

Applied Spectroscopy Spectroscopic Nomenclature

Absorbance, A

Negative logarithm to the base 10 of the transmittance: $A = -\log_{10}(T)$.
(Not used: absorbancy, extinction, or optical density). (See Note 3).

Absorptance, α

Ratio of the radiant power absorbed by the sample to the incident radiant power; approximately equal to $(1 - T)$. (See Notes 2 and 3).

Absorption

The absorption of electromagnetic radiation when light is transmitted through a medium; hence “absorption spectrum” or “absorption band”. (Not used: “absorbance mode” or “absorbance band” or “absorbance spectrum” unless the ordinate axis of the spectrum is Absorbance.) (See Note 3).

Absorption index, k

See imaginary refractive index.

Absorptivity, α

Internal absorbance divided by the product of sample path length, ℓ , and mass concentration, ρ , of the absorbing material.

$$\alpha = A_i / \rho \ell$$

SI unit: $\text{m}^2 \text{kg}^{-1}$.

Common unit: $\text{cm}^2 \text{g}^{-1}$; $\text{L g}^{-1} \text{cm}^{-1}$.

(Not used: absorbancy index, extinction coefficient, or specific extinction.)

Attenuated total reflection, ATR

A sampling technique in which the evanescent wave of a beam that has been internally reflected from the internal surface of a material of high refractive index at an angle greater than the critical angle is absorbed by a sample that is held very close to the surface. (See Note 3.)

Attenuation

The loss of electromagnetic radiation caused by both absorption and scattering.

Beer–Lambert law

Absorptivity of a substance is constant with respect to changes in path length and concentration of the absorber. Often called Beer’s law when only changes in concentration are of interest.

Brewster’s angle, θ_B

The angle of incidence at which the reflection of p -polarized radiation is zero.

Circular birefringence

$n^L - n^R$, the difference between the refractive index of a medium for left, n^L , and right, n^R , circularly polarized radiation. Like the refractive indices, circular birefringence changes with wavenumber.

SI unit: none, a dimensionless quantity.

Circular dichroism

In general, the property of different absorption of left and right circularly polarized radiation by an optically active material. Specifically, the circular dichroism is $k^L - k^R$, where k^L and k^R are the absorption indices (imaginary refractive indices) of the sample for left and right circularly polarized radiation, respectively. Note that some authors use the absorptivity or molar absorptivity instead of the absorption index. Like absorption of radiation, circular dichroism changes with wavenumber.

Complex refractive index, \tilde{n}

The complex sum of the real refractive index, n , and the imaginary refractive index, k . ($\tilde{n} = n + ik$)

Critical angle, θ_C

The angle above which a beam in an optically rare medium (low refractive index, n_1) that is incident at an interface with an optically dense medium (higher refractive index, n_2) is totally reflected. $\theta_C = \sin^{-1}(n_1/n_2)$

Diffuse reflectance

The ratio of the spectral intensity reflected by a scattering sample to that reflected by an equivalent non-absorbing reference that replaces the sample; sometimes refers to a measurement where specularly reflected radiation has been prevented from reaching the detector. The term "Remittance" may be used in place of "Diffuse reflectance" to emphasize inclusion of the specularly reflected radiation.

SI unit: none, a dimensionless quantity.

Diffuse reflection

The process in which radiation is incident on a scattering sample at a certain angle and is returned (or remitted) over all angles. Diffuse reflection is a complicated process that involves transmission, reflection, and scattering. (See Note 3).

Diffuse transmission

The process in which radiation is transmitted by a scattering sample and leaves the sample in directions other than that required by Snell's law of refraction. The process is complicated and involves transmission, reflection, and scattering. (See Note 3).

Emittance, ϵ

Ratio of the radiant flux emitted by the sample to that emitted by a black body at the same temperature. (See Notes 2 and 3).

Frequency, f , ν

Number of cycles in unit time.

SI unit: Hertz ($1 \text{ Hz} = 1 \text{ s}^{-1}$).

Imaginary refractive index, k

A dimensionless parameter indicating the amount of absorption loss when an electromagnetic wave propagates through a material. k is equal to $\alpha/2\pi\tilde{\nu}$, where α is the linear absorption coefficient (cm^{-1}) and $\tilde{\nu}$ is the wavenumber. (Also used: Index of absorption, absorption index; not used: index of attenuation.)

