

# Integrating Sphere Diffuse Reflectance Technology for use with UV-Visible Spectrophotometry

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## Key Words:

- CIE compliant
- Color Measurement
- Diffuse
- DRA
- Haze Compliant ASTM D1003
- Integrating Sphere
- Reflectance
- UV-Visible

## Purpose of the Integrating Sphere Accessory

Conventional UV-Visible spectrophotometry is carried out in transmission mode with samples that allow the light beam to pass straight through without being diverted by refraction or spread out by scattering.

Samples that are opaque may be analyzed by placing them at the back of an integrating sphere, reflecting light off them, and gathering the scattered light that bounces back. Samples that pass light, but scatter the beam as it passes through, may be analyzed by placing them at the front of the sphere and gathering the transmitted light as it emerges from the sample.

The two experiments are more similar than they may appear. In each case, the scattered light emerges from the sample in a hemispherical pattern (Figure. 1).

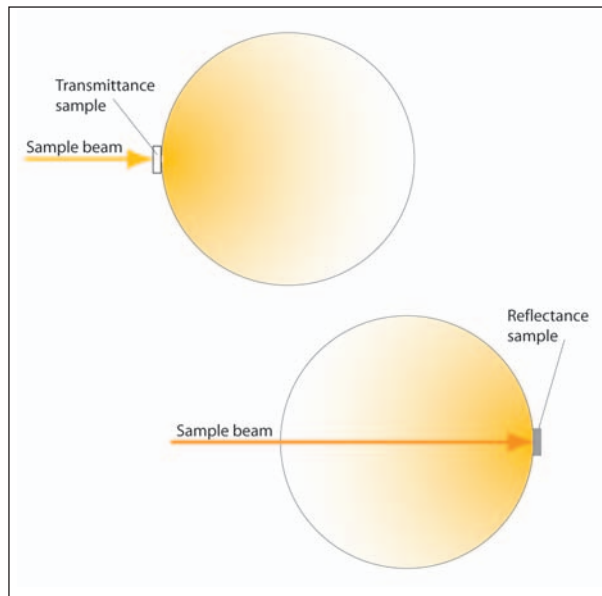


Figure 1: Paths of diffusely scattered light passing through a colloidal sample (top) or scattering off a matte surface (bottom).

An integrating sphere is a type of Diffuse Reflectance Accessory (DRA). Diffuse reflectance refers to light being reflected off a matte surface – an effect that is sometimes referred to as *Lambertian* behavior. This is distinct from *specular* reflectance that occurs from mirror-like surfaces. In this technical note, we will discuss the principles of diffuse reflectance and transmittance spectrophotometry using an Integrating Sphere accessory. Integrating spheres can also be used for specular reflectance measurements, as can a range of specialized specular reflectance accessories.



The Thermo Scientific Evolution 600 spectrophotometer is shown with the DRA-EV-600 accessory. A black acrylic monolith is mounted on the reflectance port as an example.

## Factors Influencing Integrating Sphere Performance<sup>1</sup>

The interior of the integrating sphere accessory is coated with a material with a very high diffuse reflectance. The industry-standard material is Spectralon<sup>®</sup>, made by Labsphere. This is a Teflon<sup>®</sup>-based material that reflects better than 99% of incident light from ~300 nm to ~900 nm, with performance dropping off to ~95% between 250 nm and 300 nm<sup>2</sup>. The Thermo Scientific Diffuse Reflectance (DRA-EV-600) accessory uses a Spectralon coating. Other coatings are available and may have been used in earlier spheres sold by a range of instrument manufacturers, or still be in use in some competitive spheres. For example, many competitive spheres use a barium sulfate based paint that is only 95-96% reflective in the visible region and even less reflective in the UV region.

