

TECHNICAL GUIDE

Reflectance Spectroscopy



A GUIDE TO REFLECTANCE SPECTROSCOPY

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INTRODUCTION

In his classic monograph *Reflectance Spectroscopy*, Gustav Körtum describes the two types of reflectance:

"If a parallel beam of light is allowed to fall on the smooth surface of a solid material, two limiting cases arise for the reflected portion of the radiation: it is either reflected 'specularly' (that is, as from a mirror) or it is reflected in all directions of the hemisphere uniformly. In the first case, the surface is an ideal reflecting (polished) surface, while in the second case, it is an ideal matte (scattering) surface. These two limiting cases for a surface are never attained in practice..."

In the real world, every object that we see is the result of the reflectance of light from that object reaching an extremely sensitive (if somewhat wavelength limited) photodetector, the eye. For that reason alone, the measurement of reflectance in the laboratory is important to those in business, the arts, sciences and industry. It enables us to quantify what we see, an important concept knowing that our human detector systems vary widely from individual to individual, and from condition to condition.

Reflectance Spectroscopy is a versatile tool that allows us to accurately measure the flux per wavelength of light reflected from a sample. Whether the sample be specular (as from a polished metal surface), diffuse (as from a packed powder sample), or something in between (as in a paint or plastic sample), reflectance spectroscopy can give you information about the material's chemical composition or formulation that is not available by other methods of analysis. In addition, Reflectance Spectroscopy in the 'visible' region of the spectra - that area between roughly 380 nm to 740 nm - allows quantitation of color measurement for biological, pharmaceutical, commercial, and artistic applications.

At this point, let's look at the types of reflectance measurements from materials and the information that can be gained from each.

FIGURE 1 - DIFFUSE REFLECTANCE

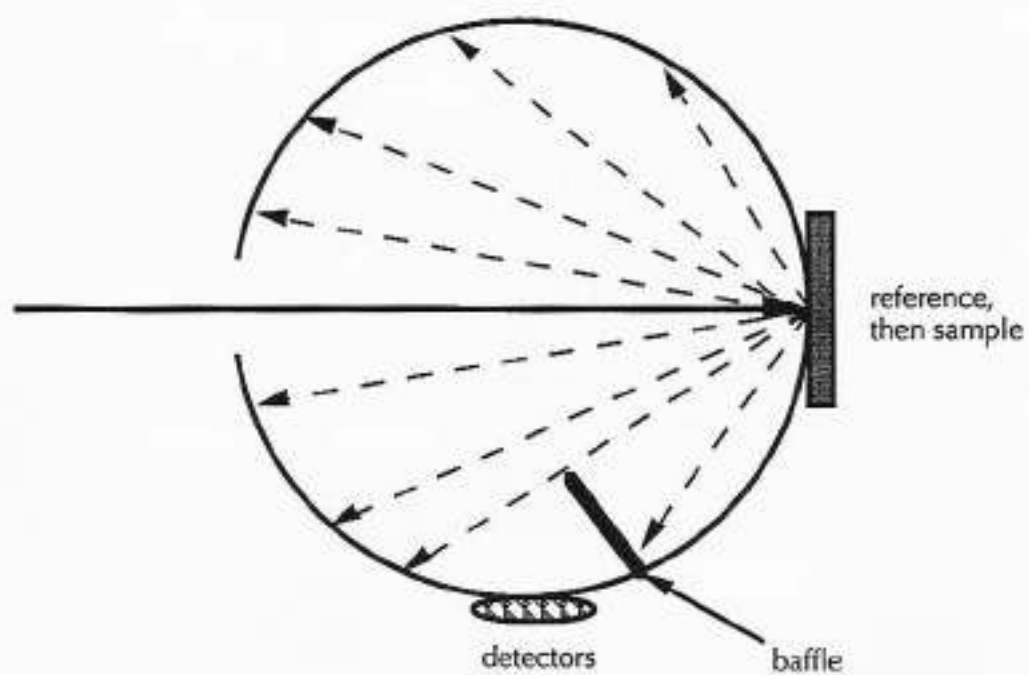
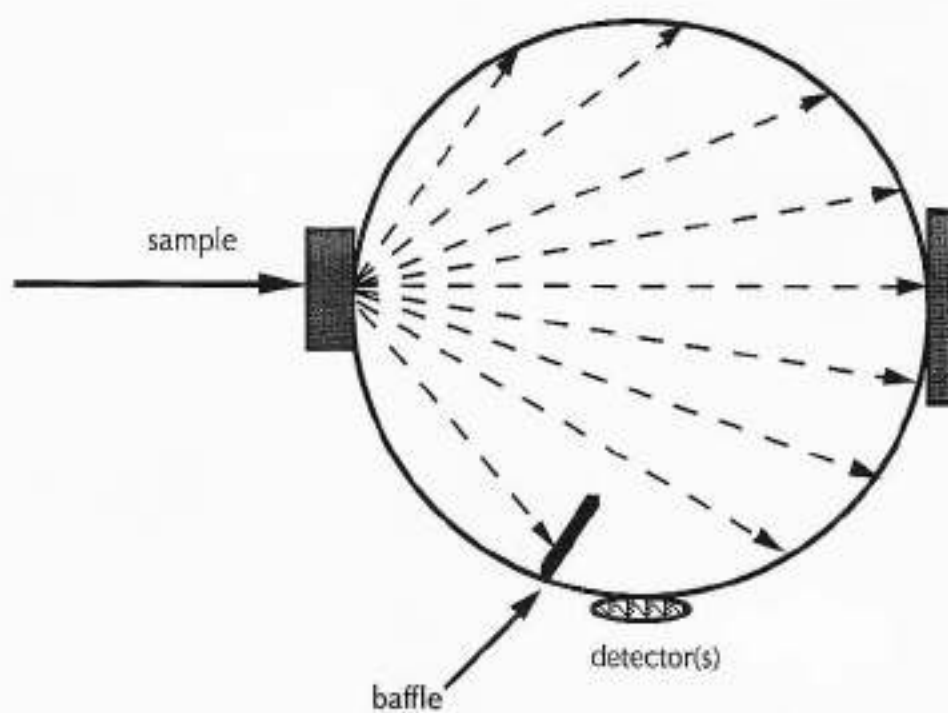


FIGURE 2 - TOTAL DIFFUSE TRANSMITTANCE



TYPES OF REFLECTANCE MEASUREMENTS

Primarily Diffuse Reflectance - Example: Matte paint sample

Diffuse Reflectance Information: Pigment composition, color matching /difference with other paints or textiles. Quality control of paint in process control by studying drawdowns from each batch. Long term applications may include study of the change in material due to weathering or photolytic bleaching, opacity of the product, etc.

Specular Reflectance Information: (From Total Reflectance minus Diffuse Reflectance) Gives indication of gloss, amount of binders and flattening agents in the formulation, quality control of spraying process on the production line.

Primarily Specular Reflectance - Example: Gold plated contacts on circuit board

Diffuse Reflectance Information: Color and composition of the gold on a fast QC basis. If the vendor has changed from 24K gold to 14K gold with copper or silver as the second component, the gold will be of a different color (along with vastly different conductance performance) which may be measured quantitatively using Reflectance Spectroscopy. The use of Reflectance Spectroscopy can be used as both a quantitative and qualitative quality control tool.

Specular Reflectance Information: Smoothness and flatness of the part. If the part has been corroded before plating, it will scatter more light, so the amount of diffuse reflectance compared to specular may give information on process control of the plated surface.

Mixed Specular and Diffuse Reflectance in a Translucent Sample - Example: Colored plastic material

Diffuse Reflectance Information: Color and degree of pigmentation for quality control of a production process. In a chemical process, is the product obtained truly the product or just an admixture of some combination of the starting materials?

Specular Reflectance Information: Degree of gloss of the sample. This may give information of the surface finish of the product- was it supposed to be a matte or glossy finish?

Diffuse Transmittance Information: Whether the sample was as opaque or translucent as desired. Is a paint build opaque enough to provide sufficient cover to prevent photochemical degradation of the substrate? Was the degree of pigmentation complete enough to make the sample totally opaque? If the process was thermoforming, did the process go to completion?

These are just some of the possible uses for Reflectance Spectroscopy. These concepts can be applied to biological/biotechnology applications in such fields as studying the color or UV-VIS-NIR spectra of culture plates that are stained to give percentages of cells which absorbed the staining media. Packed powders, such as various pharmaceutical preparations, can be measured for intensity (and thus concentration) of USDA dyestuffs used in the preparation of medicinals. Textiles and yarns can be measured using proper sample preparation techniques to give useful quantitative and qualitative data using the techniques of Reflectance Spectroscopy.

Applications Using Integrating Spheres to Measure Total and Diffuse Transmittance

In addition to reflectance measurements, an integrating sphere accessory combined with a spectrophotometer is the ideal method for the measurement of diffuse transmittance. Diffuse transmittance is defined as light passing through an object that is not absorbed but scattered upon transit. In fact, in most cases, the measurement that is needed by customers is total transmittance of a translucent article, the total transmittance being the sum of the directly and diffusely transmitted components. A normal spectrophotometer cannot accurately measure the scattered component, the detectors generally have a small subtended angle so an integrating sphere, with an effective subtended angle of 180°, is used to capture all the forward scatter and directly transmitted component. Diffuse transmittance is important in many fields. Two important applications are the total transmittance through packaging of medicinals and the transmittance through architectural glass.

In the first example, packaging of materials, the F.D.A. specifies the amount of UV that can penetrate packaging for most over-the-counter and prescription drugs as these packages are usually translucent glass or plastic, an accurate and reproducible method of measurement must be made on these materials. A standard spectrophotometer will give erroneously low values for transmittance by not accurately measuring the scattered component. An integrating sphere system will accurately give transmittance measurements.

In architectural glass, glass manufacturers have a number of specifications to meet; total transmittance over a particular spectral range, transmittance at various incident angles of radiation, transmittance/absorbance/reflectance of ultraviolet or near-infrared radiation. These measurements can all be made using current Labsphere integrating sphere technology and today's advanced spectrophotometers.

Integrating Sphere Based Diffuse Reflectance Measurement in Mid IR

A field of evolving importance is the use of diffuse reflectance in mid-infrared spectroscopy. The mid-IR region has long been used for as an analytical tool in qualitative analysis for organics and organometallics but sample handling has prevented its use as a quantitative tool except in rare instances.

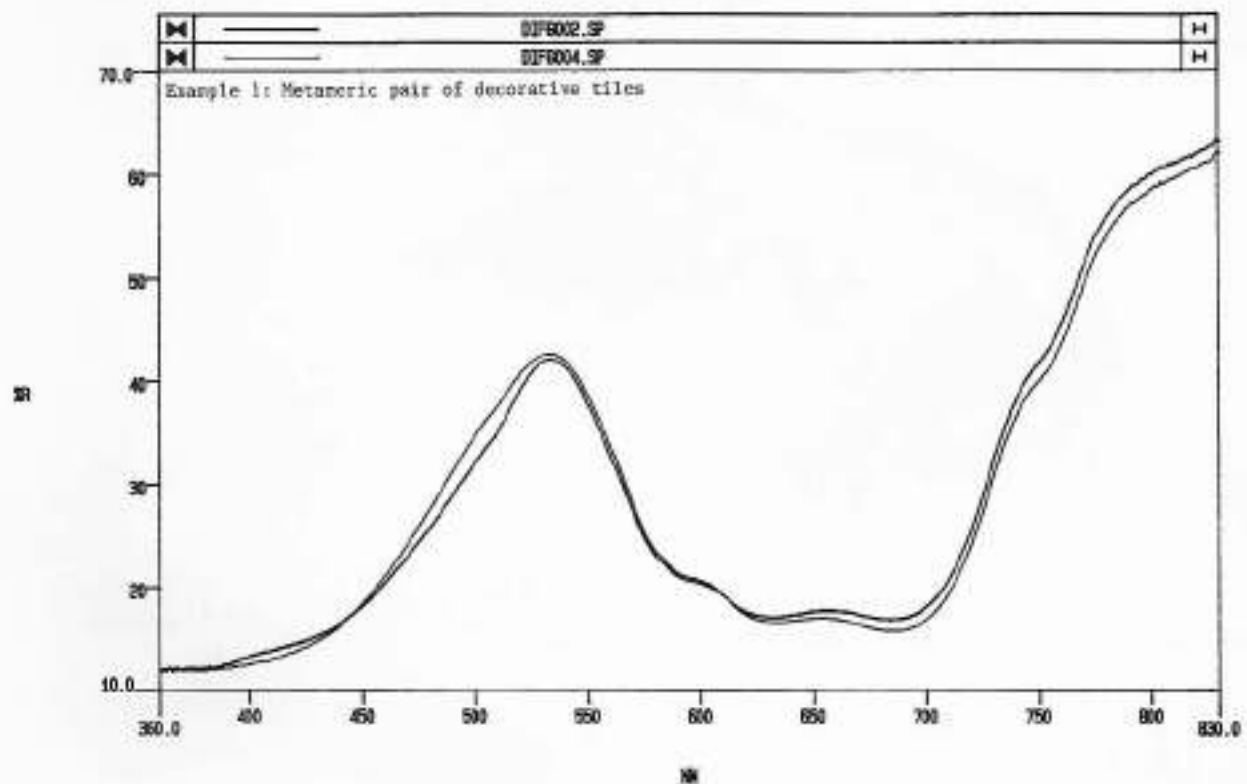
The use of an integrating sphere coupled with a Fourier Transform infrared (FTIR) spectrometer as an analytical tool is fairly new. Until recently the applications have been almost exclusively in the field of thermal analysis, predominantly of coatings and composites for the military and aerospace industries, or for analysis of minerals (especially the work by Dr. Jack Salisbury of U.S. Geological Survey and Johns Hopkins University). In the last year, however, work by Dr. Mike Fuller at Nicolet Instruments has shown that integrating spheres combined with modern FTIR technology can be a potentially powerful quantitative tool in the analysis of complex mixtures of organics, including even such difficult analyses as mixtures of carbohydrates.

