Measuring the absorption coefficient of optical materials with arbitrary shape or distribution within an integrating sphere

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Abstract: The absorption coefficient of a material is classically determined by measuring the transmittance of a homogeneous sample contained within flat optical faces and under collimated illumination. For arbitrary shapes this method is impracticable. The characterization of inhomogeneous or randomly distributed samples such as granules, powders or fibers suffers the same problem. Alternatively, an integrating cavity permits us to illuminate a sample under a homogenous and isotropic light field where the analysis simplifies. We revisit this strategy and present a new formal basis based on simple radiometric laws and principles. We introduce a new concept to describe the absorption: the optical form factor. We tackle a rigorous treatment of several regular forms, including full absorption range and the reflection at its surfaces. We also model and improve an integrating sphere setup to perform reliable measurements. Altogether, it permits achieving simple but general conclusions for samples with arbitrary shape or spatial distribution, from weak to highly absorbing, expanding the applicability of quantitative absorption spectroscopy. Finally, we validate it by measuring different sample formats made of PMMA: a cube, groups of granules and injection molding loose parts. The absorption coefficient of PMMA varies near three orders of magnitude in the explored range (380-1650 nm).

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1. Introduction

The characterization of the absorption properties of materials is relevant in many disciplines. Under the term of absorption spectroscopy, it permits the analysis, identification and quantification of substances and general materials. More specifically, in optics and its applications it is of interest the monitoring of optical materials deteriorated under different processes: the aging due to radiation damage (UV, solar, spatial), a thermal damage induced by injection molding fabrication, etc... The conventional approach to obtain the coefficient of absorption of a material is to measure the transmittance of a sample confined between flat parallel faces [1–4]. A homogeneous sample (no-scattering), a collimated light beam and a strict alignment are assumed. This limits the practical possibilities as the samples should adapt to these stringent conditions. Often, a cumbersome or even destructive sample preparation is necessary, especially for solid materials.

For low absorption samples, Elterman (1970) [5] introduced a different strategy: the integrating cavity spectroscopy. The basic idea is to enclose a material sample within a homogenous and isotropic light field (HILF). This can be provided by an integrating sphere or equivalent cavity. There are two primary advantages of using integrating cavities to measure absorption: 1) the high lambertian reflectivity of the cavity walls induces a multi-pass effect on the sample, therefore amplifying its effective absorption length; 2) the measurement should be insensitive to sample orientation or alignment. However, Elterman [5] implicitly assumed a premise generally not
An arbitrary optical material illuminated by a HILF does not lead necessarily to an internal homogeneous and isotropic light field within the volume of the material. Taking apart absorption and reflection losses, this is mainly due to refraction and total internal reflections (Fig. 1) that “distorts” and compress the light field. In other words, inside the volume of an optical element there are some locations and ray orientations that contains no light. This is illustrated in Fig. 1 where, for a cube and a sphere, there are ray trajectories inaccessible from external illumination. This problem was appreciated by Fry et al. (1992) [6] who developed a method to measure the absorption of fluids (water based mainly) by using two diffusing cavities, the first one with translucent diffusing walls that it is filled out with the fluid. The second cavity encloses and illuminates the first one. This architecture guarantees that the fluid is internally illuminated with an isotropic and homogeneous light field and thus, the formalism introduced by Elterman can be applied directly. Based on this scheme, we find numerous contributions for measuring absorption of gases and aqueous solutions filling an integrating cavity completely [6–18]. To the best of our knowledge we did not find relevant contributions applied to solids or loose samples. Emel’yanov et al. (1978) [19] measured frosted glass pieces based on the Elterman’s single cavity approach but with partial success as the results depended strongly on sample weight and location inside the cavity.

We revisit this last situation, i.e. the case of solid arbitrary samples located inside an integrating cavity and provide a formal basis to manage from low absorption to full absorption samples and as general as possible. In this contribution we will consider that the light propagates internally through ray segments (homogenous optical media) as illustrated in Fig. 1 and treated under radiometry laws for the flux transfer. In section 2, we start the analysis with simplified situations (weak absorption and non-refracting/reflecting) and incorporate complexity progressively (refracting forms, full absorption range, surface reflection, body arrangements,...). In this process we have to introduce the concept of the “optical form factor” connected to the “average path length” and the “body absorptance” which permits to simplify the analysis and frees the need to fill the integrating cavity as mentioned. In section 3, we propose an integrating sphere measurement model and set-up where both illumination and detection must be as isotropic and homogenous as possible. The consequence is that decentered samples or asymmetry induced errors are highly reduced. Several results for different shapes and absorption degrees validate both the proposed analytical basis and the measuring setup schemes. In the weak absorption range we may use a very simple formula to obtain the absorption coefficient. It only depends on the volume of the sample (compact or dispersed) and the optical form factor. For moderate to high absorption, we may proceed in some general situations but we need extra information to use very
approximate formulas, particularly the surface of the body and its hemispherical reflectance of its surface. Finally, in section 4, we present experimental validation measurements. We measure the absorption coefficient of a PMMA cube and successfully compare it with a standard transmittance method. We also check that the proposed analysis and experimental setup can measure the absorption coefficient of dispersed arrangements of granules and the result is independent of the sample weight, surface reflections and scattering among the granules (within the low absorption approximation).