Intensity, I

The radiant power that crosses unit area. Intensity and irradiance are formally the same quantity, but the term intensity is usually used for collimated beams of radiation.

SI unit: W m^{-2} .

Interactance spectroscopy

A term coined by Karl Norris to describe a variant of conventional near-infrared diffuse reflection spectroscopy applicable to scattering samples whereby the Raman scattered light is collected from a region that is displaced from the point where the NIR beam is incident on the sample.

Internal absorbance, A_i

Negative logarithm to the base 10 of the internal transmittance: $A_i = -\log_{10}(T_i)$.

Internal Absorptance, α_i

Ratio of the radiant power absorbed by the sample to the incident radiant power, fully corrected for reflection losses and any window absorption. (See Notes 6 and 7)

Internal reflection element, IRE

A transparent material of high refractive index that is used for ATR measurements. Note: These materials are often not crystalline and so should not be called ATR crystals.

Internal transmittance, T_i , τ_i

Ratio of the radiant power transmitted by the sample to the incident radiant power, fully corrected for reflection losses and any window absorption. (See Notes 6 and 7).

Irradiance, I

The radiant power received on unit area.

SI unit: W m^{-2} .

Kubelka–Munk function, Remission function, $f(R_\infty)$

This function is defined as: $f(R_\infty) = (1 - R_\infty)^2 / 2R_\infty$, where R_∞ is the diffuse reflectance from a sample of infinite depth. Theoretically, $f(R_\infty)$ equals the ratio of the linear absorption coefficient to the scattering coefficient. Under the assumptions of the Kubelka–Munk theory, if the scattering coefficient at a given wavenumber is a constant for a given set of samples, then $f(R_\infty)$ is directly proportional to the product of the absorptivities and concentrations of the components of a mixture, analogous to the behavior of absorbance under Beer's law.

Kubelka–Munk reflection or Volume reflection

The process of light penetrating into a powdered sample and re-emerging from the surface of incidence; sometimes incorrectly called diffuse reflection. The combined process of volume reflection and specular reflection is known as diffuse reflection or remission.

Linear absorption coefficient, α

The Napierian absorbance divided by the path length, $\alpha = A_e / \ell$.

Linear remission coefficient, b

The negative Napierian logarithm of the fraction of light remitted by a non-absorbing scattering sample, divided by the path length ℓ .

$$b = -\ln_e(I_R / I_0) / \ell$$

SI unit: m^{-1} .

Low-emissivity (“low-e”) glass slides

Slides that are made of glass coated with a thin Ag/SnO₂ layer. They are chemically inert and nearly transparent to visible light. However, they reflect mid-infrared radiation almost completely and thus are ideal and inexpensive substrates for transflection infrared microspectroscopy, as they allow both visual and infrared images to be collected from the same sample.

Mass concentration, c

Mass of sample divided by volume of solution or mixture.

SI unit: kg/m^3 .

Common unit: g/L; mg/L.

Mass fraction, w_B

The mass of component B divided by the total mass of the sample. Frequently given as ppm or ppb. (See Notes 8 and 9).

Molar absorptivity (preferably) or **Molar decadic absorption coefficient**, ϵ
Internal absorbance divided by the product of sample path length, ℓ , and molar concentration, c , of the absorbing material.

$$\epsilon = A_i / c\ell$$

SI unit: $\text{m}^2 \text{mol}^{-1}$

Common unit: $\text{L mol}^{-1} \text{cm}^{-1}$; $\text{cm}^2 \text{mol}^{-1}$.

(Not used: molar absorptivity index or molar extinction coefficient.)

Molar concentration, or molarity, M

Moles of sample divided by volume of solution or mixture.

SI unit: mol/m^3 .

Common unit: mol/L .

Mole fraction, χ_B

The number of moles of component B divided by the total number of moles in the mixture. (See Note 8).

Napierian absorbance, A^e

The absorbance calculated in base e , i.e., $\ln(1/T)$

Net absorption cross section, σ_{net}

The absorptivity per molecule, i.e., the molar absorptivity, ϵ , divided by Avogadro's number, usually corrected to base e through $\sigma_{net} = 2.303 \epsilon / N_A$.