The advances in detector technology along with Labsphere's enhanced Infragold sphere coatings point to the advancement of FTIR as a promising analytical tool. Sample preparation is minimal, difficult samples such as sludges, greases, large solid samples, can all be measured without the usual problems associated with such materials.

TYPICAL APPLICATIONS FOR REFLECTANCE/TRANSMITTANCE SPECTROSCOPY ACCESSORIES

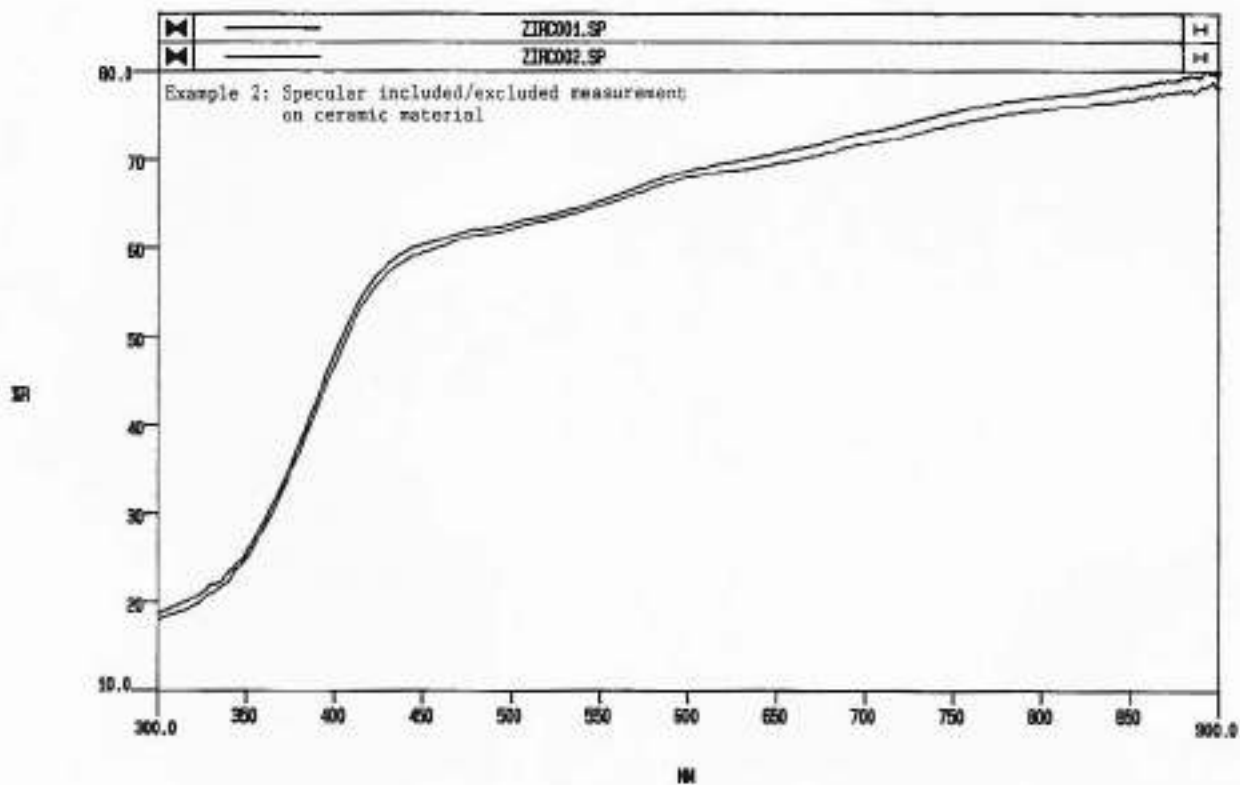
Example 1 Color Analysis by Reflectance

Vendor has supplied two "matching" green decorative tile samples. Customer returns samples saying that under fluorescent lights, the tiles don't match. By measuring the reflectance of the two tiles, it can be seen that the curves are not identical (even though visually under incandescent lights the tiles are indistinguishable), and cross at three points. The tiles are a metameric pair, likely caused by using different pigments for the two lots of tile.



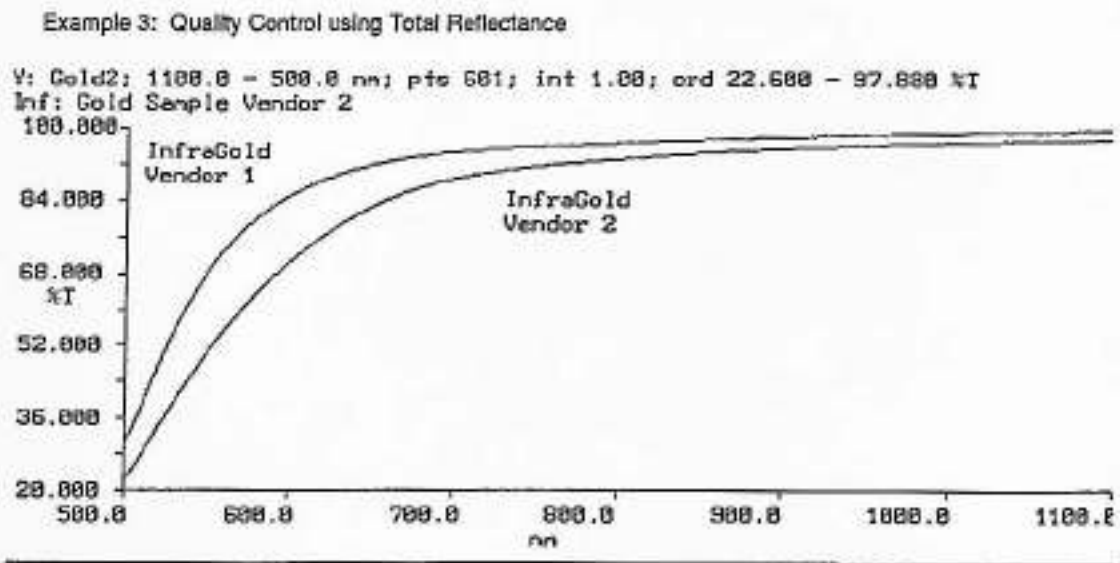
Example 2 Measurement of Gloss by Diffuse Reflectance

Vendor has been asked to provide a low gloss zirconium oxide based ceramic for use in an aerospace application. Only a small specular (non-diffuse) component is allowable to prevent inaccurate instrument readings. By measuring the ceramic in a specular-included (top curve) and specular-excluded (bottom curve), it can be shown that specular component is <3% over the wavelength range desired by the contractor.



Example 3 Quality Control Using Total Reflectance

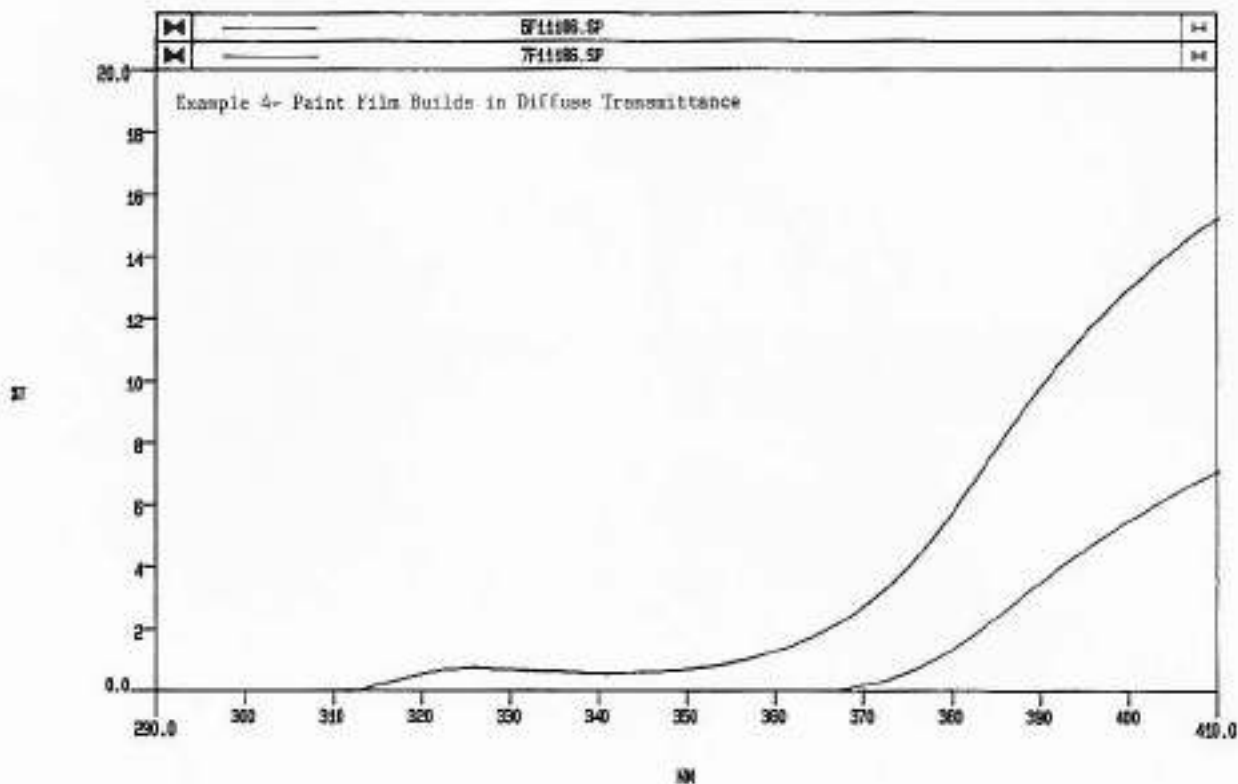
End user of gold plated parts for the electronics industry needs a quick method to check quality of incoming parts. End user knows that a minimum of 99% gold is needed to meet conductivity specs on parts. By measuring total reflectance and the shape of the reflectance curve, the customer can determine quickly if vendor has added additional copper or other metals to the plating process on test coupons that would give lower reflectance. This could be translated into lower conductivity, thus not meeting specifications.



Example 4 Diffuse Transmittance

In these days of increasingly stiff EPA regulations on volatile organics, car manufacturers have changed to water-based coatings for vehicles. With this change has come some problems. If the paint films transmit too much light in the UV, especially below 360 nm, delamination of the paint from the base metal/primer may occur, giving paint blisters. Even very low transmittance (<1%), over long exposure, may cause this delamination to occur. Consequently, UV absorbers and increased pigment loads are used to block UV. The downside is that too much of the UV blocker or an increase in pigment load can cause dulling of the paint, lessen the number of available colors and add expense to the manufacturer.

Transmittance measurement of these film builds with a standard spectrophotometer is not feasible due to the high degree of scatter due to pigment. By using an integrating sphere accessory, these measurements are easily accomplished. The spectra below shows two film builds of the same pigment with the lower curve showing sufficient pigment at UV blocker to prevent delamination, while the upper curve shows a failed film of the same color. Notice that there is significant transmittance well below the 360 nm cutoff.