2. Basic theory for arbitrary forms and distribution: the form factor

2.1. Linear absorption model for arbitrary shapes

Next, we present an alternative way to achieve some of the results already known (Elterman [5], Fry et al. [6]) that later will allow to expand the analysis to general samples and experimental setups. Consider an arbitrary optical body delimited by surface $S_B$ containing a volume $V$ (see Fig. 2). The light rays propagate, refract and reflect as in conventional optical media. This object is immersed in a homogenous and isotropic light field. The assumption of internal full isotropic illumination does not hold necessarily.

Consider first that the medium surrounding the body is of the same refractive index, particularly $n=1$ and that absorption is very low ($\alpha \rightarrow 0$). In this case rays propagate straight and isotropy and homogeneity is maintained internally. Light field is then characterized by constant radiance $L_s$.

As it is well known, the light flux $\Phi$ transmitted through a material in a length $z$ can be expressed as (Lambert-Beer law) [1–4]

$$\Phi = \Phi_0 \exp(-\alpha z), \quad (1)$$

where $\alpha$ is the absorption coefficient and $\Phi_0$ the light flux at $z=0$. The absorbed flux $\Delta \Phi$ is then

$$\Delta \Phi = [1 - \exp(-\alpha z)]\Phi_0. \quad (2)$$

In the limit of weak absorption ($\alpha \cdot z \rightarrow 0$) it may be approximated as

$$\Delta \Phi \cong \Phi_0 \alpha z. \quad (3)$$
For very weak absorption a ray is practically unaltered so the body is internally illuminated with the same radiance \( L_S \) everywhere. For a beam of radiance \( L_S \) starting at a differential surface \( dS \) and propagating at an angle \( \theta \) to the normal of \( dS \), the differential flux \( d^2\Phi_0 \) within a differential solid angle \( d\Omega \) is

\[
d^2\Phi_0 = L_S dS \cos(\theta) d\Omega.
\]

Consider a chopped internal slice “i” of a body with thickness \( dt \) (see Fig. 2) and single face area \( a_i \). From Eq. (3) and Eq. (4) we may write the differential flux absorbed by this slice within the light field, i.e. integrated to all the slice area \( a_i \) and to all ray directions (both faces Fig. 2) as

\[
d(\Delta \Phi_i) = \frac{2}{\pi} \frac{a_i}{S_B} \int_0^{\pi/2} \sin(\theta) \cos(\theta) a_i dt = \frac{4}{\pi} L_S \alpha a_i dt = \frac{4}{\pi} L_S \alpha a_i dt,
\]

where \( dV_i = a_i dt \) is the differential volume of the considered slice. Therefore, integrating to all the slices to complete the volume \( V \), the absorbed flux within the whole body is

\[
\Delta \Phi_V = \int d(\Delta \Phi_i) = \pi L_S \alpha V.
\]

This is basically the same result obtained by Elterman and Fry et al. [5,6] from different arguments [5,6]. Notice that Eq. (6) is valid for a single arbitrary shape but also for separated parts adding up a volume \( V \). The term \( \pi L_S \alpha \) corresponds to the irradiance \( E \) over any surface within the HILF. The term \( \alpha V \) has area units and then we may interpret the factor \( 4\alpha V \) (Eq. (6)) as an equivalent black surface of area \( 4\alpha V \) that absorbs all the received irradiance \( E \). (\( = \pi L_S \)).

Introducing the body surface \( S_B \) in Eq. (6) we may rewrite it as

\[
\Delta \Phi_V = \pi L_S S_B \frac{4V}{S_B} = \Phi_0 \alpha \bar{z},
\]

where the term \( \pi L_S S_B \) corresponds to the external flux \( \Phi_0 \) incident on the body surface and \( \bar{z} \) is the body chord length average (CLA). We have used the well known expression [20–23])

\[
\bar{z} = \frac{4V}{S_B},
\]

frequently referred as Cauchy’s or Dirac’s formula and originally demonstrated for convex bodies. Finally, notice the similitude of Eq. (7) characterizing the absorption in a volume with Eq. (3) valid for a straight ray single pass.

We now consider the more general case of optical bodies with refractive index \( n > 1 \) relative to ambient and we first assume no external reflection. As we mentioned the light beams now refract and this has a primary consequence: the internal light field is no longer homogeneous and isotropic, there are blind zones (see Fig. 1). Further, the possible total internal reflection complicates the analysis as ray trajectories are not always single straight-lines between surface points (z chords) but composed of several ray segments before exit. The mathematical concept of chord length is thus insufficient and Eq. (6) or Eq. (7) should be adapted to consider these geometrical optical effects. Instead of the chord length, we define the path length \( d \) as the total length of a ray trajectory along the body from input to exit, considering total internal reflections if any.

We may rewrite Eq. (6) to describe the total absorbed flux inside of a refractive body as

\[
\Delta \Phi_V = \pi L_S n^2 4\alpha VF,
\]

where \( n \) is the refractive index of the body (relative to outer medium) and the term \( L_S n^2 \) is the radiance of an internal beam as stated by the radiometry laws [4]. In other words, a thin beam

\[
\text{(9)}
\]
refracting from air to \( n \), compress its solid angle by a factor \( n^2 \) and the flux transfer between two differential surface elements increases in that factor. Finally, the parameter \( F \) is a correction factor with a strict geometrical meaning and represents the filling efficiency of the light field inside the body (\( F \leq 1 \)). The form factor \( F \) depends on the particular shape of the body and the refractive index \( n \) and must be estimated apart. Equation (9) differs from Eq. (6) just in the term \( n^2 F \). We will call it the optical form factor and represents the factor that absorption increases compared to the same body but with \( n=1 \). Later we will use this last strategy to estimate the optical form factor (analytically or by ray tracing simulations).