In this technical note, we consider “scattered” light to mean light distributed inside the sphere in either transmittance or reflectance mode. What happens after a light beam is scattered by the sample is what makes the sphere detector unique. Light is re-scattered again and again until it escapes the sphere through an open port or is absorbed either by the reflecting surface or by some sort of optical component or baffle built into the interior of the sphere. This multiple reflection causes the intensity of the light inside the sphere to rapidly reach a steady state level at all points inside the sphere. It also results in this intensity being higher than what one would predict based on the simple *dilution* of a typical 2 mm x 7 mm beam across the interior surface of the sphere. How much light is integrated by the sphere in this way is calculated as the *sphere multiplier*, *M*.

Sphere Diameter	Sphere Surface Area (mm <sup>2</sup> )	Port Fraction <i>f</i>	Sphere Multiplier <i>M</i>	% of Incident Light Falling on 64 mm <sup>2</sup> Detector Port
60 mm	11310	11.3	8.1	4.6
70 mm	15394	9.3	9.7	4.0
<b>75 mm*</b>	<b>17671</b>	<b>3.6</b>	<b>21.7</b>	<b>7.9</b>
150 mm	70686	2.5	28.5	2.6

Table 1: Theoretical percent of incident light falling on an 8 mm x 8 mm detector for representative spheres with port fractions and sphere multipliers as listed in the table.

\*Thermo Scientific DRA-EV-600. In reality, the detector port on this sphere is 242 mm<sup>2</sup>, so 29.6% of the incident light falls on the detector.

## Sphere Diameter

The surface area of a sphere is equal to  $\pi \times d^2$ . Table 1 shows the surface areas of several spheres and the percentage of the incident light that falls upon an 8 mm x 8 mm detector port after factoring in the sphere multiplier.

Typical integrating spheres in the marketplace have values of *M* ranging from 10-30. From the data in Table 1, we see that integrating spheres transmit only 2-8% of the incident light. Differently stated, an integrating sphere has an *absorbance* of 1.1 to 1.7. The spectrophotometer using an integrating sphere accessory must therefore have sufficient beam intensity, stray light control and a detector that provides meaningful data in the range > 2.0 absorbance units.

### The Sphere Multiplier (larger numbers are better)

A photon inside a perfectly reflecting, closed sphere would, in theory, reflect around inside the sphere forever. This fact is what puts the “integrating” in *integrating sphere*. The photons that are striking an arbitrarily chosen point on the surface are not only those that are being fed into the sphere at that instant, but also those that entered the sphere over the period since the light source was turned on.

A real sphere is neither perfectly reflecting nor closed, so photons do escape or are absorbed by the surface or interior baffles or optics. As such, the flux seen in the sphere is a steady state quantity, with steady state being reached in a matter of a few nanoseconds – fast enough that the sphere works perfectly with both xenon flash lamps and chopped beams running at several tens of hertz.

A full discussion of the mathematics of calculating the sphere multiplier (*M*) is given in reference 1. For the purposes of this technical note, the important message is that *a higher value of M means increased energy throughput, which is good*, and that *M is directly proportional to reflectance of the interior coating and inversely proportional to the magnitude of the port fraction* (see separate box).

## Detector Choice

Two terms measuring detector performance are worth defining here. *Dynamic Range* is the ratio of the highest to the lowest light level over which the detector is able to discriminate changes in incident light. *Sensitivity* is a measure of the detector’s signal-to-noise ratio at a particular light level.

The most common detectors in mid- to high-range instruments are silicon photodiodes or photomultiplier tubes (PMTs). A PMT has a wider dynamic range, is approximately five orders of magnitude more sensitive compared to a photodiode, and produces very low noise amplification of the signal. With a sample in place, an integrating sphere transmits less than 1% of the sample beam, so a detector with good sensitivity in the absorbance range > 2 is necessary to provide high quality results. This means that while a PMT is significantly more expensive it is almost always a superior choice of detector. Most integrating spheres will have their own integrated detector built into the sphere.

