ Some additional references relating to emittance and its measurement are ASTM E307,¹⁷⁶ ASTM E423,¹⁷⁷ Clarke and Larkin,⁸⁵ DeWitt,¹⁷⁸ DeWitt and Richmond,¹⁷⁹ Hornbeck,¹⁸⁰ Millard and Streed,¹⁶⁸ Redgrove,¹⁸¹ Sparrow et al.,¹⁶⁴ Stierwalt,¹⁸² and Wittenberg.¹⁸³

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