Similarly to Eq. (7) we may rewrite Eq. (9) as

\[
\Delta \Phi_V = \pi L_s S_B a \bar{d},
\]

where \( \bar{d} \) is now the average path length inside the optical body under external isotropic illumination and expressed as

\[
\bar{d} = zn^2 F = \frac{4V}{S_B} n^2 F,
\]

i.e., the average path length \( \bar{d} \) is thus the average chord length \( \bar{z} \) corrected by the optical form factor \( n^2 F \).

Another useful concept to introduce is the body absorptance \( A_B \) applicable to a whole object. Consider the total flux absorbed within the volume of a body (\( \Delta \Phi_V \)) that is illuminated all along its surface \( S_B \) by an irradiance \( \pi L_s \) (within HILF) so it get inside a flux of \( \pi L_s S_B \). We define the body absorptance \( A_B \) as

\[
A_B \equiv \frac{\Delta \Phi_V}{\Phi_0} = \frac{\Delta \Phi_V}{\pi L_s S_B}.
\]

In the weak absorption limit (linear model) the body absorptance is therefore (from Eq. (10))

\[
A_B = \alpha \bar{d}.
\]

### 2.2. Reciprocity principle and implication on HILF preservation

We wonder now how the immersion of a body may distort the HILF around it. Consider a general non-absorbing body (Fig. 3(a)) illuminated by a HILF and an arbitrary incident ray (numbered 0 in Fig. 3(a) coming from this light field. This incident ray is bifurcated (or scattered) multiple times leading to an infinite number of ray outputs (numbered as 1, 2, 3... in Fig. 3(a) covering the full angular space. Now consider reversing the directions of the exit rays (1, 2, 3...) by feeding them with the HILF. From the Stokes–Helmholtz reversion–reciprocity principle [24,25] we know that the trajectories may be reversed and the energy balance \( \rho \) between an incident original ray 0 and any of its outputs (\( m=1, 2, 3... \)) is preserved in reversed mode, i.e. \( \rho(0,m)=\rho(m,0) \). We use the notation \( \rho \) that recalls a reflectance factor as the input and output beams are in the same space. The consequence is that all these reverse contributions add to the incident point an exit ray 0* which is an exact copy of the incident ray 0 (same energy) but propagating in opposite direction (Fig. 3(a)), i.e. the same situation as if the body were not present outside its surface. Therefore, as ray 0 is arbitrary, we conclude that the HILF as a whole maintains its properties and keeps unaltered (homogeneity and isotropy) around a non-absorbing body. As mentioned in the introduction this is not the case inside the body (\( n>1 \)). As a corollary, an indeterminate number of side by side non-absorbing bodies do not alter the external HILF, including the space between them (Fig. 3(b)). Their distribution or orientation is not relevant either. In practice this is easy to check, we may see how non-absorbing bodies introduced inside an integrating sphere disappear to vision.

Alternatively we may think on the following argument. Consider a virtual surface enclosing a non-absorbing body. Under a HILF, the incoming radiance is constant. We could expect that
outgoing radiance is different due to refractions and reflections in the body. However, energy is preserved in the process and, as outgoing radiance cannot be higher than incoming one [4], this forces to have the original radiance all along the enclosing surface.

Therefore, for any arrangement of weakly absorbing bodies "\(i\)" the HILF should be practically unaltered or weakly modified and we may use the linear model (Eq. (9) or Eq. (10)) to estimate the absorbed flux. The total absorbed flux is the addition of all the particular contributions \(\pi L_s 4 \alpha (n^2 F \cdot V)\). In practice, we may see the volume \(V\) in Eq. (9) as a totalizing quantity (sum of \(V_i\)) assuming the same optical form factor \(n^2 F\) for all the parts "\(i\)" or at least a reasonable average. This means that for relatively homogenous particle aggregates (dispersed similar granules, powders,...) it would be enough to know its net volume (=weight/density) and an estimation of its average optical form factor.

In the following sections (2.3-2.4) we analyze in detail several regular shapes and obtain some formulas for the absorption and the optical form factors (assumed no external reflection). Finally, in section 2.5 we explore its behavior considering reflection at surfaces and full absorption range. These results will permit to get a better insight applicable to more general forms and situations.

2.3. Sphere: absorption and optical form factor

Consider a sphere of radius \(R\) and refractive index \(n\) (see Fig. 4). The flux absorbed for a light beam between \(dS_1\) and \(dS_2\) as described in Fig. 4 is

\[
d^2\Phi_{ABS} = L_s n^2 \frac{dS_1 \cos \theta dS_2 \cos \theta}{(2R \cos \theta)^2} (1 - \exp(-\alpha^2 R \cos \theta)), \tag{14}
\]

where \(L_s\) is the external constant radiance (HILF). Light illuminating \(dS_1\) comes from all directions and refracts at corresponding \(\theta\) just until the critical angle \(\theta_C\) \((\sin(\theta_C) = 1/n)\). There are not total internal reflections. Integration in \(dS_2\) till the critical refraction angle \(\theta_C\) gives this expression

\[
d\Phi_{ABS} = \pi L_s n^2 dS_1 \int_0^{\theta_C} 2 \cos(\theta) \sin(\theta)(1 - \exp(-\alpha^2 R \cos \theta)) d\theta. \tag{15}
\]