REFLECTANCE/TRANSMITTANCE MEASUREMENT TECHNIQUES

REFLECTANCE MEASUREMENT TECHNIQUES

- Solid samples can generally be measured in the comparison method if the user can place the sample flush to the port of the integrating sphere. If the sample is translucent, it should be backed with a light trap to prevent room light from entering through the sample and giving a false high reflectance reading.
- Powdered samples may be pressed into pellets and measured in the normal fashion. Problems may arise as reflectance is a function of the packing density and that a specular surface on the pressed pellet may give inaccurate readings.
- Loosely packed powders may be measured in a cuvette but reference should be measured in identical cuvettes.
- Powder sample holders (generally a Teflon or aluminum block with quartz or glass windows) give accurate, reproducible measurements. Reference sample can be made to fit sample holder. This type of holder is also effective for measuring pastes and thick slurries.
- Fabric samples can be stretched across a frame to give a flat, non-wrinkled surface (back sample with light trap to assure external light does not affect measurements).
- Yarn or pile samples can be bunched, bound, then cut flat across the pile to give a flat surface to present to the sphere port.
- Small solid samples should be masked (with identical mask for reference) so that the masked sample fills the sample port.
- Clear liquids and transparent (non-scattering) solids can be measured in cuvettes
- Turbid liquids or translucent solids can be measured in cuvettes or larger liquid cells. Remember, %T/A is a function of path length or thickness of sample.

SAMPLE PREPARATION FOR REFLECTANCE

Small Samples

Small samples may be measured by means of masking techniques.

To do this, the reference (blank scan) must also be measured behind the same mask.

Generally a black mask is used to prevent reflectance from the mask adding to the reflectance of the sample. Simple and effective masks can be prepared from a piece of cardboard (a manila file folder is excellent in that it is thin and easily manipulated) large enough to fill the port painted black with flat black Krylon™ paint.



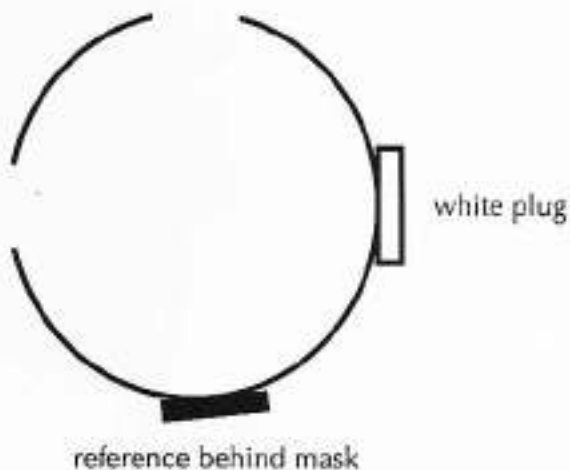
sample in mask



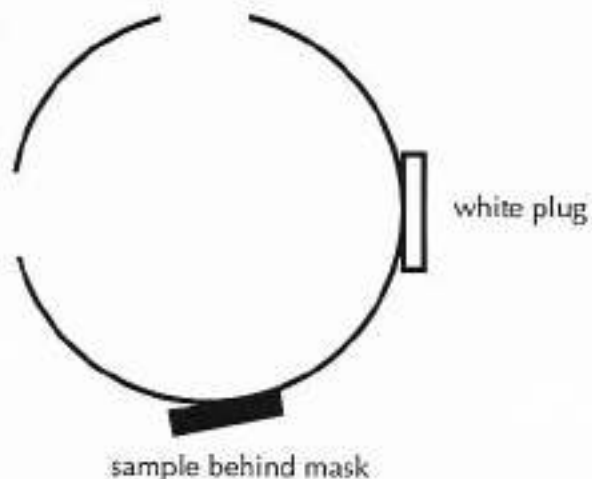
reference

While this method uses the substitution method, the area of the sample is generally so small that the substitution error is insignificant. With a double beam sphere accessory a background correction should be performed with masked reference in place before sample is measured..

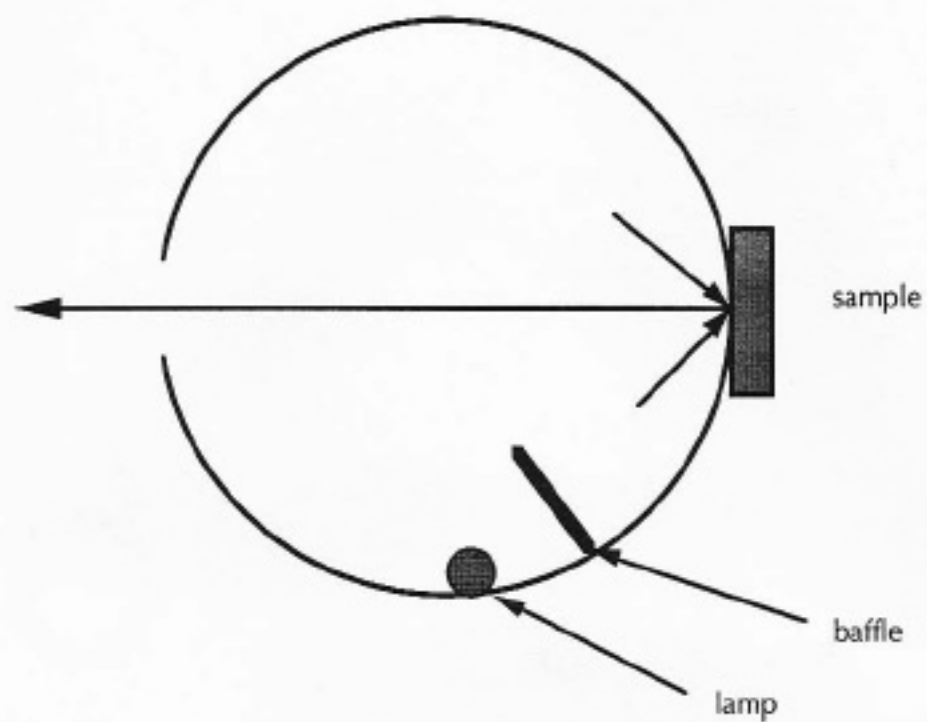
1. Sphere configuration for blank



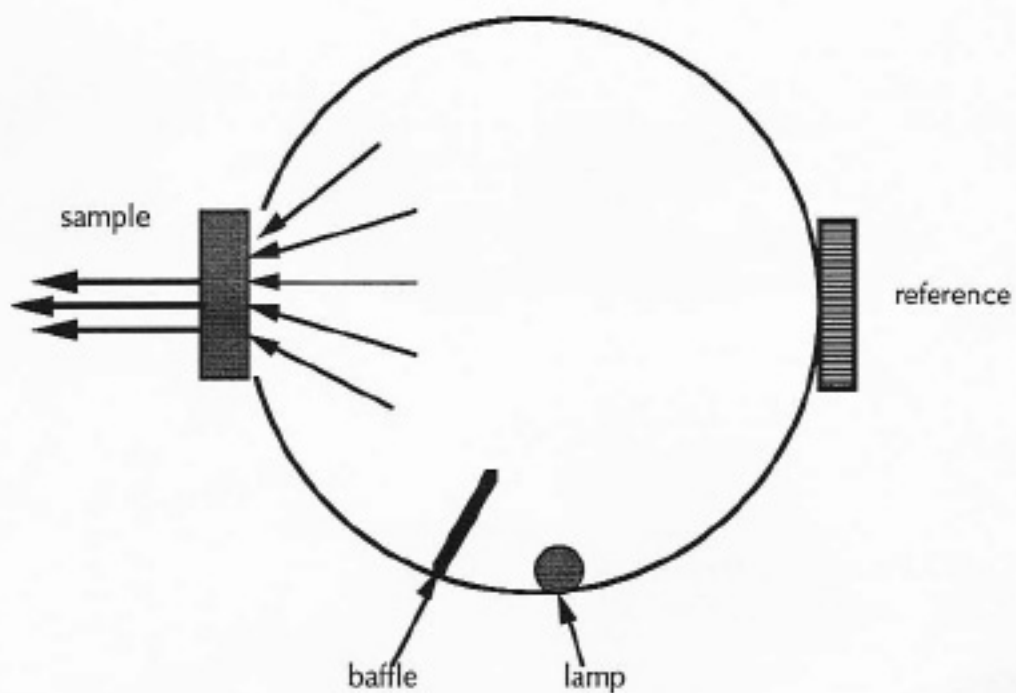
2. Sphere configuration for measurement



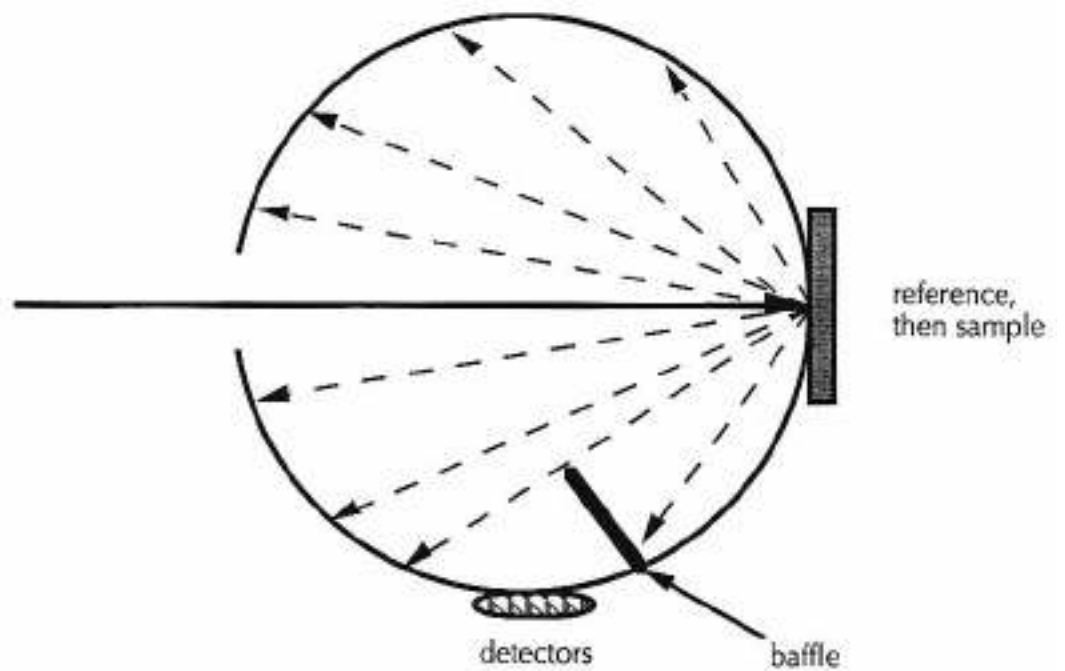
DIFFUSE REFLECTANCE
(Source in Sphere)



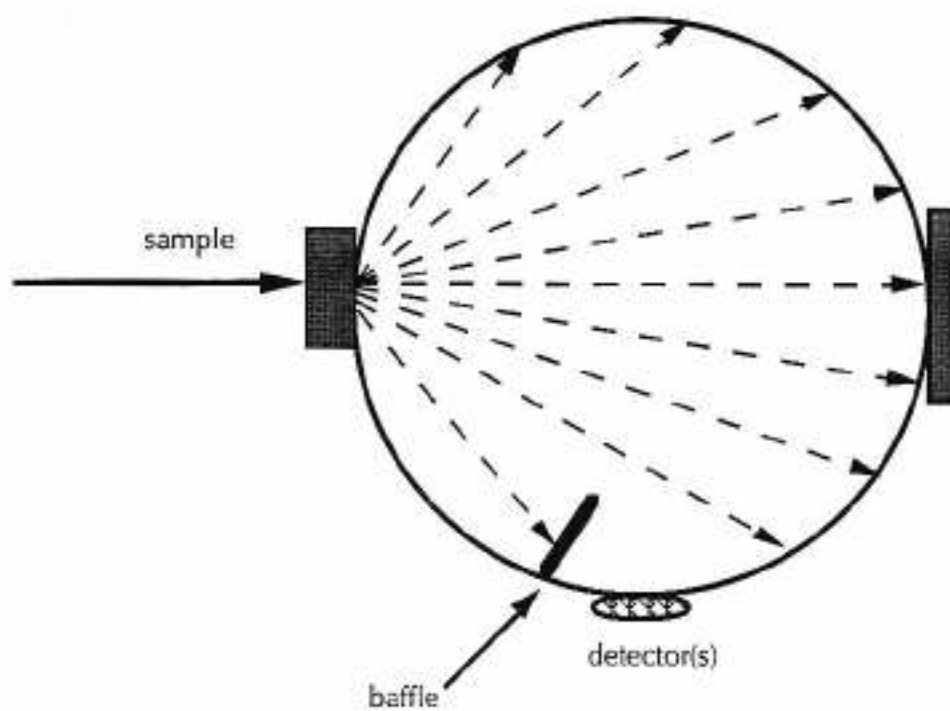
TOTAL TRANSMITTANCE
(Source in Sphere)



