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A Discussion of Center Mount Sample Holder Designs and Applications

The Use of Center Mount Sample Holders in Reflectance Spectroscopy

Center mount sample holders are used to position a sample inside an integrating sphere for measurements. Positioning the sample at the center of the sphere, rather than at the sphere's transmittance or reflectance port, offers the user several measurement advantages unavailable with smaller integrating sphere accessories. These advantages include the ability to measure hemispherical reflectance as a function of incidence angle, as well as the ability to measure the transmittance and reflectance ("transflectance") of a sample simultaneously. In addition, the absorbance of turbid liquids can be measured using the center mount configuration. Center mount sample holders are available for Labsphere reflectance spectroscopy accessories with sphere diameters of 150 mm or greater. Options for center mount sample holders include variable angle or fixed angle (generally 0°) versions. All of Labsphere's UV-VIS-NIR center mounts have a Spectralon®(1) base and are coated with Spectraflect™(2) diffuse reflectance coating for high reflectance over the entire 200–2500 nm wavelength range.

Measurements with Center Mount Sample Holders

Spectral Calculations

Consider an "ideal" solution to be one that is transparent. For standard UV-VIS-NIR measurements of ideal solutions, transmittance and absorbance are related by the following equation:

$$A = -\log T = -\log(1-At) \qquad \text{Equation 1}$$

Where, At is the absorptance, the faction of the light absorbed At + T = 1 or I(absorbed) + I(transmitted) = I(0). However, for non-ideal samples, such as turbid liquids, or translucent or opaque solids, this equation ignores any light reflected from the sample. Integrating spheres can be used to measure the total hemispherical reflectance, as well as total hemispherical transmittance, of such samples. If both the reflectance and transmittance of a sample are measured, the sample's total absorptance can be calculated as described below in the Kirchoff relationship:

$$At + T + R = 1 \qquad \text{Equation 2}$$
$$\text{or } T + R = 1 - At$$

For smaller integrating sphere accessories, with sphere diameters less than 150 mm, the calculation of total absorbance requires separate reflectance and transmittance scans. Separate scans can often lead to measurement errors due to geometry or sampling differences, especially if the spot size or sampling location differ in the reflectance versus the transmittance measurement.

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The center mount sample holder can eliminate such measurement variables. By positioning the sample at the center of the sphere, both the transmittance and reflectance of the sample are measured simultaneously. This "transflectance" measurement (transmittance plus reflectance, TR) allows the sample's absorbance to be derived directly and efficiently, following the equations given below:

$$A = - \log (T + R) = -\log(1-At) \qquad \text{Equation 3}$$
$$\text{or } A = - \log TR$$

Thus, for translucent solids, turbid liquids, or other non-ideal samples, the center mount sample holder allows very simple and efficient calculations of absorbance based on a single measurement.

If an opaque sample is measured in the center mount configuration, the transmittance term falls to zero; hence, for opaque samples, absorbance can be derived directly from the reflectance data:

$$A = - \log R \qquad \text{Equation 4}$$

The transflectance data is also related to the sample's absorptance, which is defined as the ratio of the absorbed radiant or luminous flux to the incident flux (ASTM E 284-95a). Absorptance can be calculated according to Equation 5, below:

$$\text{Absorptance} = 1 - (T + R) \qquad \text{Equation 5}$$
$$\text{or Absorptance} = 1 - TR$$

Consult ASTM E 903-82 (Reapproved 1992) for further information regarding absorptance measurement procedures.

Sources of Sphere Errors

Approaching the "Perfect" Sphere and Center Mount

A perfect integrating sphere would have no ports and no baffles. As this is a physical impossibility, it is necessary to find a way to optimize the sphere so that it will allow accurate center mount measurements. Sphere errors can be reduced by minimizing both the number and the sizes of ports and baffles in the sphere. Each Labsphere reflectance accessory is designed with this goal in mind. For an application using the center mount, all sphere ports except the beam entrance ports should be filled with Spectralon reflectance standards, the same material as the sphere wall. This helps to keep the sphere errors to a minimum by filling the reflectance and specular ports with highly reflective, diffuse material. Another sphere error is avoided by making the center mounts self-baffling. To prevent the sphere's detectors from viewing directly the first strike radiation on the sample, each center mount sample holder is equipped with a baffle underneath the sample.

Substitution Errors

When a center mount sample holder is introduced into this near-perfect sphere system, it acts as a large baffle. The center mount holder and the sample itself undergo multiple interactions with the light in the sphere, even after the sample beam's first strike on the sample. If these secondary reflections are not corrected spectrally, by use of a double beam integrating sphere, then substitution error will occur and the measurement results will be erroneous.