This finds an analytical solution. Integrated to all the sphere surface \((S_B=4\pi R^2)\) we have

\[
\Phi_{ABS} = \pi L_s n^2 4\pi R^2 \left[ (\sin \theta)^2 - \frac{1}{\alpha R} \left( \cos \theta + \frac{1}{\alpha 2R} \right) \exp(-\alpha^2 R \cos \theta) \right] \bigg|_0^{\theta_C}. \tag{16}
\]
Fig. 4. Light transfer between two differential surfaces in a refracting sphere ($n > 1$). An external homogenous and isotropic light field illuminates $dS_1$ and light propagates to $dS_2$ at an angle of refraction of $\theta$. This angle goes from zero to the critical angle $\theta_C$ ($\sin(\theta_C) = 1/n$).

Let’s consider Eq. (16) in some simplifying situations. For the case of weak absorption and gaseous material ($n=1$, $\theta_C=\pi/2$) we get

$$\Phi_{ABS} = \pi L_S 4\pi R^2 \frac{4}{3} R = \pi L_S S_B a d = \pi L_S 4a V,$$

as expected according to the general Eq. (6) ($S_B=4\pi R^2$ and $z=4R/3$). For a solid sphere of refractive index $n$ but still within the limit of very weak absorption we get

$$\Phi_{ABS} = \pi L_S \frac{4}{3} R n^2 \left(1 - \left[1 - \frac{1}{n^2}\right]^{3/2}\right) = \pi L_S S_B a z n^2 F = \pi L_S 4a V n^2 F,$$

as expected according to Eq. (9). Thus, the optical form factor $n^2 F$ for the sphere is

$$n^2 F_{sphere} = n^2 \left(1 - \left[1 - \frac{1}{n^2}\right]^{3/2}\right) = n^2 (1 - \cos^3 \theta C).$$

2.4. Infinite plate and the rectangular cuboid: absorption and optical form factors

For the case of an infinite plate of thickness $t$ we may come back to Eq (5) but now the integral is between $\theta=0$ and the critical angle limit $\theta_C$. For weak absorption and to a given surface $S_B$ (single face) we get the following absorbed flux

$$\Phi_{ABS} = \pi L_S 2S_B a 2n^2 (1 - \cos \theta_C) (= \pi L_S a 4V n^2 F),$$

where $2S_B$ is the exposed surface of the film (both sides) and $S_B t$ is the illuminated volume $V$. We may appreciate that the average chord length is twice the thickness of the plate $t$ ($z = 2t$) and the average path length is $d = 2n^2 (1 - \cos \theta_C)$, thus the optical form factor is

$$n^2 F_{\infty\text{Plate}} = n^2 (1 - \cos \theta C).$$

The case of a rectangular cuboid (faces intersect at 90°) can be based in the analysis of an infinite plate. The light entering a face reach the parallel opposite face directly or totally reflected.
in other faces while keeping the same angle of incidence due to the orthogonal distribution of the faces. For a refractive index of \( n > 1.4142 \) all the internally reflected light is under total reflection. Considering the 3 couple of parallel faces of a cuboid we have (from Eq. (20))

\[
\Phi_{\text{ABS}} = \pi L_s \cdot 4 \alpha (S_1 t_1 + S_2 t_2 + S_3 t_3) \cdot n^2 (1 - \cos \theta_C),
\]

(22)

where \( S_i \) and \( t_i \) refer to the three characteristic face areas and thicknesses of a cuboid. As \( S_i t_i \) is the volume of the cuboid \( V \) we may compare Eq. (22) with

\[
\Phi_{\text{ABS}} = \pi L_s 4 \alpha V \cdot n^2 F,
\]

(23)

and obtain the optical form factor of a cuboid as three times that of an infinite plate:

\[
n^2 F_{\text{Cuboid}} = 3n^2 (1 - \cos \theta_C).
\]

(24)

2.5. Consideration of multiple reflections and full range absorption: sphere and cube

Let consider now the effect of reflection at a real surface and a full range of absorption. The illuminating light that is reflected at the surface first clearly is not absorbed within the volume. However, we will see that the light internally reflected and trapped may compensate this effect and, for low absorption, the solid material behaves as no reflections were present. For this purpose, consider incoherent light multiply reflected in a cube (with \( n > 1.4142 \)) or in a sphere (Fig. 5). In both cases, the absorptance \( A \) \((A=1-R-T)\) for an arbitrary ray locally incident at an angle of incidence \( \varphi \) can be written as [4]

\[
A(\varphi) = \frac{1 - R_0(\varphi)}{1 - R_0(\varphi) \exp(-\alpha d(\varphi))} [1 - \exp(-\alpha d(\varphi))],
\]

(25)

where \( R_0(\varphi) \) is the reflectivity for unpolarized light (typically computed from known Fresnel formulas [4]) that is the same at input and exit for successive rays and \( d \) is the path length from input to output (including total reflection trajectories). For the cube we have \( d = D/\cos(\varphi') \) and for the sphere \( d = D \cos(\varphi') \) where \( D \) is the size of the cube or the sphere (Fig. 5). For low absorption the first term in Eq. (25) tends to 1 and remains what is the absorptance for a corresponding non-reflection model. In real application we should integrate Eq. (25) weighted for all the angles of incidence and over the body surface to obtain the body-absorptance under a hemispherical illumination. Particularly, for both the cuboid and the sphere we may write

\[
A_B = \frac{\Delta \Phi_V}{\Phi_0} = \frac{\pi L_s n^2 S_B}{\int_0^{\pi/2} dS \int_0^{\pi/2} A(\varphi) 2 \cos \varphi \sin \varphi d\varphi}.
\]