### The Port Fraction (small numbers are better)

Integrating spheres require at least one port for the beam to enter. If measuring reflectance, a second port is required for the sample, and if using a reference beam to eliminate substitution error, a third port is required. The area occupied by the detector, being non-reflecting, also functions as a port for the purposes of calculating port fraction. Even a very good integrating sphere coating will not provide exclusively *diffuse* reflectance. There will always be some element of specular reflectance which is undesirable unless one is doing a total reflectance measurement. For purely diffuse reflectance measurements, the specular portion of the reflectance should be directed out of the instrument.

Photons should also undergo at least two bounces within the sphere before detection, so baffles are installed to prevent direct illumination of the detector port from either the entry port (for transmission experiments) or the reflectance port (for reflectance). Ports and baffles are non-reflecting and poorly reflecting components of the integrating sphere and represent ways for photons to be lost from the system. The port fraction *f* is the sum of these areas expressed as a fraction of the total sphere area. A more complete mathematical description is contained in reference 1.

In making comparisons between spheres, *a smaller value of f is a good thing*. Increasing the number of ports on the sphere will make *f* larger, as will inclusion of additional baffles or optics inside the sphere to support special applications or configurations. Because ports are of finite size, typically about 8 mm x 8 mm, all other things being equal, increasing the sphere diameter will reduce the value of *f* simply because the open ports occupy a smaller portion of the total surface area of the sphere.

## Double Beam Versus Single-beam Experiments In Integrating Spheres

A single-beam reflectance experiment in an integrating sphere is depicted in Figure 2.

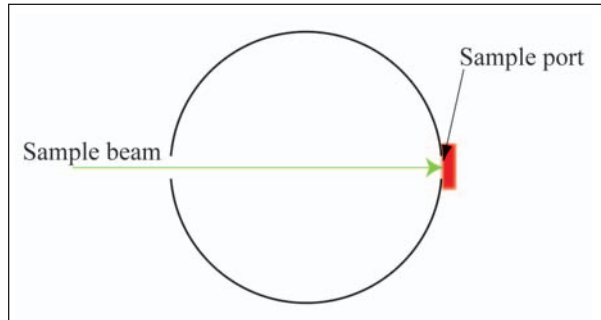


Figure 2

In *both* single- and double-beam experiments, the sample port is covered with a reference material such as a piece of Spectralon and a baseline scan is recorded and saved. The sample port is then covered with the analyte and the resulting data displayed by the associated software is the difference between the two scans.

Placing the sample material on the sample port reduces the total internal reflectivity of the sphere (because most samples will be less reflective than the Spectralon used as a reference). This lowers the sphere multiplier and reduces the energy throughput of the sphere. In a single-beam sphere, this *substitution error* makes all samples appear to be less reflecting than they really are. Reflectance measurements generally use a y-axis scale of percent reflectance (%R). Substitution error will *lower* the displayed value of %R relative to the true value.

In a double-beam experiment (Figure 3), a reference beam is fed into the sphere through a second entry port and reflects off the sphere wall. This means that reference reflectivity data is obtained with the sample in place and substitution error is avoided. Double-beam operation of an integrating sphere also brings all the advantages of a conventional double-beam experiment in terms of a chopped beam that alternates between sample and reference permitting off-frequency noise cancellation in software. A double-beam sphere requires additional optics and an additional port to get the reference beam into the sphere. This adds to the complexity and cost of the sphere but, for absolute accuracy of the %R data, a double-beam configuration is a requirement. The DRA-EV-600 accessory is a double-beam sphere with an integrated PMT detector. It does not suffer from substitution error.

Note that Figure 3 displays the incident angles at which the beams strike the sample and wall (for the reference) as being non-normal. The DRA-EV-600 uses an 8° incident angle<sup>3</sup>, a fairly common choice that allows inclusion or exclusion of the specular component of the scattered light.