Substitution error, sometimes referred to as the single beam sample absorption error, is a systematic, predictable and non-random error inherent in single beam integrating spheres measuring reflectance or transmittance. When a sample is placed in the center mount sample holder, it changes the overall *throughput* of the sphere, defined as the flux reaching the detector. If the sample is not in the sphere when the baseline correction scan is performed, the sphere has a different throughput than when the sample is placed into the sphere during the actual measurement. Substitution error due to this change in sphere throughput is thus introduced into the single beam sphere system.

Double beam spectrophotometers, or those instruments which chop between the sample beam and the reference beam, have both beams present in the sphere at essentially the same time. In this case, since the sample beam and the reference beam each "see" the

same sphere, there is no substitution error. The presence of the reference beam in the sphere eliminates any throughput differences caused by the introduction of the sample into the integrating sphere. While all of the center mount sample holders available for Hitachi, Perkin-Elmer, and Varian instruments are used for double beam spectrophotometers without substitution error, Labsphere's six inch diameter reflectance/transmittance "RTC-060-SF" sphere may be used in either the single or double beam modes.

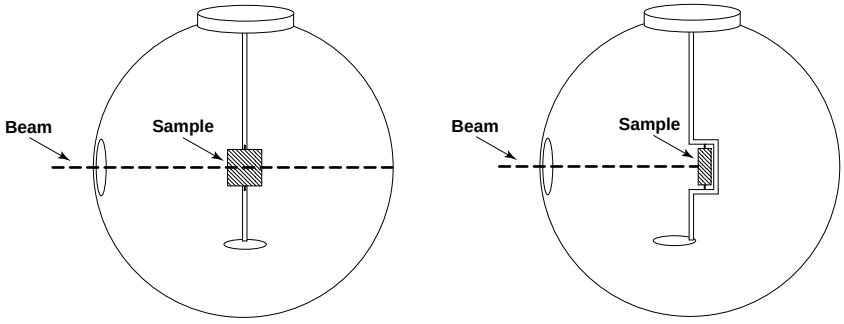
The substitution error present in the single beam integrating sphere can be corrected to a great extent with the proper center mount sample holder design. The multiple light interactions between the sample beam and the center mount holder or sample can be overcome by placing the sample in the center mount sample holder *but out of the path of the sample beam* while the instrument baseline correction is performed.

Center Mount Design

Eliminating Substitution Error in Single Beam Spheres

Substitution error due to the introduction of the sample into the single beam sphere can be overcome by using either a Gier-Dunkle or an Edwards center mount sample holder. Both of these center mount attachments work to eliminate substitution error by putting the sample into the sphere, but away from the sample beam's first strike, during the instrument baseline correction. To measure the sample after the baseline is collected, the Gier-Dunkle or Edwards center mount is pivoted so that the sample beam now impinges on the sample at the desired angle. This procedure is depicted in *Figure 1.* Any changes in sphere throughput due to the sample are now eliminated, since the sample is already present in the sphere during the baseline scan. In this configuration, the throughput changes in the sphere which occur between the baseline and sample scans are directly contributed to the first strike on the sample and not due to any subsequent interactions of the reflected radiation with the sample.

FIGURE 1
Diagram of Gier-Dunkle center mount sample holder—procedure to elimate substitution error



Baseline Scan—
Beam bypasses sample

Sample Scan—
Holder rotated 90 degrees

Beam Geometry for Center Mount Measurements

Ideally, the beam geometry for a reflectance accessory should be optimized for the user's sample application or prime method of measurement. For center mount sample measurements, it would be ideal for the beam to be focused at the center of the sphere, on the front surface of the sample. However, when Labsphere designs reflectance accessories, we try to accommodate the most general usage of the accessory. Thus, while a center mount may be used for measurements, the beam geometry is not always "ideal" for that application. Usually the beam geometry of an accessory has been optimized for measuring reflectance samples on the wall of the sphere and to allow for efficient specular subtraction in that geometry.