(26)

Alternatively, we may resort to the path length distribution function (PLDF) of a given shape. In the case of an arbitrary solid without reflections at its external surface we may express the body absorptance as

\[
A_B = \frac{\int_0^\infty \text{PLDF}(s)[1 - \exp(\alpha s)]ds}{\int_0^\infty \text{PLDF}(s)ds}.
\]

(27)

Under this scheme, the average path length is

\[
d = \frac{\int_0^\infty \text{PLDF}(s)ds}{\int_0^\infty \text{PLDF}(s)ds}.
\]

(28)

and for low absorption Eq. (27) leads again Eq. (13). For the particular case of a cube with \( n=1 \) we may calculate \( A_B \) only with Eq. (27) and we will use Eq. (26) in other cases. Thus,
specifically for the cube with \( n=1 \) we should know its PLDF function. Anyhow, it is relevant to our discussion to explore how the PLDF depends on the refractive index \( n \) for both shapes. In the case of the sphere and the cube we find analytical expressions [26] for the PLDF. These functions are represented in Fig. 6 for \( n=1 \) and \( n=1.5 \) and the corresponding average path lengths are \( d=2D/3 \) for \( n=1 \) and for \( n=1.5 \) \( d=0.879D \) (sphere) and \( d=1.146D \) (cube).

Notice the PLDF spread in Fig. 6 for \( n=1 \) and how it narrows for \( n=1.5 \). This narrowing can be expected for other general refractive bodies as \( n \) increases. Based on this result and on Eq. (25) we propose the following semi-analytical formula as a good approximation to estimate the body absorptance in a general situation,

\[
A_B \approx \frac{1 - R_H}{1 - R_H \exp(-\alpha \bar{d})} [1 - \exp(-\alpha \bar{d})],
\]

where \( R_H \) is the averaged reflectance of the body surface (hemispherical reflectance) and \( \bar{d} \) is the average path length. Clearly, the average of exponential terms is not the exponential of the arguments average but, thanks to the narrowing of PLDF in refractive bodies, (29) will prove
quite adequate and simple to use in many situations. Thus, knowing the body absorptance $A_B$ and the hemispherical reflectance $R_H$ we may obtain the absorption coefficient $\alpha$ as (from Eq. (29))

$$\alpha \bar{d} = \ln \left( \frac{1 - R_H(1 + A_B)}{1 - R_H - A_B} \right).$$ (30)

The Eq. (30) will be referred in the following as the non-linear model. For weak absorption Eq. (30) simplifies Eq. (13), i.e., the linear model ($\alpha \bar{d} \rightarrow 0$)

$$\alpha \bar{d} = A_B,$$ (31)

independently of the reflectance of the surface $R_H$. Thus, under low absorption a body behaves as if there were zero reflectance at its surface. The light lost at first reflection tends to be compensated by the light trapped in multiple reflections inside the body and finally absorbing the same flux.

We tested the validity of Eq. (29) compared to rigorous integration (Eq. (26) or Eq. (27)) for the cube and the sphere and the results are shown in Fig. 7. For the sphere, the path length distribution is quite different to that of the cube (Fig. 6) and nevertheless, we achieve similar conclusions. Equation (29) works better at the sphere compared to the cube and improves further when the refractive index increases. Remind that the PLDF narrows around the path length average (Fig. 6) as $n$ increases and necessarily Eq. (29) gives better results. However, even for the wide spread of the PLDF of the “gaseous” cube or sphere (Fig. 6(a)) Eq. (29) predicts the body absorptance $A_B$ far better than the linear model. In the worst situation ($\alpha \bar{d} \sim 2$ for the gas cube) the error is still below 15% (Fig. 7(b)). For the simpler and convenient linear model we may establish its validity range (error below 10%) for $\alpha \bar{d} < 0.15$ (Fig. 7(b)).

![Fig. 7.](image)

This analysis also suggest that shapes with aspect ratio far from 1 like plates, flakes and fibers should be treated differently when considering high absorption. In those cases the PLDF is typically bi-modal and a single average may not be adequate enough to deal with a moderate to high body absorptance.
3. Integrating sphere model and measuring procedure

3.1. Integrating sphere model

For a practical measurement of the body absorptance $A_B$ we will use integrating spheres to provide isotropy both for illumination and for detection. The integrating sphere theory can be synthesised in the following equation [27,28]

$$E_S = \pi L_S = \Phi_0 \frac{1}{S_S (1 - \rho(1 - f))} = \Phi_M,$$

that describes the wall irradiance ($E_S$) or internal lambertian radiance ($L_S$) of an integrating sphere of area $S_S (= 4\pi R^2)$, where $\Phi_0$ is the introduced light flux from a wall spot and $\rho$ is the reflectance factor of the lambertian diffusing wall. The factor $(1-f)$ represents the port plug losses where $f$ is the ratio of the projected port area $a_i$ over the sphere area $S_S$. For $N$ ports:

$$f = f_1 + f_2 + \ldots f_N = \frac{a_1 + a_2 + \ldots a_N}{S_S},$$

$M_0$ is the characteristic amplification factor of an integrating sphere, i.e.:

$$M_0 = \frac{1}{1 - \bar{\rho}(1 - f)} = \frac{1}{1 - \bar{\rho}},$$

where $\bar{\rho} = \rho(1 - f)$ is the average reflectance of the sphere wall considering its ports. In practice, the ports may not be fully black, therefore the parameter $a_i$ represents the effective area (totally absorbent) of an element with partial absorption and it is a spectrally dependant parameter as it is $\rho$.