SI unit: m^2 .

Optical absorption depth, μ_β

The depth in a sample at which the radiant intensity is reduced to $1/e$ of its value at the surface of the sample. It equals the reciprocal of the linear absorption coefficient.

SI unit: m .

Common unit: μm .

Percent transmission

Transmittance $\times 100$. (Not used: Percent transmittance)

Penetration depth, d_p

In attenuated total reflection, the distance from the boundary with the internal reflection element at which the mean square electric field intensity of the evanescent wave, i.e., the intensity of a collimated radiation beam, is reduced to $1/e$ of its value at the boundary.

In photoacoustic (PA) spectroscopy, an analogous definition may be cited for strongly absorbing samples. For weakly absorbing PA samples, the depth of penetration is given by the thermal diffusion depth. In practice, the depth below the surface that gives rise to most of the measured PA spectrum is the smaller of

the thermal diffusion depth and the optical absorption depth. SI unit: m. Common unit: μm .

Photoacoustic spectroscopy

A form of spectroscopy in which the measured signal is caused by the increase in temperature of a sample caused by the absorption of radiation.

p-Polarized Radiation

Polarized radiation where the plane of polarization is parallel to the plane of incidence.

s-Polarized Radiation

Polarized radiation where the plane of polarization is perpendicular to the plane of incidence.

Pressure fraction

The partial pressure of component divided by the total pressure of the sample. Frequently given as ppm or ppb. (See Notes 8, 9, and 10).

Raman wavenumber shift, $\Delta\tilde{\nu}$

The vacuum wavenumber of the exciting light minus the vacuum wavenumber of the Raman scattered light.

SI unit: m^{-1} .

Common unit: cm^{-1} .

Reflectance, R , ρ

Ratio of the radiant power reflected by the sample to the incident radiant power. (See Notes 2 and 3).

Reflection

The redirection of a beam of electromagnetic radiation at an interface; hence “reflection spectrum” or “reflection mode”. (Not used: “reflectance mode” or “reflectance spectrum”, unless the ordinate axis of the spectrum is Reflectance.) (See Note 3).

Reflection–absorption

A sampling technique used to investigate films on flat metallic surfaces in which radiation is passed onto the surface of the sample at grazing incidence. Usually applied to the case where the thickness of the film is much less than the wavelength of the radiation. (See Note 3.)

Reflection–absorption at grazing incidence; Infrared reflection–absorption spectroscopy (IRRAS); Reflection–absorption infrared spectroscopy (RAIRS)

Reflection–absorption with very thin layers of an absorbing material on a metallic surface and the angle of incidence between 70° and 90° ; i.e., with the incident

radiation beam traveling nearly parallel to the surface. The electric vector of the radiation is then either parallel or nearly perpendicular to the surface, which allows improved discrimination between species at the surface and those in the bulk.

Refractive index, n

The ratio of the phase velocity, c , of radiation in a vacuum to the phase velocity in the medium itself.

Remission

The process by which radiation that is incident on one side of a scattering sample is redirected to leave the sample on the same side; often called diffuse reflection. (See Note 3).

Remission fraction or remittance, \tilde{R}

The fraction of the incident radiation that undergoes remission. The sum of the remission fraction, the transmittance, and the absorptance equals one.

SI unit: none, a dimensionless quantity.

Sample path length, b, ℓ

The length of sample through which the radiation passes.

SI unit: m.

Common unit: μm ; mm; cm.

Savitzky–Golay filter

A method first published in 1964 to smooth data using a digital filter that is applied to data points in order to increase the signal-to-noise ratio.

Signal-to-noise ratio, SNR or S/N

The ratio of the signal of interest to the noise level. The noise level may be the root-mean-square noise or the peak-to-peak noise, but which of these is used must be stated, along with the spectral region over which the noise is measured.

SI unit: none, a dimensionless quantity.

Spatially offset Raman spectroscopy (SORS)

A variant of conventional Raman spectroscopy applicable to scattering samples whereby the Raman scattered light is collected from a region that is displaced from the point where the laser is incident on the sample.