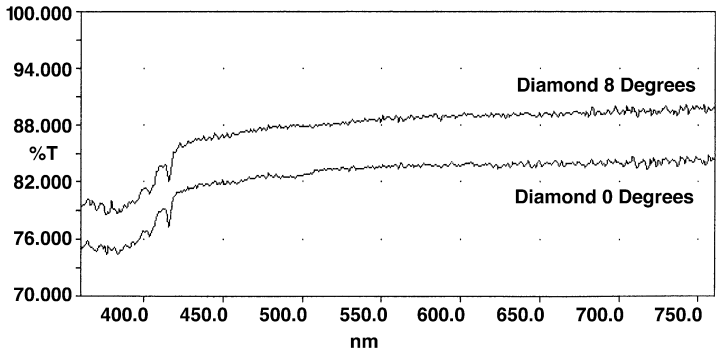
A solution to this problem is the placement of a lens into the sample beam path in order to focus the radiation at the center of the sphere. Labsphere has provided such small spot kits for a number of UV-VIS-NIR reflectance accessories. Other reflectance accessories have moveable sample beam optics which allow the beam to be focussed at either the transmittance, center mount, or reflectance sample positions of the sphere. A list showing the availability of accessories with these beam focussing options is provided on page 7.

Types of Center Mount Sample Holders

Variable Angle Center Mounts

Variable angle center mount sample holders enable the sample's reflectance or absorbance to be studied at various beam incidence angles. The effects of incidence angle on reflectance are important factors, for example, in the measurements of gems and of pearlescent pigments, such as those used in the automotive industry. The typical variable angle center mount sample holder utilizes a rotating dial to allow the user to very quickly set the desired incidence angle to the nearest 1° increment. Depending on the sample size and the instrument's beam characteristics, the user can choose to perform measurements at beam incidence angles ranging from ≈ 0 - 60°; the larger incidence angles are achieved by using a small spot kit in conjunction with the reflectance accessory to focus the beam completely on the sample, thus preventing overfilling of the sample. At a 0° incidence angle, the specular or shiny component of reflectance is removed from the measurement, whereas sample angles exceeding 8° include the sample's total reflectance in measurements. The contribution of specular reflectance to the overall appearance of a master diamond is shown in *Figure 2.*

FIGURE 2
A comparison of total reflectance of master diamond (top spectrum) versus diffuse, specular excluded reflectance (lower spectrum)



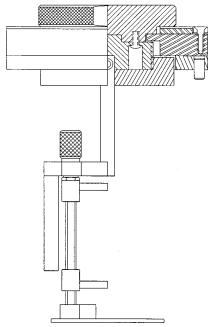
For double beam integrating spheres, variable angle center mount sample holders are available with a jaw or a clip sample restraining mechanism. The jaw mechanism is used to clamp rigid samples. A clip-style variable angle sample holder can be used for films or thin, flexible samples which do not have the rigidity to be held by the jaw mount. For single beam integrating spheres, the Gier-Dunkle and Edwards variable angle center mount sample holders are available. While the Gier-Dunkle center mount can be designed to measure any sample type, the Edwards sample holder design can accommodate only rigid, opaque samples.

The user's choice of center mount sample holder design should be based on the type of sample to be measured and on whether reflectance or absorbance measurements are desired.

Jaw Center Mounts

The jaw-style variable angle center mount sample holder allows hemispherical reflectance factor measurements to be performed as a function of incidence angle. The jaw mount sample holder is designed to hold rigid, opaque samples which can be clamped, such as silicon wafers, mirrors, or painted metal samples. If samples are translucent rather than opaque, an optional light trap can be used during reflectance measurements to capture and eliminate any transmitted component of radiation. The design of Labsphere's jaw center mount sample holder is shown in *Figure 3.*

FIGURE 3
Diagram of jaw center mount sample holder



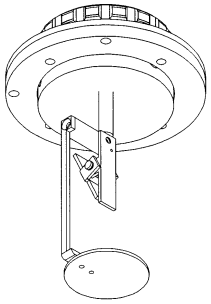
Variable angle reflectance factor measurements are performed relative to a calibrated reflectance standard, such as packed PTFE (polytetrafluoroethylene), Spectralon, or a calibrated first-surface aluminum mirror. A background scan is collected with the reflectance standard in the sample holder, which has been set to the angle of interest. The standard is then replaced by the sample, and the measurement is taken at the same incidence angle. Ideally, the reflectance standard should be calibrated at the same incidence angle at which the measurements are to be collected. However, because Spectralon shows highly lambertian behavior, its calibration is essentially independent of beam angle and therefore its measurements will not show any angular variations.

To avoid substitution errors during these reflectance measurements, the sample should be placed in the same type of holder as the reference. A Spectralon reflectance standard removed from its cup is ideal for use as a reference, as all surfaces are relatively diffuse.