An absorbing sample introduced in the sphere will behave similarly to an extra port. More specifically, consider a sample situated at the center of an integrating sphere with a uniform wall or with finely distributed ports with an average reflectance $\bar{\rho} = \rho(1 - f)$. For sake of simplicity we consider first the case of a spherical black ball of a completely absorbing surface $S_{BB} = 4\pi r^2$. Let’s define the ratio $f_B$ as $S_{BB}/S_S$ where $S_S$ is the surface of the integrating sphere. From any differential surface spot at the wall, considered as a light source, the ball casts a shadow of exactly the lateral area of the ball ($S_{BB}$). Similarly, the ball observed from any point on the wall behaves as a virtual black port of surface $S_{BB}$. Considering this and adding up the multiple lambertian reflections we get for the average irradiance on the wall

$$E_B = \pi L_{SB} = \Phi_0 \frac{(1 - f_B)}{S_S (1 - \bar{\rho}(1 - f_B))}.$$  

Consider now a general absorbing body or sample. Now, we lose the symmetry of the ball, the sample also refracts and reflects rays and further it may not be well centered. A non-absorbing sample has no effect in irradiance distribution as we saw in section 2.2. However, an asymmetric or decentered absorbing sample induces a gradient in the wall irradiance $E_B$. If the sample gets closer to the wall, it is expected to have lower irradiance there and the opposite happens at the opposite side. Our hypothesis is that to first order, the average irradiance over the sphere is still the established by Eq. (35). Therefore, an isotropic illumination and detection is important to average these possible irradiance gradients. Practical implementation of isotropy will be done by situating several detection and illumination spots surrounding the sample.

For a general absorbing sample we re-define $f_B$ attending to its surface $S_B$ and body absorptance $A_B$ as

$$f_B = \frac{S_B A_B}{S_S},$$

$S_B A_B$ can be seen as an equivalent black area of the sample ($a_B$) and is wavelength dependant.
3.2. Experimental procedure

In practice, we measure the ratio of irradiances before and after introducing a sample \((E_S \text{ and } E_B\) respectively). We denote this ratio as the integrating sphere transmittance \(T_S\). From Eq. (32) and Eq. (35)

\[
T_S \equiv \frac{E_B}{E_S} = \frac{(1 - \bar{\rho})(1 - f_B)}{1 - \bar{\rho}(1 - f_B)} \tag{37}
\]

together with Eq. (34) we obtain

\[
\frac{1 - T_S}{T_S} = M_0 \frac{f_B}{1 - f_B} \tag{38}
\]

Defining \(f_B^* = \frac{f_B}{1 - f_B}\) and the observable \(U_B = \frac{1}{T_S} - 1\), we rewrite Eq. (38) as

\[
U_B = M_0 f_B^* \tag{39}
\]

For low absorption \(f_B^* \approx f_B\) and the effective absorption area can be written as \(a_B = S_B A_B = 4\alpha V n^2 F\). Introducing \(f_B = a_B / S_S\) in Eq. (38) we finally get

\[
\frac{1 - T_S}{T_S} = M_0 \alpha \frac{V}{S_S} n^2 F \tag{40}
\]

This equation is basically the same result of Elterman’s [5] with the difference of the necessary form factor \(F\) introduced in section 2.1.

Given a measurement of \(T_S\), we obtain the sample absorption factor \(f_B\) as (Eq. (37))

\[
f_B = \frac{1}{1 + \frac{T_S}{1 - T_S} M_0} = \frac{1}{1 + \frac{M_0}{1 - f_B}} \tag{41}
\]

that together with Eq. (36) and Eq. (30) (non-linear model) gives an explicit formula for the absorption coefficient

\[
\alpha = \frac{S_B}{4V n^2 F} \ln \left[ \frac{1 - R_H \left(1 + \frac{S_B}{S_S} f_B\right)}{1 - R_H - \frac{S_B}{S_S} f_B} \right] \tag{42}
\]

Alternatively, this expression can be expanded and written as

\[
\alpha = \alpha_L \left(1 + \frac{1}{2} \frac{1 + R_H}{1 - R_H} \alpha_L \bar{d} + \frac{1}{3} \frac{1 - R_H^3}{(1 - R_H) \alpha_L \bar{d}} \frac{1}{(1 - R_H^2)^3} \left(\alpha_L \bar{d}\right)^2 + \ldots \right), \tag{43}
\]

where \(\bar{d}\) is the average path length determined from Eq. (11) and \(\alpha_L\) stands for the linear absorption coefficient estimated for example from Eq. (36) and Eq. (31) as

\[
\alpha_L = \frac{S_S}{4V n^2 F} f_B \tag{44}
\]

As already mentioned, within the linear or low absorption regime, it is not necessary to know the surface area of the sample \((S_B)\) neither its hemispherical reflectance \(R_H\), just the volume of the sample and its optical form factor.
3.3. N bodies set: the influence of the sample container

Consider the case of \( N \) bodies grouped inside the integrating sphere configuring a sample \( "m" \). For low absorption \( f_m^* = f_m \) and from Eq. (39) we have that the observable \( U_m \) (N bodies set) is the sum of its independent isolated measurements \( U_1, U_2, \ldots U_N \), i.e.

\[
U_m = M_0 f_m^* = M_0 (f_1 + f_2 + \ldots + f_N).
\]  

(45)

This result is coherent with section 2.2 and useful when considering loose particles, as we will see in the experimental results. Multiple reflections, internal and between bodies can be disregarded based on the results obtained in sections 2.2 and 2.5.