Specular reflection

The process in which radiation is reflected from the front surface of a sample in which the angle of incidence equals the angle of reflection.

Specular reflectance, R

The ratio of the spectral intensity of radiation reflected from the front surface of the sample to that reflected by an appropriate reference material.

Spectrometry

The measurement of a spectrum.

Spectroscopy

The art or science of interpreting spectra qualitatively or quantitatively.

Thermal diffusion depth; Thermal wave decay length, μ_s

The distance traveled by a thermal wave in photoacoustic spectrometry at which its amplitude is reduced by $1/e$.

SI unit: m.

Common unit: μm .

Transflectance

The ratio of the spectral intensity of the transflected beam to the spectral intensity of the incident beam in a transflection experiment. "Transflectance" has also been used to mean "transflection"; this is clearly confusing and is strongly discouraged. (See Note 3).

Transflection

A sampling technique used to investigate relatively thick films on a reflecting surface of either a metal or "low-e" glass substrate (for mid-infrared measurements) or a diffusely reflecting substrate such as a ceramic disk for near-infrared measurements. The thickness of the film is large enough to yield an interpretable spectrum. (See Note 3).

Transmittance, T , τ

Ratio of the radiant power transmitted by the sample to the radiant power incident on the sample. The incident radiant power is usually obtained as that transmitted by a non-absorbing reference material. (Not used: transmittancy or transmission). (See Notes 2 and 3).

Transmission

The passage of electromagnetic radiation through a medium (unless the ordinate axis of the spectrum is Transmittance). (Not used: "transmittance mode" or "transmittance spectrum", unless the ordinate axis of the spectrum is Reflectance.) (See Note 3).

Transmission fraction, Total transmittance, Total transmission fraction, T

The fraction of the spectral intensity incident upon a scattering sample that leaves the opposite side of the sample.

SI unit: none, a dimensionless quantity.

Two-dimensional (2D) correlation spectroscopy

A form of spectroscopy in which spectra are recorded at different levels of an applied external perturbation of the sample and are processed to yield a 2D

correlation spectrum. The applied external perturbation may be cyclic or non-cyclic, and for vibrational spectroscopy changes of temperature, pressure, or mechanical strain have been used. The technique is applicable to all forms of vibrational spectroscopy.

Two-dimensional (2D) correlation spectrum

A three-dimensional surface in which two of the dimensions show wavenumber $\tilde{\nu}_1$ and wavenumber $\tilde{\nu}_2$ and the third axes shows a correlation function of the spectral intensities observed at $\tilde{\nu}_1$ and $\tilde{\nu}_1$. The shape of the surface shows whether the bands at the two wavenumbers are or are not correlated, and hence allows deductions to be made about the extent to which the different parts of the molecule are linked in their response to the applied external perturbation.

Vibrational circular dichroism, VCD

Circular dichroism, $(k^L - k^R)$ or $(A^L - A^R)$, for vibrational transitions.

Volume fraction, ϕ_B

The volume of component B divided by the total volume of the sample. Frequently given as ppm or ppb. (See Notes 8 and 9).

Wavelength, λ

Smallest distance in the direction of propagation between equivalent points on a wave at constant time.

SI unit: m.

Common unit: μm , nm. (See Note 11).

Wavenumber, σ or $\tilde{\nu}$

Number of waves in unit length, i.e., $\sigma = 1/\lambda$. σ is used for wavenumber in medium of refractive index n ; $\tilde{\nu}$ is used for wavenumber in vacuum, i.e., $\tilde{\nu} = 1/n\lambda$. When used to characterize radiation, the wavenumber is defined as the reciprocal of the wavelength in vacuum and the symbol $\tilde{\nu}$ is used. (Not used: wavenumbers.)

SI unit: m^{-1} .

Common unit: cm^{-1} . (See Note 11).