Clip Center Mounts

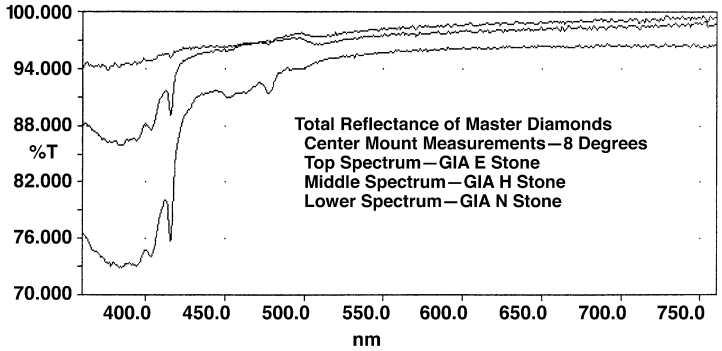
The clip-style variable angle center mount sample holder is designed for transflectance or absorbance measurements of translucent samples. A typical clip center mount sample holder is pictured in *Figure 4.* The clip holder is especially well suited for films and thin, flexible samples; gems can also be measured in this configuration by adapting the sample holder to include gem clips (tweezers).

FIGURE 4
Diagram of clip center mount sample holder



The gem measurement configuration as described above, was used to compare the total reflectance spectra of master diamonds which had been rated by the GIA (Gemological Institute of America) for color. The results of the reflectance analysis are depicted in *Figure 5.*

FIGURE 5
Comparison of reflectance spectra of master diamonds, grades E, H, and N.



When the clip-style variable angle center mount sample holder is used in a double beam sphere system, the measurements are absolute, not relative to a reflectance standard as described above for the jaw mount's reflectance measurements. In the case of the clip center mount, the background scan is performed with the empty clip sample holder placed in the sphere and rotated to the desired angle of incidence. The sample scan is then run with the sample placed in the clips of the sample holder, which has been rotated to the same incidence angle, usually 8° for total transflectance measurements. Because this measurement compares the sphere's reflectance both before and after addition of sample, there is no need for a reflectance standard; any differences in measured absorbance are directly attributable to the sample's presence in the sphere.

It is important that flexible samples hang straight beneath the center mount clip, exactly perpendicular to the sample beam. Any twisting, bending, or drooping of the sample will interfere with the accuracy of the measurement. A film sample can be mounted into a frame if it needs to be held taut, as long as the sample beam strikes only the sample and not part of the film holder.

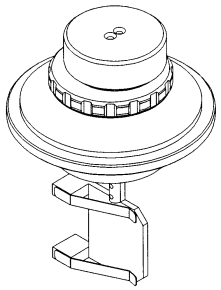
Gier-Dunkle Center Mounts

The Gier-Dunkle center mount has a C-shaped sample holder which projects from its rotating axis. A sketch of this design is given in *Figure 1.* This design allows the sample to be moved either in or out of the sample beam path for correction of single beam substitution error. Because the sample is always present in the sphere during the baseline or sample measurements, the Gier-Dunkle center mount provides the absolute reflectance (or transflectance) of the sample. Both translucent and opaque samples can be measured with this sample holder, and the sample holder can be designed to hold either rigid or flexible samples.

Edwards Center Mounts

The Edwards-style center mount can be used to measure the variable angle reflectance of diffuse or specular samples. The Edwards design of the center mount sample holder shown in *Figure 6* places the sample in the holder back-to-back with the reference. The reference material on the Edwards attachment is composed typically of the same material as the sphere wall. This sample holder, with exposed reference on its back, is rotatable 180° so that the sample is present in the sphere during the baseline scan but it is not in the sample beam's direct path. This design is ideal for single beam spheres, as it eliminates any throughput differences caused by the introduction of the sample into the integrating sphere.

FIGURE 6
Diagram of Edwards center mount sample holder



Because the reference material on the Edwards attachment is diffuse Spectralon or Spectraflect like the sphere wall, only primarily diffuse samples can be measured using this sample holder in a comparison mode, which fully eliminates substitution error. Specular reflectance samples may be measured with the Edwards attachment if it is used in a substitution mode and the sample measurement is performed relative to the proper specular reflectance standard.

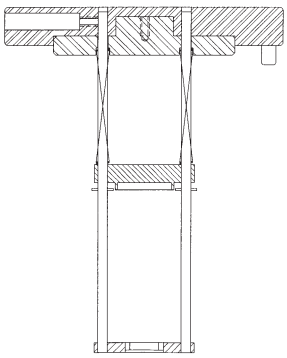
Due to its back-to-back design, the Edwards attachment is not appropriate for the transflectance measurements of translucent samples; the reflectance sample must be opaque.