In a real measurement, any kind of sample must be held by a container \( "c" \). We may subtract its contribution by using the Eq. (45). For a weakly absorbing container \( (f_c \rightarrow 0) \) and a general absorbing sample we have

\[
U_m = M_0 f_m^* = U_{m,c} - U_c,
\]  

(46)

where \( U_c \) is for a measurement of the container alone, \( U_{m,c} \) for the sample in the container and \( U_m \) is the observable for the sample itself.

3.4. Integrating sphere setup for experimental validation

We have used a specific integrating sphere setup (Fig. 8) for experimental validation. The original integrating sphere (from Labsphere Inc.) has 4 ports, spectralon walls, 135 mm in diameter and we liberate the internal flaps. The sample is centered in the integrating sphere and lies on a weakly-absorbing holder. Typically, we use quartz recipients (from proQuarz GmbH) with very low absorption. The light source (a commercial 50 W halogen lamp stabilized in continuous mode) is projected by means of a condenser lens over a port and the incident flux beam is split in 3 beams by means of a plastic prismatic array (cube-corners in reverse mode) as illustrated in Fig. 8. Approximately, 6 W are introduced inside. Three beams are symmetrically distributed around the sample (Fig. 8). A fiber optics senses the irradiance on the sphere wall at four different locations that surround the sample (Fig. 8). Similarly, we use micro-prismatic array (retro-reflective sheeting in reverse) as beam splitters to integrate these four sensing spots (Fig. 8). The effect of the prism array is to split the natural field of view (FOV) of the optical fiber. The retro-reflective sheeting provides 6 spots or views, but we blocked 2 of them [29]. Overall, this allows reducing asymmetry effects due to a bad centering of the sample, irregular shapes or spatial arrangements. A final spectrophotometer gets the spectra to estimate the sphere transmittance \( T_S \). In our set-up, a bifurcated fiber output was connected to a double channel spectrophotometer to cover from 380 nm to 1650 nm spectral range (AvaSpec-NIR256-1.7-RM and AvaSpec-1024-USB2-RM from Avantes). Fiber optics are of 600 µm core and NA=0.22. Current illumination setup implicitly assumes non-fluorescent samples, anyhow they may be also considered by introducing monochromatic radiation. Also notice that both the internal illumination or detection beams should avoid the sample. This imposes a limit to the sample size.

To know the amplification factor \( M_0 \) of the integrating sphere we may just measure a known sample, for example an opaque black ball \( (T_S = E_{BB}/E_S) \) and then applying Eq. (38) to get \( M_0 \). The loss factor for the ball is \( f_B = (S_{BB}/S_S)(1-R_{HB}) \) where \( R_{HB} \) is the hemispherical reflectance of the ball surface and we know the surface area. We used a decorative black ball nominally termed “obsidian black” (40 mm diameter). By comparing the spectra provided by the ball and by an open port plug (ideal black) we checked that the ball has achromatic reflectance. The hemispherical reflectance \( R_H \) of the ball was obtained in the following way: we center the ball inside the illuminated integrating sphere and observe it from an auxiliary port. We take a picture with a calibrated CCD camera and compare the ball image gray levels to its surroundings (i.e. the integrating sphere walls taken as reference). By averaging the values inside the contour of the ball we directly obtain the hemispherical reflectance as \( R_{HB} = 0.12 \). We use later this value in the
Fig. 8. Integrating sphere setup for experimental measurements. A weakly-absorbing quartz holder supports the sample in a centered position. Introduced illumination is split in three beams that spots on the sphere equator. A fiber optics collects light by sensing 4 spots of the integrating sphere wall at a meridian. These illuminating and detection spots are symmetrically disposed around the center to average and reduce the effect of de-centering and other sample asymmetries. These beams do not intersect the sample.

analysis of the experimental data. In our experimental setup \( M_0 \) varies approximately from 20 at near UV to 30 in the near IR.

4. Experimental results

For experimental validation the shape of a cube is appropriate. It can be measured by conventional direct transmittance and by our procedure. We tested a commercial PMMA (acrylic glass) cube of \( \sim 40 \) mm side and fire polished. In the measured spectral range this material provides near 3 orders of magnitude of variation in the absorption coefficient. We used the integrating sphere setup of Fig. 8(b) to obtain the absorption coefficient \( \alpha \) and compare it to a direct transmittance or conventional method as a reference.