Notes

1. For collimated beams, the *radiant power* can be replaced by intensity. It is usually measured as the unratiod spectrum obtained from a Fourier transform spectrometer or a single-beam spectrum from a dispersive spectrometer.
2. If scattering and luminescence can be neglected, $T + \alpha + \rho = 1$.
3. A spectrum should generally be termed a *transmission spectrum*, an *absorption spectrum*, a *reflection spectrum*, a *diffuse reflection spectrum*, an *attenuated total reflection spectrum*, or an *emission spectrum*. The same adjectives should be used with *spectra* when more than one spectrum is meant. The terms *transmittance spectrum*, *absorbance spectrum*, *reflectance spectrum*,

diffuse reflectance spectrum, attenuated total reflectance spectrum, or emittance spectrum, should only be used when the ordinate explicitly presents the transmittance, absorbance, reflectance, diffuse reflectance, attenuated total reflectance, or emittance spectrum.

4. Once the instrument on which the spectrum has been measured has been defined as, for example, an FT-IR spectrometer (e.g., in the Experimental section), spectra should subsequently be referred to as “infrared spectra” or simply “spectra”, not “FT-IR spectra”.

5. The *radiant flux* can be replaced by radiant power if the sample and the black body have the same area, and by *intensity* if in addition the emission is measured as a collimated light beam.

6. In optical spectroscopy, internal properties such as the internal transmittance, T_i and internal absorptance α_i are defined to exclude surface effects and effects of the sample cell such as reflection losses or vignetting. Thus, $T_i + \alpha_i = 1$ if scattering and luminescence can be neglected. This leads to the usual form of the Beer–Lambert law, $I_r / I_0 = T_i = 1 - \alpha_i = \exp(-\epsilon c \ell)$.

7. In gas-phase spectroscopy in which the sample cell remains in the light beam between spectra, the ratio of the spectrum of the cell full of sample to the spectrum of the empty cell gives the internal transmittance without correction. This is usually the case in GC/FT-IR, for example. Similarly, the spectrum of a cell full of a solution of a dilute solute divided by the spectrum of the same cell full of solvent gives the internal transmittance of the solute directly, provided that the position of the cell in the beam is unchanged. In both cases, the internal absorptance is obtained directly as $\alpha_i = 1 - T_i$. However, to obtain the internal transmittance of a cell full of a neat liquid, or of the solvent of a solution, the transmittance spectrum obtained with a suitable reference requires correction for reflection effects.

8. Authors should use the American billion, 10^9 , in preference to the European billion, 10^{12} , and the American trillion, 10^{12} , in preference to the European trillion, 10^{18} . Thus 1 part per billion (ppb) is one part in 10^9 and 1 part per trillion (ppt) is one part in 10^{12} . Parts per thousand should be abbreviated as ppth to distinguish it from parts per trillion.

9. Fractions are dimensionless quantities. Terms like ppm and ppb should only be used to describe dimensionless quantities. The frequently used terms ppmg, ppbv, etc., to mean parts-per-million grams, parts-per-million volume, etc., are ambiguous because they are used to describe sometimes mass fractions or volume fractions and sometimes ratios of mass to volume. Thus, their use should be avoided unless their meaning is clearly defined in the paper. In particular the use of ppmv to conveniently describe a ratio of mass to volume in the units mg/L should be avoided unless it is clearly stated that ppmv describes the mass concentration in mg/L.

10. The pressure fraction is usually essentially equal to the mole fraction through Dalton's Law of partial pressures.

11. The label on spectra for which the abscissa is wavenumber should be Wavenumber (cm^{-1}), not Wavenumbers (cm^{-1}).

How to define Emittance and Emissivity

Merriam-Webster's dictionary defines them as follows:

EMITTANCE: the energy radiated by the surface of a body per second per unit area:

EMISSIVITY: the relative power of a surface to emit heat by radiation : the ratio of the radiant energy emitted by a surface to that emitted by a blackbody at the same temperature

Wikipedia was not all that helpful as one entry states that "the term emissivity is generally used to describe a simple, homogeneous surface such as silver. Similar terms, **emittance** and **thermal emittance**, are used to describe thermal radiation measurements on complex surfaces such as insulation products." Another entry states that "**thermal emittance** or **thermal emittivity** is the ratio of the radiant emittance of heat of a specific object or surface to that of a standard black body. Emissivity and emittivity are both dimensionless quantities given in the range of 0 to 1, but emissivity refers to a material property (of a homogeneous material), while emittivity refers to specific samples or objects.

Emissivity versus Emittance

The term emissivity determines the characteristics of a material while emittance refers to the characteristics of a target object. Hence, emissivity is only one variable which helps in finding out emittance of a specific object."