REFLECTANCE DISPERSIVE SPECTROPHOTOMETER



DIFFUSE (TOTAL) TRANSMITTANCE/ DISPERSIVE SPECTROPHOTOMETER

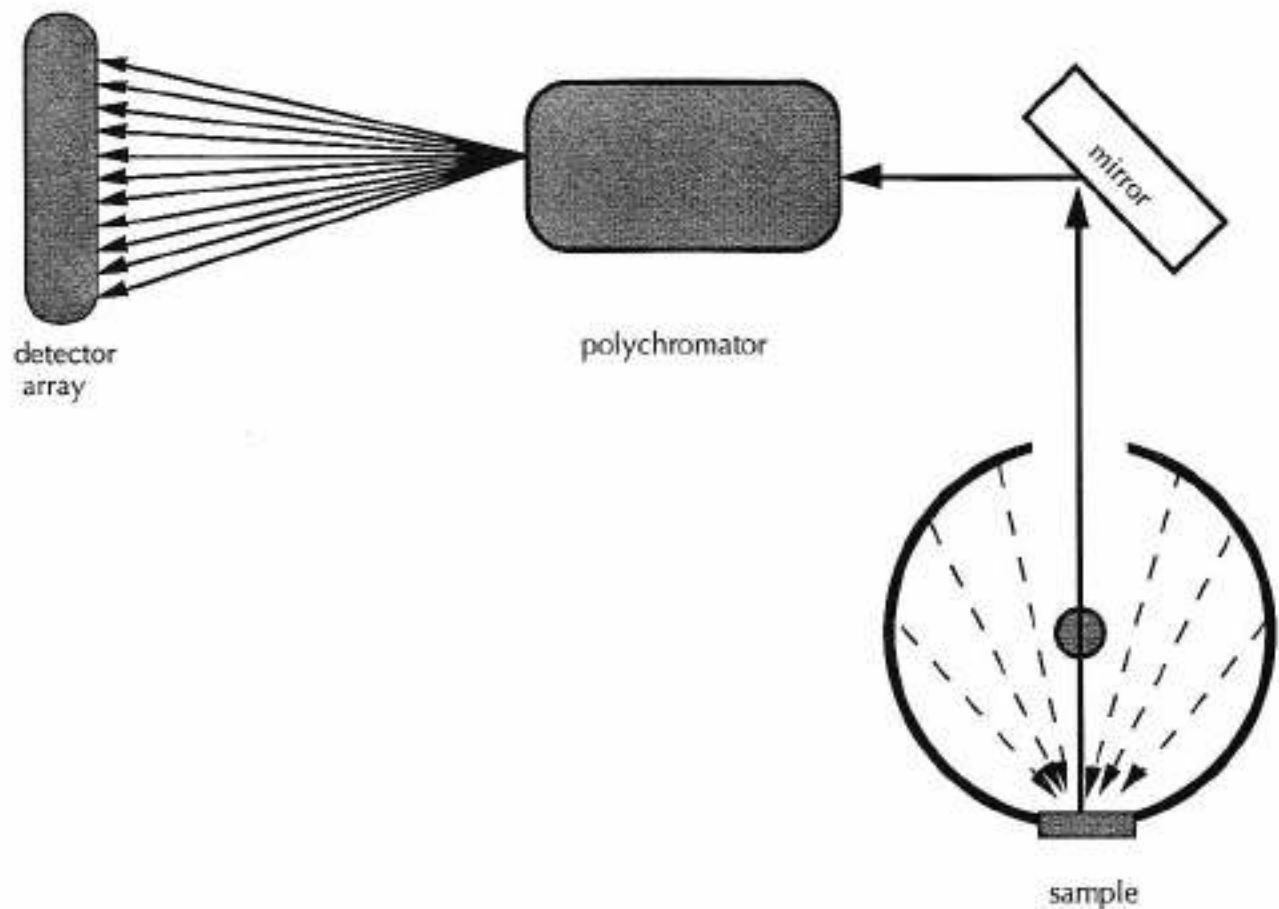


REFLECTANCE MEASUREMENTS WITH DIODE ARRAY SPECTROMETER

Unlike most reflectance measurement devices which illuminate the sample using monochromatic light, diode array instruments make use of a tungsten-halogen lamp (or a xenon arc lamp) located inside the sphere to produce polychromatic illumination. The sample is viewed at either 8° or 0° to give measurement of either total reflectance or specular subtracted reflectance. These two geometries are known as diffuse/ 8° and diffuse/normal (or 0°), respectively.

Advantages of diffuse/ 8° or normal geometries accompanied by a diode array detector system include speed of sample measurement and some ability to look at the fluorescent component of reflectance.

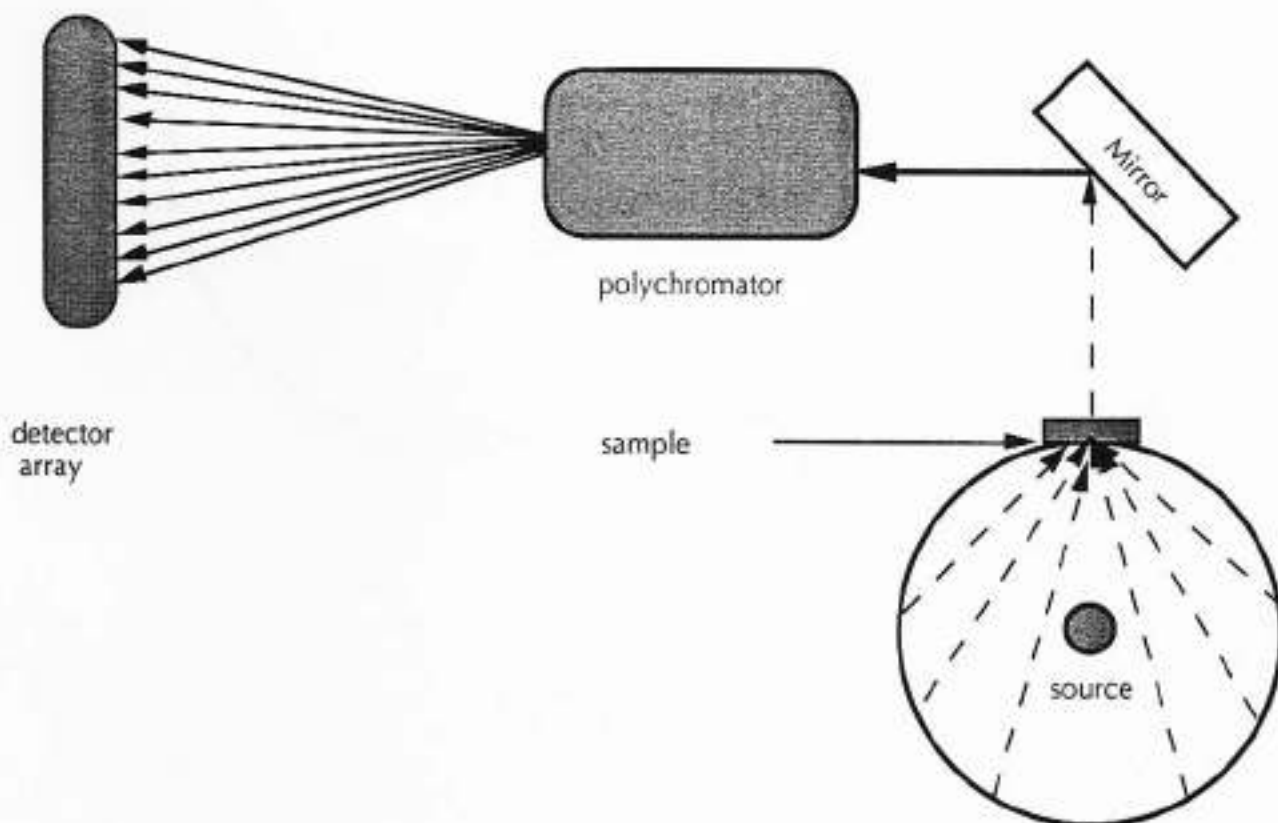
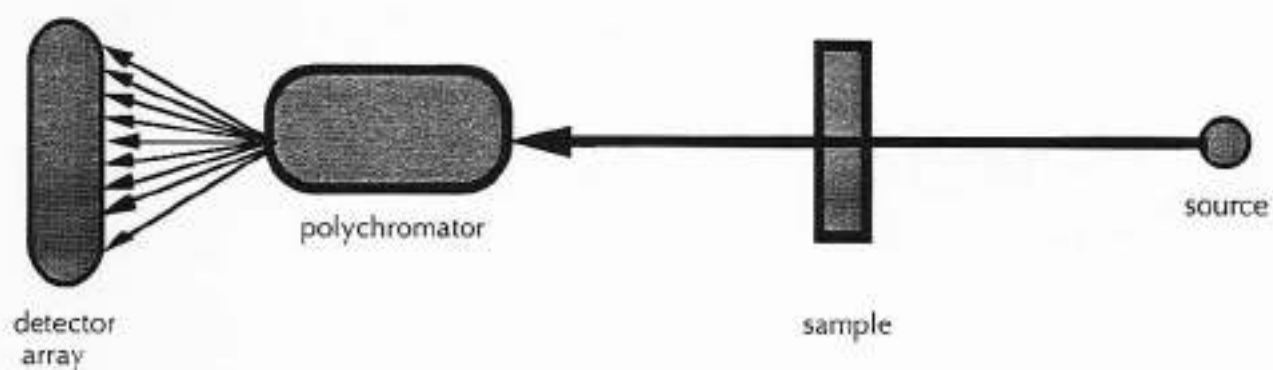
Sphere as Source - Diffuse Illumination



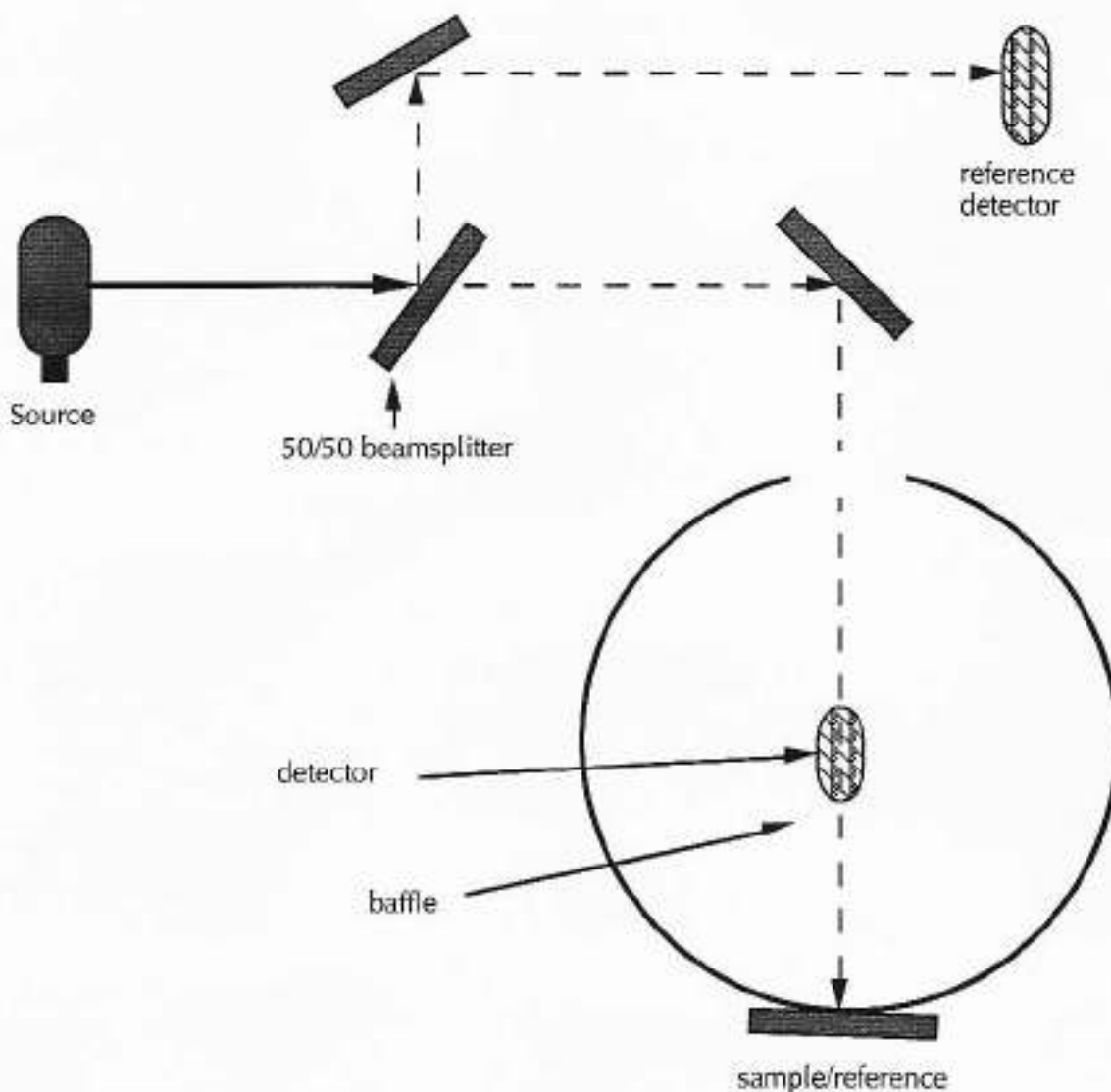
TRANSMITTANCE MEASUREMENTS WITH DIODE ARRAY SPECTROMETER

Sphere as Source - Diffuse Illumination

This schematic diagram shows the measurement of transmittance (either diffuse or normal) using a diode array spectrophotometer accessory. The geometry is diffuse/normal.