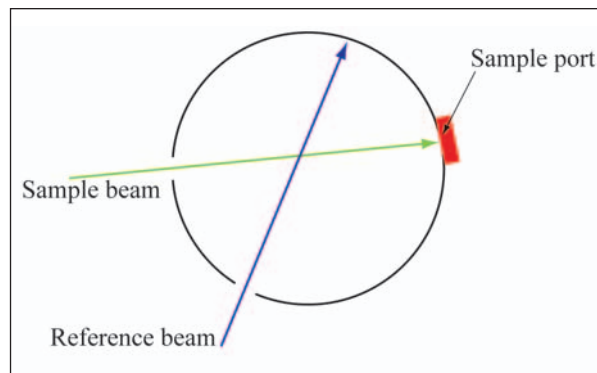


Figure 3

## Sample Mounting Geometry

Most DRAs bring the sample beam in on the xy (horizontal) plane. This means the sample is held in a vertical position against the side of the sphere. The sample holder is generally spring loaded and samples are pressed hard against the sample port. The accessory is also generally mounted entirely inside the sample compartment of the instrument so sample size is limited by what can physically fit into the available space. Spheres do exist with a *look-down* geometry where the sample port is on the bottom of the instrument. Such a *horizontal* geometry is useful for looking at powder surfaces that are difficult to adapt to a vertical mount. The DRA-EV-600 accessory has a unique combination of a horizontal *look-up* geometry and a raised sphere that stands above the plane of the instrument. This arrangement permits non-destructive analysis of very large or thick samples which would not be possible with other instruments (Figures 4 and 5). It also permits