Yet another Wikipedia entry states:

"**Emissivity** is a variable which is considered very crucial for infrared temperature calculations of a target object. It is basically defined as "the ratio of the energy radiated by an object at a given temperature to the energy emitted by a perfect radiator, or blackbody, at the same temperature".

The value of emissivity for all objects ranges between 0.0 and 1.0. The emissivity of a blackbody is found to be 1.0 as it happens to be very near to the emissivity range of infrared. Objects having higher emissivity values can be easily handled for infrared temperature measurements while the objects having lower emissivity values are difficult to deal. Therefore blackbodies offer trouble free temperature measurements while extremely reflective and shiny metals like chrome, silver and aluminum having lower emissivity values poses problems in correct temperature measurements. However, almost all IR radiation thermometers provide compensation for varying emissivity values for diverse materials."

The following was taken from the **International Flame Research Foundation** (<http://www.handbook.ifrf.net/handbook/cf.html?id=146>):

Combustion Handbook:

The meaning of emissivity

In the analysis of radiative heat transfer, it is essential to be clear about the definition of emissivity because the term is often used ambiguously. The emissivity of a surface or body is always defined as the ratio of the radiation emitted by the surface to the maximum possible, that is, from a black body at the same temperature. However, since temperature, wavelength and direction may all affect this ratio, they should all be included in a fully comprehensive definition. Arising from this requirement, a number of individual definitions may be encountered in the literature.

- For radiation from a body at a particular temperature, the **directional monochromatic emissivity** (or spectral emissivity) relates to radiation at a defined wavelength and direction (usually expressed as an angle, q , to the normal).
- If radiation over the whole range of thermal wavelengths but in a specific direction is considered then the appropriate term is the **total directional emissivity**.
- Similarly, if all the radiation emitted at a particular wavelength into the hemisphere beyond the surface is involved, the appropriate definition is that of the **monochromatic hemispherical emissivity**.
- The value used in many analyses of radiative heat transfer in furnace enclosures is the simplest one. It relates to radiation at all wavelengths and in all directions and is the **total hemispherical emissivity**. It is the value used to multiply σT^4 in the Stefan–Boltzmann expression, and it is often referred to simply as the emissivity.
- Measurement of emissivity is frequently made with the surface orientated perpendicular to the radiometer, in which case the **normal emissivity** (total or monochromatic) is determined.

For real surfaces, the ratio of radiation emitted by the surface to that emitted by a black body at the same temperature is often called the **emittance**, although the definition is exactly the same as for emissivity. In this text, emissivity will be used throughout because most industrial and research workers use it.

3. The Definition of Surface Emissivity

The emissivity of a surface may be defined as the ratio of the **radiance** from the surface to that from a **black body** viewed under identical optical and geometrical conditions and at the same temperature. The total black body **radiation flux**

density, or **emissive power** $E_b(T)$ at a fixed absolute temperature, T , is obtained from integration of the black body **spectral flux**, $e_b(\lambda, T)$, over all wavelengths λ

$$E_b(T) = \int_{\lambda=0}^{\infty} e_b(\lambda, T) d\lambda$$

This leads to the expression

$$E_b(T) = \sigma T^4$$

where σ is known as the **Stefan–Boltzmann constant**.

Based on the definition of emissivity, the total temperature dependent emissivity of a surface, $e_t(T)$, may be written in terms of the black body emissive power and **spectral flux density** of the surface, $e(\lambda, T)$, as

$$E_b(T) = \frac{1}{E_b(T)} \int_0^{\infty} e(\lambda, T) d\lambda$$

Integration of $e(\lambda, T)$ over the spectral band limits (λ_1, λ_2) will yield the spectral emissivity $e_{ij}(T)$

$$E_{\lambda_j}(T) = \frac{1}{\Delta E_{b\lambda_j}(T)} \int_{\lambda_1}^{\lambda_2} e(\lambda, T) d\lambda$$

where λ_j is the nominal wavelength position defined by

$$\lambda_j = (\lambda_1 + \lambda_2) / 2$$

and $\Delta E_{b\lambda_j}(T)$ is the black body band emissive power over the same wavelength range.