Cuvette Center Mounts

Cuvette holders are the most common form of fixed angle center mount sample holders. The cuvette center mount design, which can accommodate standard 10 mm pathlength cuvettes, is shown in *Figure 7.* The cuvette-style center mount can be used to measure the absorbance of turbid liquids, such as proteins or environmental samples, in the transflectance mode. The measurement procedure used for the cuvette center mount sample holder matches that of the clip-style center mount, as the sample holder and cuvette are present in the sphere for both the background and the sample scans.

In general, the angle of incidence for cuvette sample holders is set to 0°. This allows the specular component of reflection from the cuvette's shiny surface to be eliminated from measurements.

FIGURE 7
Diagram of Cuvette center mount sample holder



Sample Size Limitations

The size of a sample which can be measured using a center mount sample holder is proportional to the size of the integrating sphere. For measurements with an Edwards sphere, ASTM E 903 recommends that "the area of the specimen shall be limited to 0.01 of the surface area of the sphere (Section 7.2). Thus, for a 200 mm diameter sphere, the required specimen size would be ≤ 20 mm in radius." Center mount sample holders for Labsphere's 150 mm integrating sphere accessories are able to accept samples up to 50 mm (H) by 50 mm (W) by 12 mm (D) in size with the jaw-style center mount and up to 35 mm (H) by 35 mm (W) by 8 mm (D) in size when using the clip-style sample holder. The cuvette fixed angle center mount sample holder is designed to hold standard 10 mm pathlength cuvettes. All other center mount holders would follow similar size restrictions as described above. Samples exceeding the recommended ASTM specimen dimensions may block the sphere's reference beam and will begin to interfere with the sphere's high reflectance and homogeneity, leading to measurement errors.

Availability

Both fixed or variable angle versions of the jaw, clip, or cuvette-style center mount sample holders are available as options for each 150 mm diameter integrating sphere accessory described below. Custom center mounts can be designed for specific customer applications.

The center mount sample holder can be used in conjunction with Labsphere's six inch diameter reflectance/transmittance "RTC" integrating sphere, RTC-060-SF. This sphere is described in our Sphere Systems and Instrumentation Catalog.

In addition, Labsphere offers several reflectance spectroscopy accessories for commercial spectrophotometers which can accept the center mount sample holder option:

Manufacturer	**Accessory**	**Spectrophotometer**
Hitachi	RSA-HI-40	U-4001
Perkin-Elmer	RSA-PE-18*	Lambda 18
	RSA-PE-19*	Lambda 9 or 19
	PELA 1000*	Lambda 900
Varian	DRA-CA-30†	CARY 1/3 or 100/300
	DRA-CA-50†*	CARY 4/5 or 400/500

* Indicates that a small spot kit is available for this accessory.
† Indicates that the accessory has moveable sample beam optics which allow the beam to be focussed at the center mount position.

Additional Reading

Center Mount Sample Measurements:

Edwards, D.K., Gier, J.T., Nelson, K.E., and Roddick, R.D., "Integrating Sphere for Imperfectly Diffuse Samples," *Applied Optics* 51, 1279 (1961).

Safwat, H.H., "Effect of Centrally Located Samples in the Integrating Sphere," *Journal of the Optical Society of America* 60 (4), 534 (1970).

ASTM E 903-82 (Reapproved 1992), "Standard Test Method for Solar Absorptance, Reflectance, and Transmittance of Materials Using Integrating Spheres."

Errors in Reflectance Measurements:

Clarke, F.J.J. and Compton, J.A., "Correction Methods for Integrating-Sphere Measurement of Hemispherical Reflectance," *Color Research and Application* 11 (4), 253 (1986).

Goebel, D.G., "Generalized Integrating Sphere Theory," *Applied Optics* 6 (1), 125 (1967).

Roos, A., Ribbing, C.G., and Bergkvist, M., "Anomalies in Integrating Sphere Measurements on Structured Samples," *Applied Optics* 27 (18), 3828 (1988).

Diffuse Reflectance:

Brunsting, A., Hernaiz, R.S., and Dossman, A.J., "Small Area Measurements of Diffuse Reflectance from 410 nm to 700 nm," *Applied Optics* 23 (1984).

Erb, W. and Budde, W., "Properties of Standard Materials for Reflection," *Color Research and Application* 4 (3), 113 (1979).

Kortum, G., *Reflectance Spectroscopy*, Springer-Verlag (1969).

(1) Spectralon is a proprietary diffuse reflecting material ideal for applications ranging from the UV-VIS to the NIR wavelength region.

(2) Spectraflect is a diffuse white reflectance coating ideal for applications over the UV-VIS and NIR wavelength region. Complete specifications and application information can be found in the Labsphere Diffuse Reflectance Materials and Coatings Catalog.

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