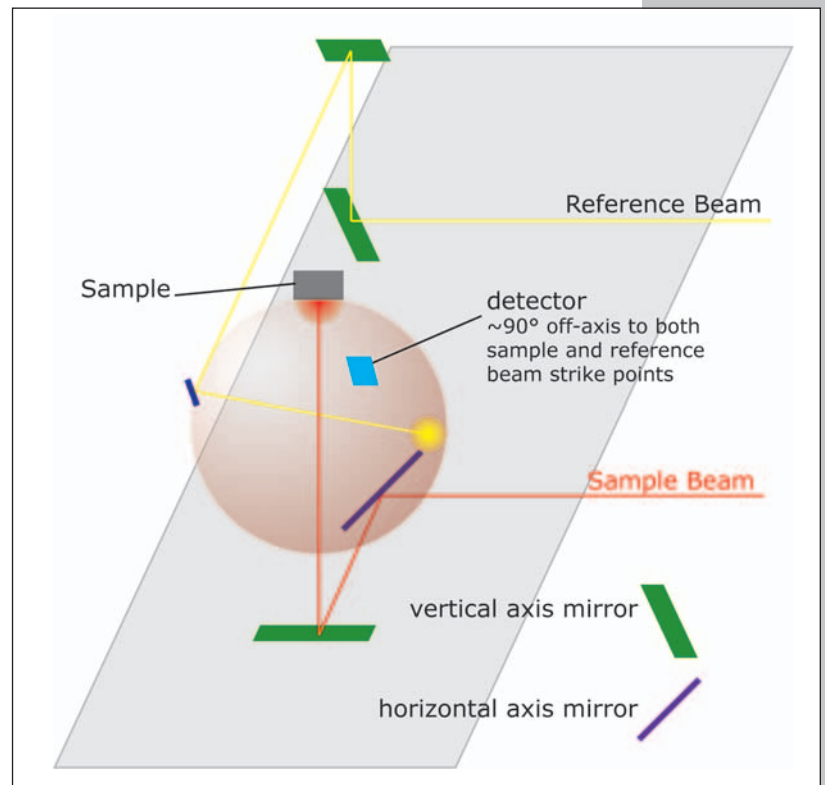


Figure 4

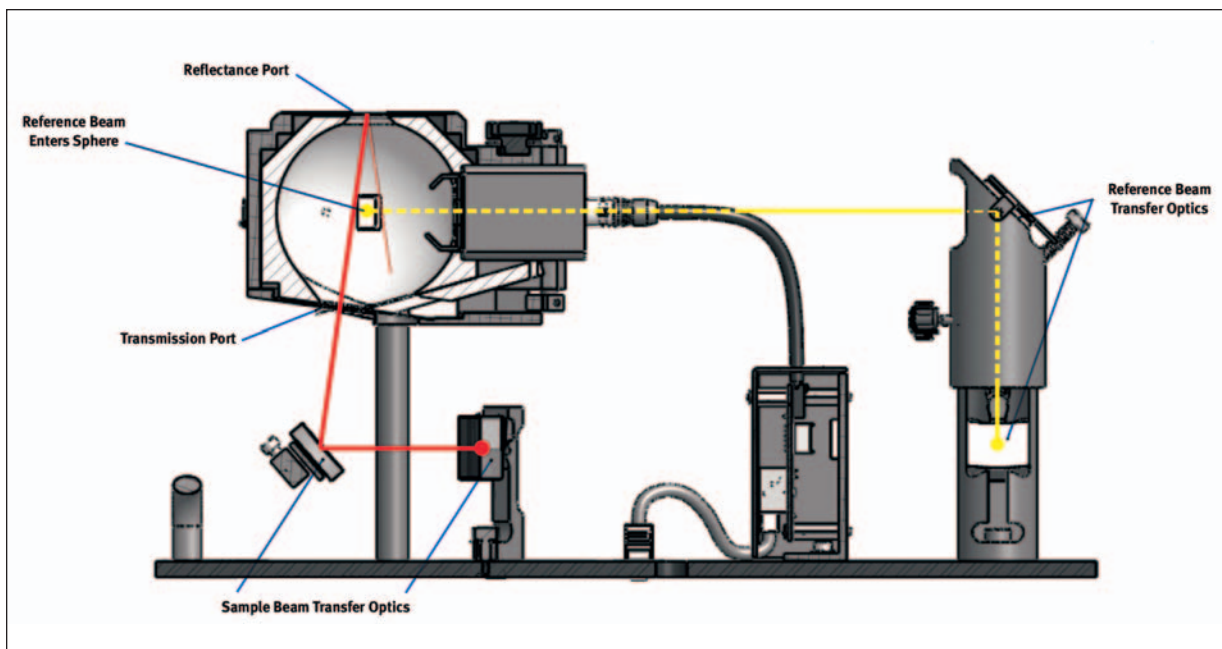


Figure 5

measurements on fragile samples that would be damaged by a sprung mount. Successful quick analyses of powders inside glass containers, where the bottle is simply placed on top of the reflectance port, are also possible.

### Compliance With International Standards

Commission Internationale de l'Eclairage (CIE), an international color-standards group, regulates the international standards for the minimum hardware specifications required for color measurements. CIE methods for color measurements using integrating spheres require that the port fraction be  $< 10\%$ . For Haze measurements on transparent plastics, ASTM-D1003 method requires that the port fraction be  $\leq 4\%$ . Most integrating spheres require a sphere diameter of 150 mm to achieve Haze compliance. The DRA-EV-600 accessory integrating sphere ( $f = 3.6$ ) achieves Haze compliance with a 75 mm sphere.

### Summary

DRAs are useful for measuring the UV-Visible absorption spectrum of diffusely transmitting materials and the reflectance spectrum, including quantitative color measurements, of diffusely reflecting materials. The high light loss inherent in the use of a DRA requires a spectrophotometer with an intense light source and excellent stray light control. Integrating sphere function is optimized by a highly reflecting coating, a low port fraction and appropriate sample mounting geometry. The Thermo Scientific Diffuse Reflectance (DRA-EV-600) accessory is designed with a very low port fraction that maximizes energy throughput and gives compliance with international standards for color and Haze measurements. Its upward viewing geometry and above-the-instrument mounting make it uniquely suited to performing reflectance measurements on large samples.

### References

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3. *Diffuse Reflectance UV-Vis Accessory Product Specification Sheet* (Part Number: PS51248\_E 04/07M), Thermo Fisher Scientific Corp., 2007

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