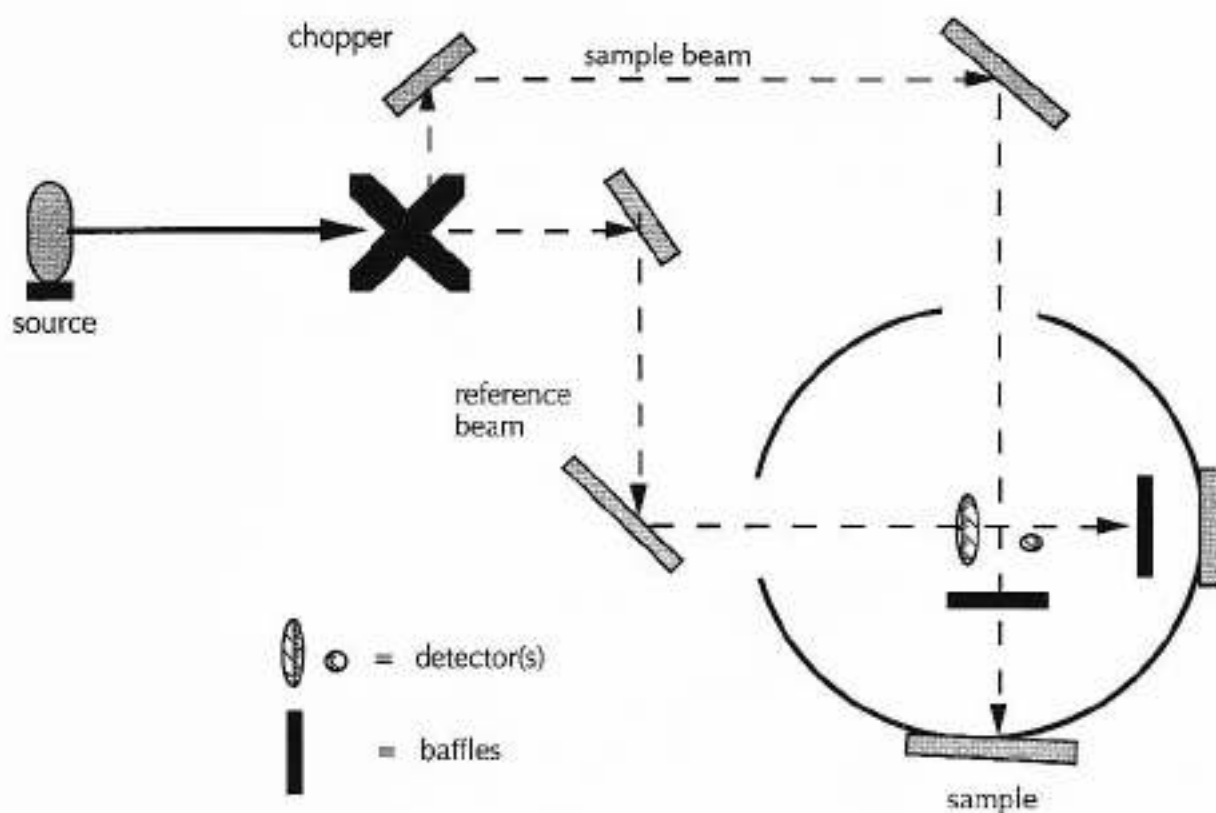


DUAL BEAM SPECTROPHOTOMETER INTEGRATING SPHERE ACCESSORY



Dual beam (DC/ non-chopped beams) spectrophotometers necessitate a design modification from chopped double beam instruments. The reference beam is led to a detector external to the sphere (usually using one of the original instruments detectors) while a second identical detector with its own amplification circuit, is placed within the integrating sphere.

DOUBLE BEAM SPECTROPHOTOMETER INTEGRATING SPHERE ACCESSORY

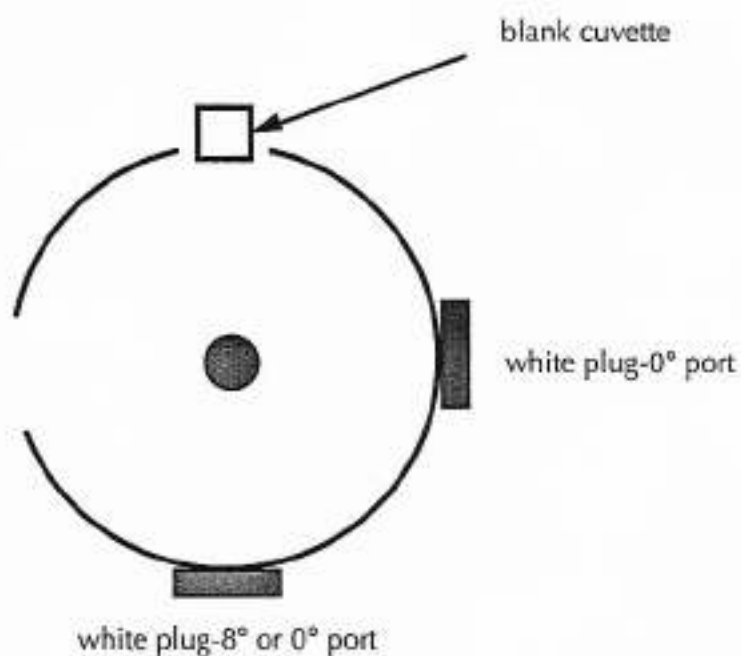


Chopped signal allows for sample and reference to be measured concurrently. This allows for comparison measurements of sample and reference without moving samples. This generic sphere design, with some modifications of sphere/optical geometry, is used for all double beam integrating sphere accessories made by Labsphere.

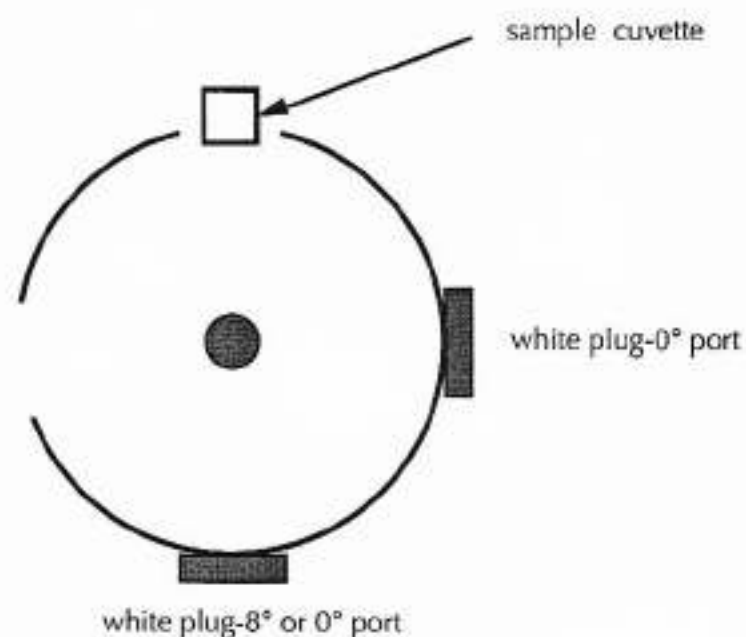
MEASUREMENT OF TRANSMITTANCE OF LIQUID SAMPLES USING A LABSPHERE INTEGRATING SPHERE ACCESSORY

Transmittance of liquid samples in cuvettes can be measured in the same manner as sample measured on the spectrometer without the sphere accessory. The sphere merely acts as the illumination source.

BLANK SCAN



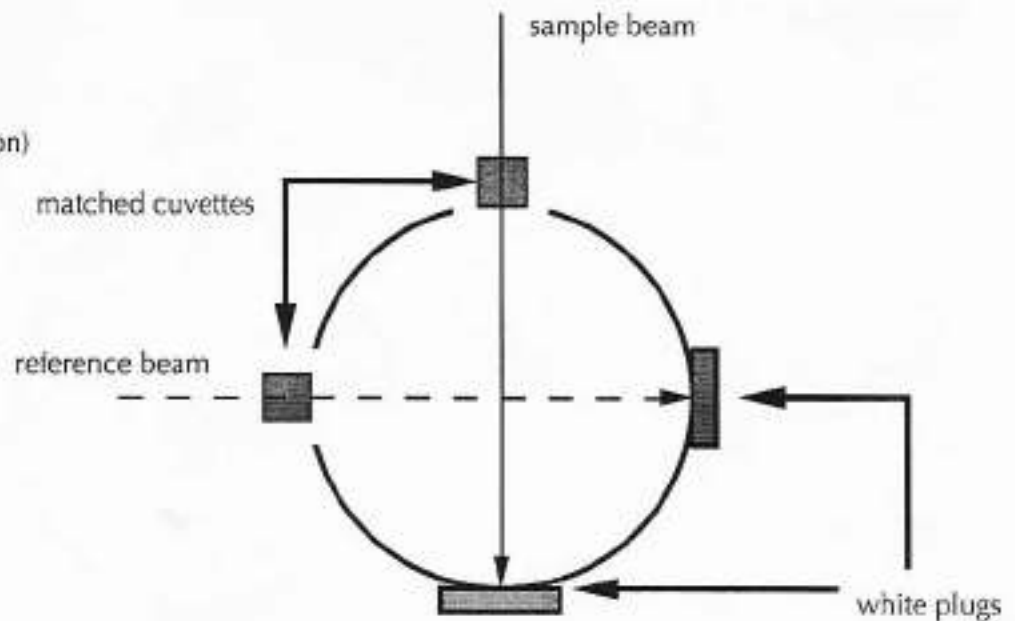
SAMPLE SCAN



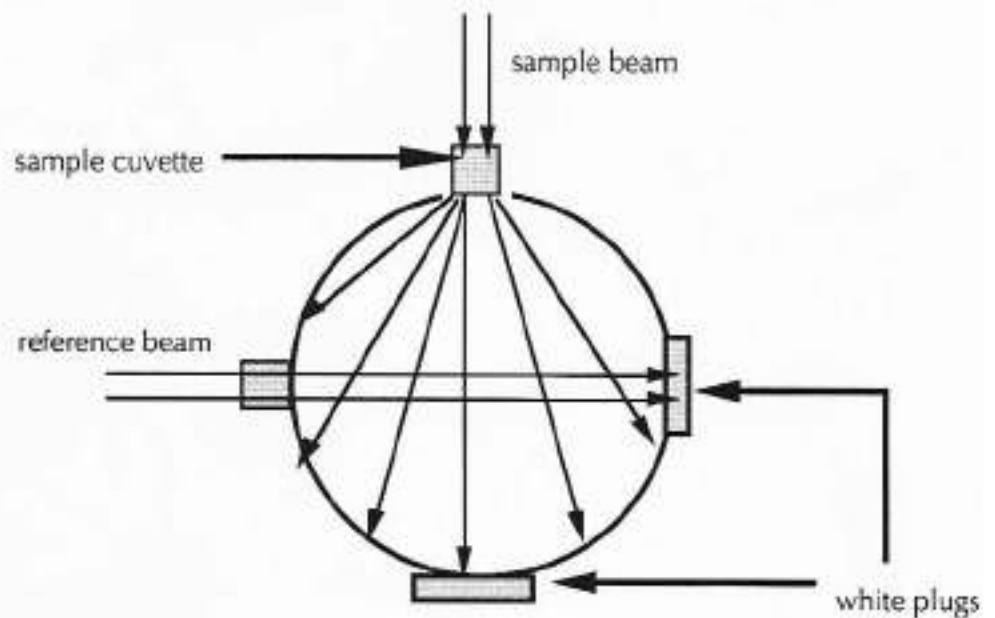
MEASUREMENT OF TRANSMITTANCE FOR LIQUID SAMPLES USING DOUBLE BEAM SPHERE ACCESSORIES

Transmittance of liquid samples in cuvettes can be measured in the same manner as without the sphere accessory. The sphere merely acts as a larger, more efficient detector for scattering samples.