In conventional determination of internal transmittance we face the typical difficulty of consider the reflection losses and compensate them to correctly calculate internal transmission, especially critical at low absorption. We follow a strategy that proved to work better than this classical approach. We sandwiched the cube between cleaned glass slides of good optical quality and match the surfaces optically with glycerol (its absorption contribution can be neglected). A reference sample consisted of the same sandwich but without the cube. To gain in reliability the setup consists in a small integrating sphere port as a primary light source collimated and later focused on the ports of the mentioned fiber (finally connected to the spectrophotometer). Under this scheme we get the internal transmittance within a \( \pm 0.15\% \) uncertainty. After determining direct internal transmittance \( T_D \) we finally get the absorption coefficient as \( \alpha = -\ln(T_D)/l \) where \( l=40 \) mm. Rayleigh scattering was also estimated and its contribution is quite below the measured absorption coefficient (\( \sigma < 3 \cdot 10^{-5} \text{ mm}^{-1} \) in the blue part of the spectrum).

For the integrating sphere measurement of \( T_S \) we followed the procedure described before (section 3). We get 3 spectra proportional to the integrating sphere walls: the integrating sphere
empty, the sample in its container and for the container alone. The sphere transmittance $T_S$ was basically stable (within ±0.15%). Only for the very absorption peaks in the IR (cube practically opaque), $T_S$ showed deviations within ±1% when de-centering the cube sample about ±20% of the radius of the sphere from its center (vertical and horizontally). In the forced case of placing the sample in the floor of the sphere (maximum decentering), we observe deviations in $T_S$ below ~10% only for the highly absorption peaks and unobservable deviations in the low absorption part of the spectrum. This served as a reliability check for the setup, concerning asymmetry and sample decentering.

In Fig. 9 we show and compare the results for the absorption coefficient of the PMMA cube. According to Eq. (24) we apply an optical form factor of 1.722 ($n=1.492$). The relative discrepancy between the full absorption range formula Eq. (42) (non-linear model) and the reference method is within ±9% along most of the spectrum (in the interval extremes and for high absorption discrepancies are higher). The simpler linear model (Eq. (44)) is fine for absorption values of $\alpha d<0.15$ as expected (in Fig. 9 corresponds to $\alpha<0.004$ mm$^{-1}$).

![Fig. 9. Measurement of the absorption coefficient for a PMMA cube (40 mm side). Comparison of the classical or direct transmittance method (□) versus the method proposed (-): linear model (blue line) and non-linear model (red line).](image)

Finally, we show the applicability to measure loose samples (random pieces, granules, powders, . . . ) and confirm the validity of Eq. (45) under the linear model (weak absorption). In Fig. 10 we compare the results for PMMA granules (trade name 8N, from Evonik) with different sample weights (10, 20 and 50 g). We applied a nominal density of 1.19 g/cm$^3$ to obtain the net volume from the sample weights. The granule size is typically $3 \times 4$ mm chopped rods and we estimate an average optical form factor of 1.6 (by ray-tracing simulations). The three independent measurements lead to the same absorption coefficient with a noise uncertainty correlated to the sample size as expected. At about 900 nm, we observe a slight discrepancy, due to the departure of the linear model range for $\alpha d>0.15$ approximately. We also show in Fig. 10 the result for an injection-molded light guide (same nominal material) used in automotive designs and cut in manageable pieces for the measurement. In this case we considered an optical form factor of 2.2.
We may appreciate a clear change of transparency at visible range, probably due to a thermal degradation in the injection process.

Fig. 10. (a) Absorption coefficient of granules of PMMA (8N) obtained for different sample weights (10, 20, 50g as expressed in the legend) and a compared result for the same material processed after injection molding (light guide used in automotive) and cut for handling (35g). (b) Sample preparation for the light guide. (c) Sample preparation of PMMA granules for 10g.

5. Conclusions

We have expanded the analytical basis and the experimental possibilities to perform quantitative absorption spectroscopy on general materials. With an appropriate integrating cavity it permits to estimate the absorption coefficient \( \alpha \) of loose materials with arbitrary shapes or spatially disperse. The absorption depends in the first order on the volume of the sample \( V \) and on the shape and refractive index through a single parameter: the optical form factor \( n^2F \).

Some simple and regular shapes were studied in detail to develop and validate rigorous models of body absorption and extrapolate some of the conclusions to more irregular forms and situations. In the limit of low absorption \( (\alpha \tilde{a} < \sim 0.15) \) the shape, the surface reflection, the number of objects and its distribution are all irrelevant. In this case, a simple linear model links the coefficient of absorption \( \alpha \) and the net volume of the sample \( V \) and the optical form factor \( n^2F \). The range of variation of \( n^2F \) is very limited, thus a reasonable estimation would be adequate in many situations. Higher absorption can also be managed but we need some extra information to obtain the absorption coefficient, particularly the surface of a single body \( S_B \) and its hemispherical reflectance \( R_H \).

The experimental setup is critical to obtain reliable results. Illumination and detection must be as isotropic as possible. In our case, an integrating sphere with a discrete distribution of illumination and sensing spots around a centered sample proves to be adequate. The theoretical models were tested by measuring a PMMA absorbing cube and compared the results with a regular transmittance measurement. The achieved agreement is within \( \pm 9\% \) for near 3 orders of magnitude of variation in \( \alpha \). We also checked experimentally that dispersed objects (PMMA granules) lead to the same result independently of the sample weight or size (low absorption). This is a remarkable result and, although out of the scope of this contribution, it opens the possibility to analyze other particle aggregates, powders, fibers, etc… in a reliable manner. This
approach also allows adjusting the size and the final volume of samples to improve accuracy and simplify the data analysis.

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**Data availability.** Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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