BLANK SCAN (background correction)



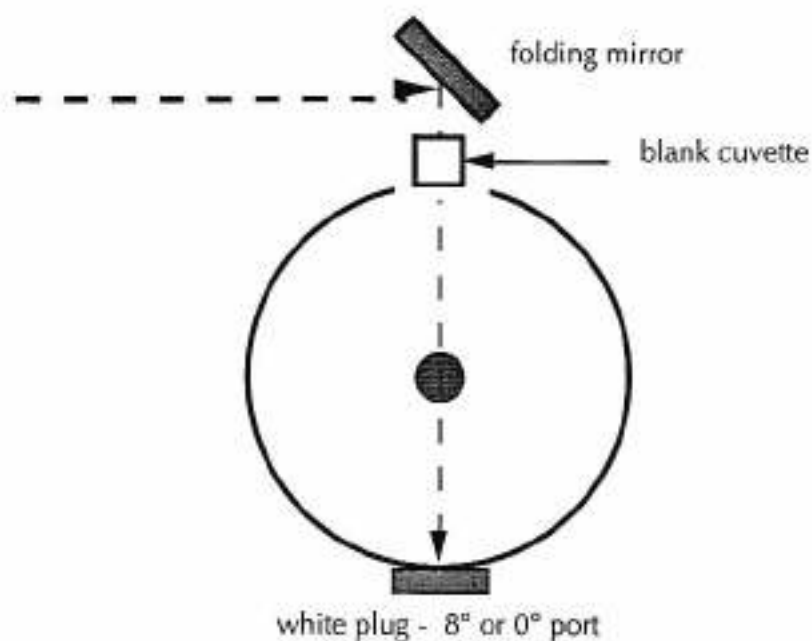
SAMPLE SCAN



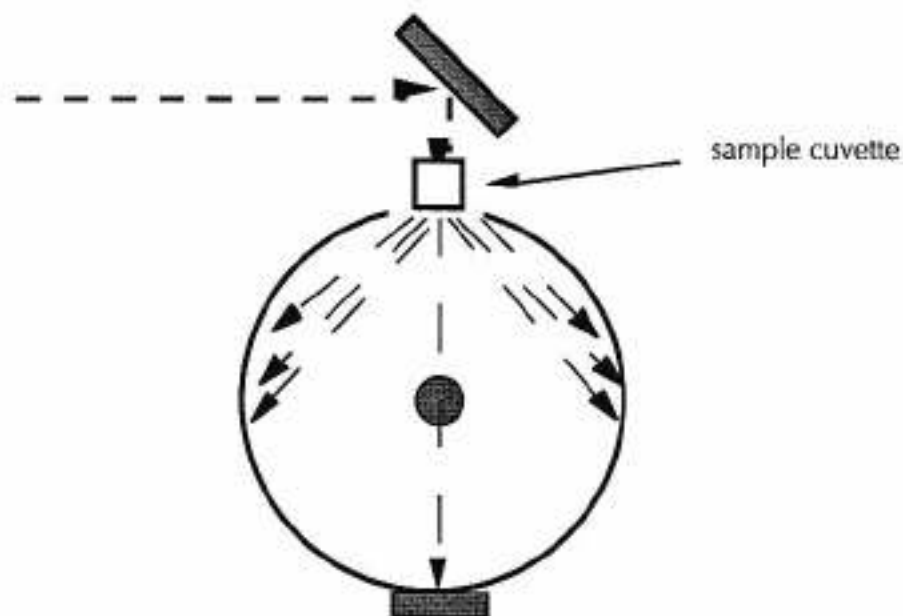
This method is the most efficient method available for the measurement of translucent or scattering liquid samples. This method is also applicable to translucent solids and films without the use of reference cuvetts. Air is the standard reference for transmittance of solids.

MEASUREMENT OF TRANSMITTANCE OF LIQUID SAMPLES USING SINGLE BEAM ACCESSORY

BLANK SCAN



SAMPLE SCAN



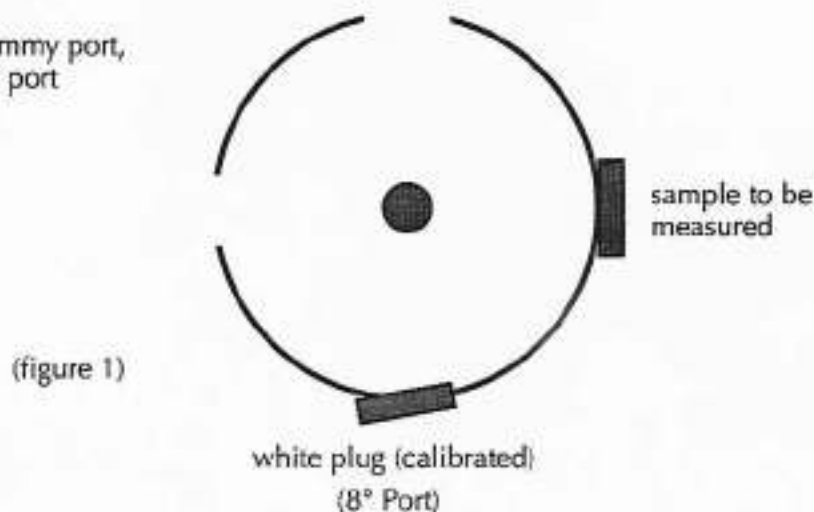
This technique may be used for either transparent or translucent (diffusely transmitting) liquids. Unlike solid samples, if a blank cuvette is used, the single beam sample substitution error is effectively eliminated and no correction factors need be applied to the measurements.

COMPARISON METHOD OF DIFFUSE REFLECTANCE MEASUREMENT

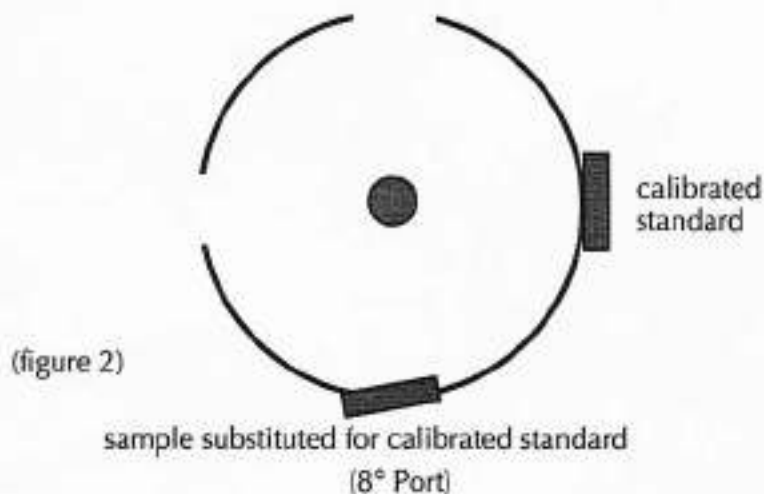
The comparison method of reflectance measurement provides accurate results with only a slight increase in the time needed for the actual measurement. As the geometry of the sphere is identical in both measurement of the blank and the sample, no calibration curves need be generated as in the substitution method. Samples can be run in either specular included (diffuse/8°) or specular excluded (diffuse/normal) mode.

RUN BLANK SCAN

Sample to be measured in dummy port,
calibrated standard in sample port



RUN SCAN



Reflectance equals (measured reflectance) * (Reflectance of Reference)

No Substitution Error - sphere throughput is the same in figure 1 and 2.

Advantages: Highly accurate measurement of reflectance; sphere geometry the same in both blank and measurement configurations.

Disadvantages: Not as fast as substitution method (requires rescanning blank with each new sample).

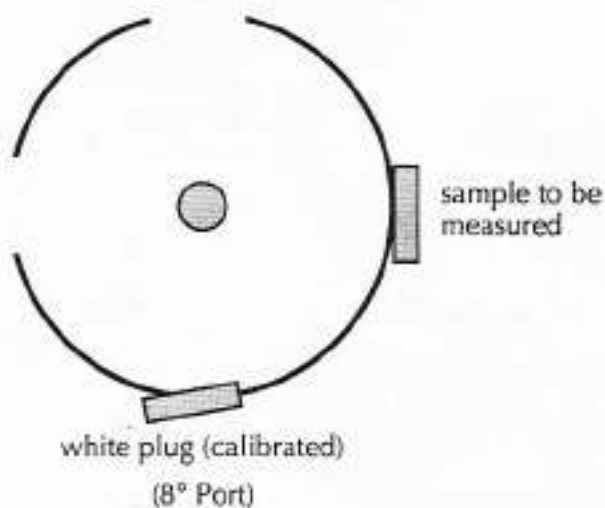
SPECULAR SUBTRACTED MEASUREMENT OF REFLECTANCE (MEASUREMENT OF GLOSS)

There are many instances that samples need be measured in two modes—with the specular component of reflectance included (total reflectance) and with the specular component excluded. The difference between these two measurements (total minus specular excluded) is the specular component of the sample, which is a good approximation of the gloss. Specular excluded reflectance is frequently required in the measurement of paints, coatings, and other materials that owe some of their visual appearance to the glossy component of their reflectance.

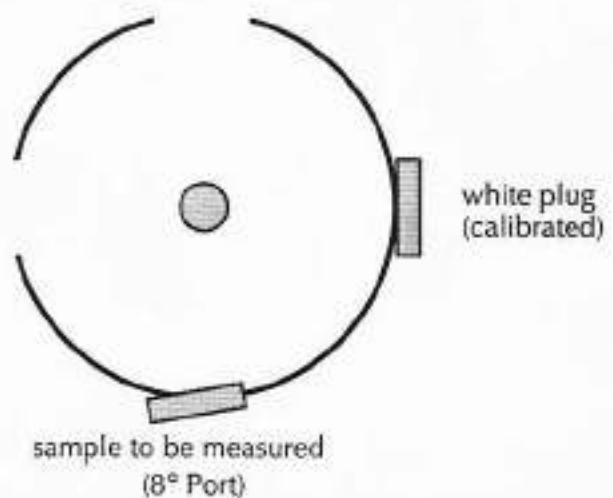
MEASURE TOTAL REFLECTANCE

Measure total reflectance with 8° port on sample port

BLANK SCAN



SAMPLE SCAN



SPECULAR SUBTRACTED MEASUREMENT OF REFLECTANCE II (MEASUREMENT OF GLOSS)

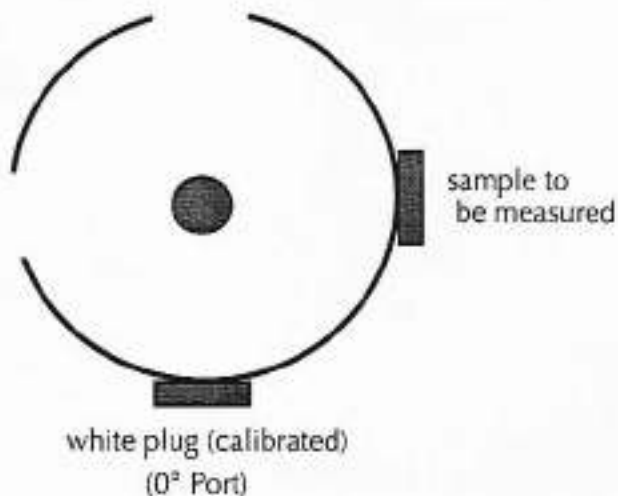
The second scan is a measurement of reflectance with the specular component removed. The gloss is defined as (total reflectance)-(specular excluded reflectance).

These measurements are important in the accurate measurement of color of glossy materials. The gloss component may artificially add brightness to a material, thus paints and coatings are often specified with both color and gloss components.

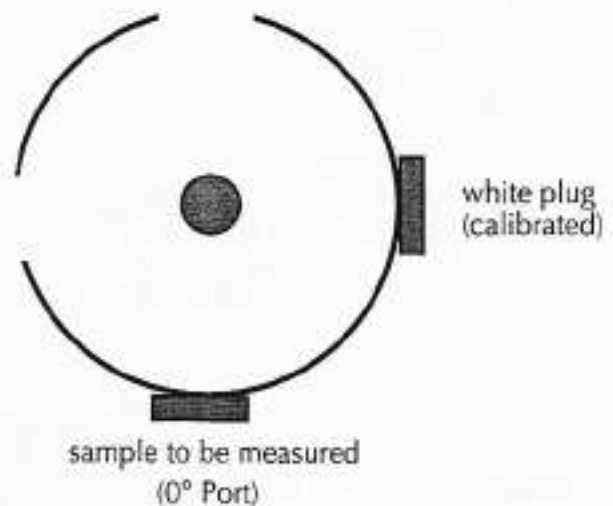
SPECULAR SUBTRACTED REFLECTANCE

Measure reflectance with 0° port on sample port

BLANK SCAN



SAMPLE SCAN

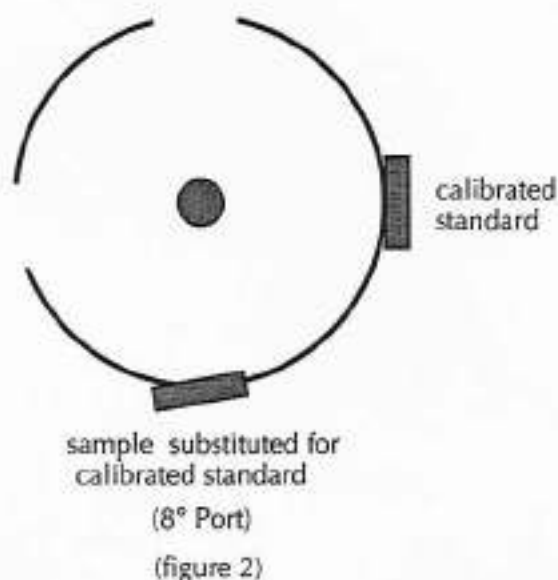
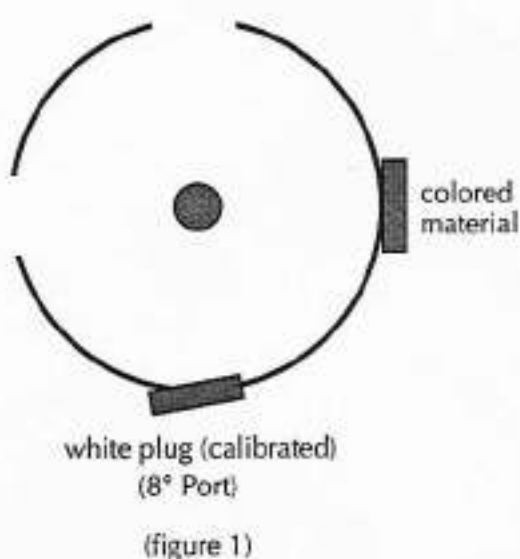


COLOR MEASUREMENTS BY USE OF COMPARISON METHOD OF DIFFUSE REFLECTANCE

Color measurements can be easily made using diode array instruments using the comparison method. As standard color measurements of solids are simply mathematical treatments of reflectance data, the obtained spectra can be converted to ASCII files using the standard spectrophotometric software and processed to give tristimulus, $L^*A^*B^*$, $L^*U^*V^*$, or other desired colorimetric data.

RUN BLANK SCAN

Sample to be measured in dummy port, calibrated standard in sample port



Reflectance of Sample equals (measured reflectance) * (Reflectance of Reference)

Standard accessories easily cover both CIE and ASTM wavelength ranges for color measurement (either 400-700 or 360-780 nm).

CIE specifies three different data intervals - (1 nm, 5 nm, or 10 nm) - all can be done using most instruments software (the 1 nm data can be interpolated). Most commercial color measurement instruments have a 10 to 20 nm bandpass.

Diode array accessories offer the end user a fast, inexpensive, accurate colorimeter for the production/quality control workplace.

CALCULATION OF ACTUAL REFLECTANCE

When a measurement is made using the comparison method, the displayed reflectance is not the actual reflectance of the material. It is actually the reflectance factor divided by the reflectance of the reference. To get the actual reflectance, one must multiply by the reflectance of the reference material.

EXAMPLE 1

A matte paint sample is measured using the provided Spectralon® reference material. Data and calculations are shown below:

<u>Wavelength</u>	<u>Measured Reflectance</u>	<u>Reference Reflectance</u>		<u>Actual Reflectance</u>
400	.452	.990	=	.447
450	.551	.991	=	.546
500	.600	.991	=	.595
550	.611	.992	=	.606
600	.625	.992	=	.620
650	.675	.992	=	.670
700	.700	.991	=	.694
750	.653	.992	=	.648
800	.523	.991	=	.518

EXAMPLE 2

A specular sample is measured in comparison mode using calibrated first surface mirror as reference.

<u>Wavelength</u>	<u>Measured Reflectance</u>	<u>Reference Reflectance</u>		<u>Actual Reflectance</u>
400	1.000	.957	=	.957
450	.993	.958	=	.951
500	.992	.939	=	.931
550	.975	.927	=	.903
600	.963	.921	=	.862
650	.965	.908	=	.876
700	.975	.894	=	.871
750	1.011	.881	=	.891
800	1.023	.827	=	.846

In all cases using the comparison method, the reflectance factor is:

$$(R_{\text{measured}}) \times (R_{\text{reference}})$$

SUBSTITUTION ERROR

The 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. The error is caused by the difference between the throughput of the sphere when the reference makes up a portion of the wall and the throughput when the sample is substituted for the reference. For reflectance measurements the throughput is usually lower when the sample is present since a reference material of high (nearly 100%) reflectance is usually used. For transmittance measurements the throughput is usually higher when the sample is present since an open port (zero reflectance when viewed from inside the sphere) is usually used as a reference.

Methods of Correction

When the sample and reference are of similar reflectances the substitution error is negligible, at worst it may reach only three or four percent and in many cases it is simply ignored. In quality control applications where a threshold value is used, the substitution error can be incorporated into this threshold. For chemical analysis where the locations of absorption peaks, not necessarily their exact absorbance values, are important the error can also be ignored. Where correction of the substitution error is necessary, the following techniques are available.

Double Beam

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 reference beam each "see" the same sphere, there is no substitution error.

Dummy Port

When room permits, single beam spheres can be designed with an additional "dummy" port. The background correction is performed with the sample to be measured in the dummy port and the physical reference in the sample port. A scan is then run with the positions of the two switched. In this comparison method the average reflectance (hence the throughput) of the sphere remains unchanged from the reference scan to the sample scan. This technique requires that a separate reference scan be run for each sample (unless the samples are all very similar and the residual substitution error caused by sample-to-sample differences can be ignored).

Matched Sample

If a reference is used which is very close in reflectance to the sample, the substitution error is negligible.

Low Reflectance or Transmittance

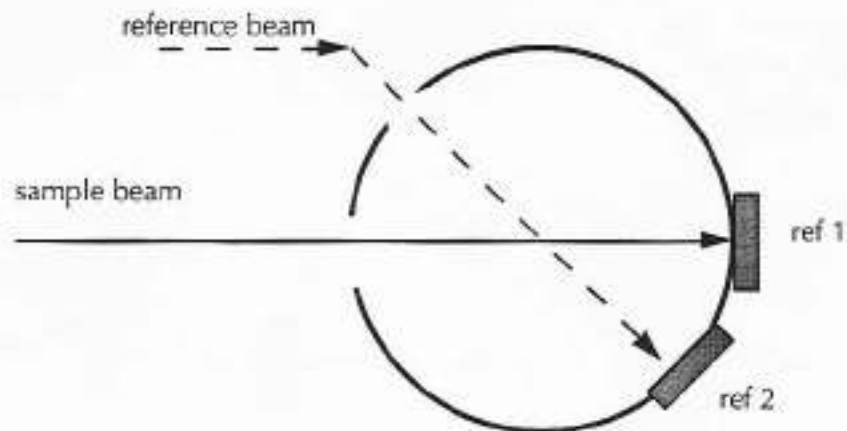
For samples with very low reflectance or transmittance, the substitution error will be very small. For a sample with zero reflectance or transmittance, there is no substitution error at all. For low reflectance and transmittance samples, the substitution error is so small that it probably falls within the random noise of the instrument.

Calibrated Standards

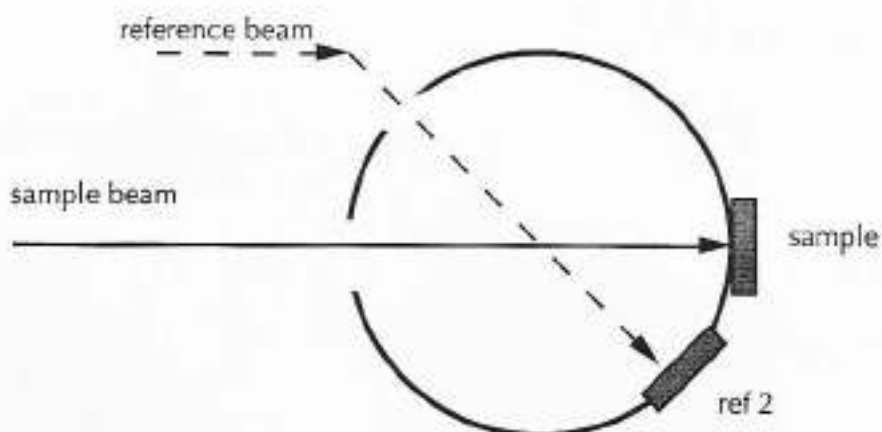
For single beam spheres without dummy ports in applications where substitution error is a concern, the spheres can be calibrated with a set of standards such as one of Labsphere's Reflectance Standards Sets, which has been measured on a sphere without substitution error. With these standards, a table of measured vs. actual readings can be generated and used to correct for substitution error.

COMPARISON VS SUBSTITUTION MEASUREMENTS

Comparison Method - all double beam accessories plus some diode array accessories



Baseline run with two 'identical' samples in sample reference ports

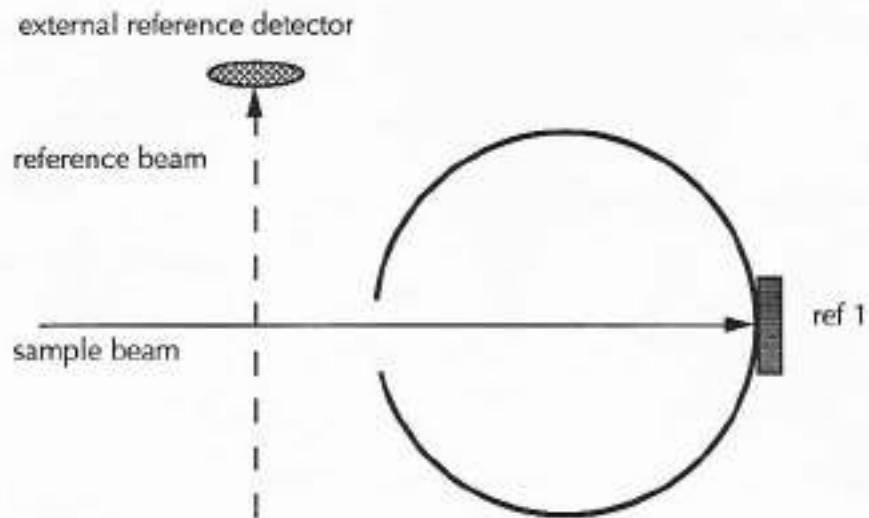


Sample replaces one plug, samples are actively compared by chopped beams

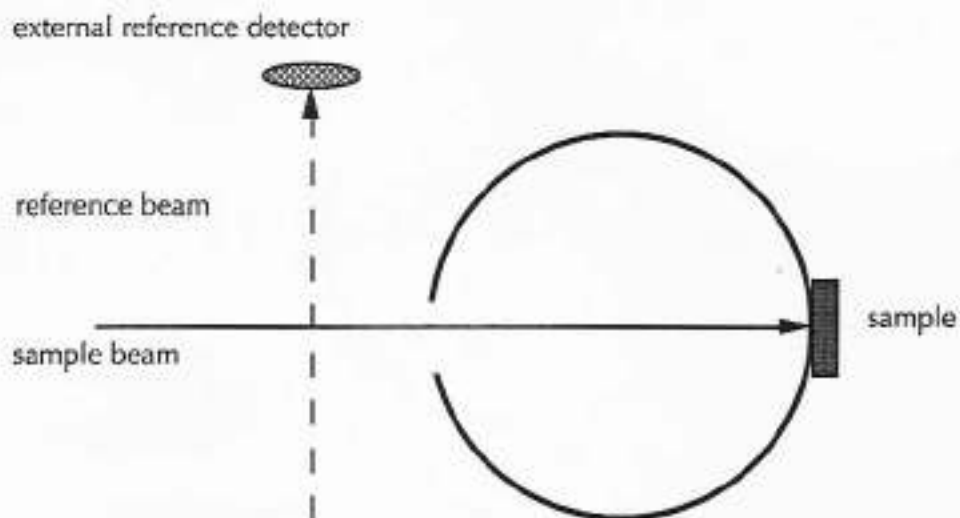
Reflectance of sample is simply ratio $I(s)/I(r)$

COMPARISON VS SUBSTITUTION MEASUREMENTS

Substitution Method - all single beam accessories, dual beam and diode array accessories.



Baseline run with reference in single port



Sample replaces reference, second measurement taken

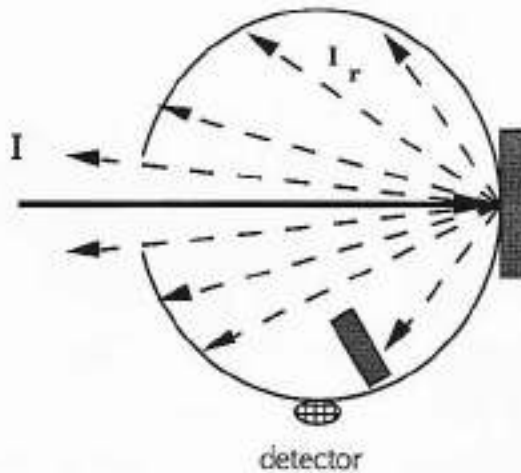
Reflectance of sample is ratio $I(s)/I(r)$ * a function called single beam substitution correction.

SINGLE BEAM SUBSTITUTION ERROR

Function of:

- Sphere Diameter
- Reflectance of Coating
- Reflectance of First Strike
- Wavelength (f reflectance)
- Port Fraction (# of holes)

SINGLE BEAM SUBSTITUTION ERROR



BASELINE

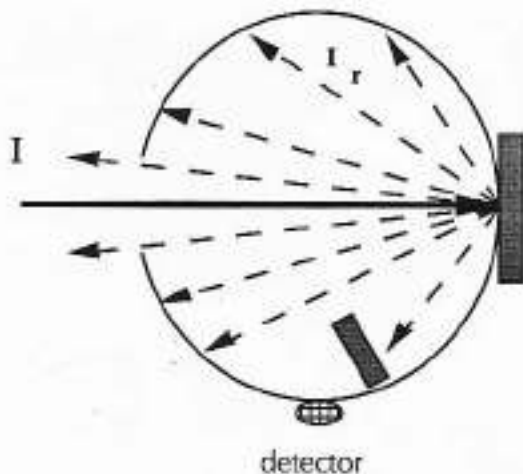
D = total flux incident on detector

$$D = f(I \cdot R_{st})f(I \cdot R_c)f(Pf)f\lambda$$

R_{st} = Reflectance of standard

R_c = Reflectance of coating

Pf = port fraction



LOWER REFLECTANCE SAMPLE

D = total flux incident on detector

$$D = f(I \cdot R_s)f(I \cdot R_c)f(Pf)f\lambda$$

R_s = Reflectance of sample

R_c = Reflectance of coating

Pf = port fraction

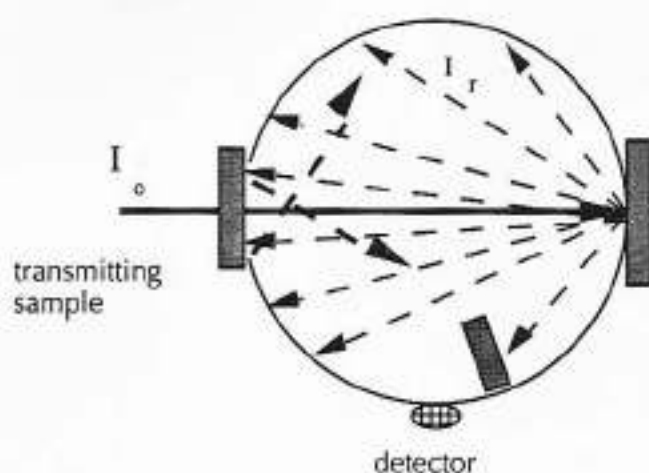
Pf decreases as ∂R of sample

Average R_c decreases with size and R_s of sample

Since R_s is $f\lambda$, then you get $\partial\lambda$ also

SINGLE BEAM SUBSTITUTION ERROR

TRANSMITTING SAMPLE



D = total flux incident on detector

$$D = f(I \cdot R_{ts})f(I \cdot R_c)f(Pf)f\lambda$$

R_{ts} = Reflectance of transmitting sample

R_c = Reflectance of coating

Pf = port fraction

Pf decreases as ∂R_{ts} of sample

Average R_c increases with size and R_{ts} of sample

Since R_{ts} is $f\lambda$, then you get $\partial\lambda$ also

Net Result is that %T is higher than actual %T !!!

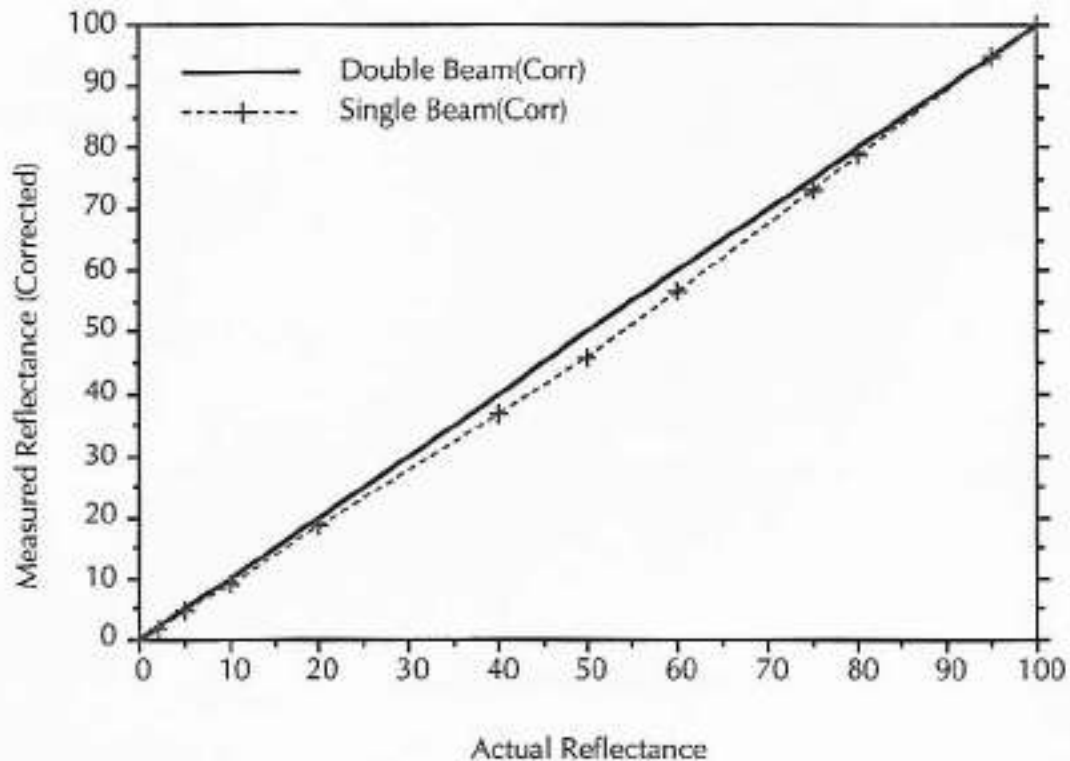
Solution: If sample is *non-scattering*, move it 5 mm. or so

in front of the port. Since R_s is f [distance from port],

$$\Delta R_{ts} \approx 0 \text{ and } D = D_{\text{trans}} \quad * \text{ transmittance baseline}$$

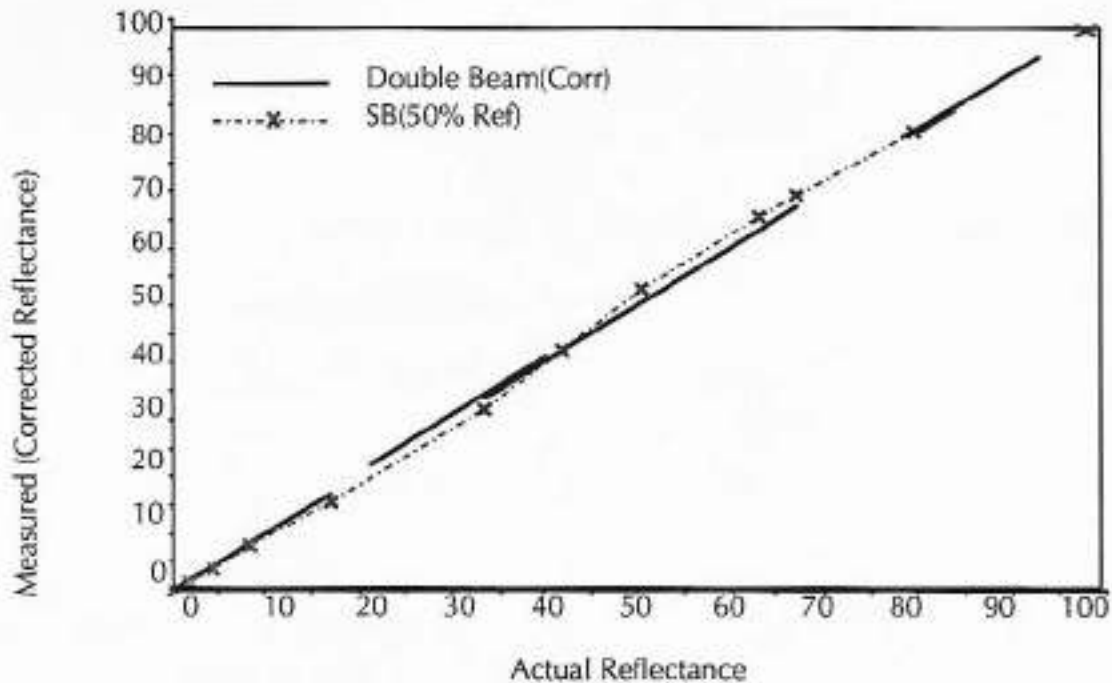
With liquid samples using cuvettes, the problem is not that severe, as the major contribution of reflectance is from the specular component of cuvette.

SINGLE BEAM SUBSTITUTION ERROR WITH 100% REFLECTOR AS REFERENCE



Using a white standard as the reference (blank), the deviation from the actual reflectance is maximum as the sample approaches 50% reflectance and is closer to the actual reflectance at both high and low reflectance values. By using a standard of intermediate reflectance, the measured reflectance of a material is closer to the actual the nearer one can approach the reflectance of the sample and reference. This allows the user to set up a series of calibration curves that allows the substitution method to approach in accuracy the comparison method.

SINGLE BEAM SUBSTITUTION ERROR 50 % REFLECTOR AS REFERENCE



Using a 50% reflectance material as a standard, the measured curve deviates from the actual less at the middle and more in nodes centering at 25% and 75%.

By making a series of reflectance curves over the wavelength range desired, an accurate measurement of reflectance using the substitution method can be developed.

LIMITATIONS OF SPHERE ACCESSORIES IN HIGH ABSORBANCE MEASUREMENTS

While sphere accessories have few limits in reflectance measurements, there are some guidelines in using a sphere for the measurement of low transmittance/high absorbance samples.

<u>Instrument Linearity</u>	<u>60 mm sphere</u>	<u>150 mm sphere</u>
3A	~3A	~2.5A
4A	~3.5A	~3A
5A	~4A	~3.5A
6A	~4.5A	~4A

These values can be slightly increased a bit using reference beam attenuation, but generally if your sample is characterized by >5-6A, a sphere is not the ideal measurement tool.

TYPES OF STANDARDS

- **Primary Standards**
- **Secondary Standards**
- **Working Standards**

PRIMARY STANDARDS

Calibrated by National Laboratories (N.I.S.T., N.P.L., etc.)

Type	Standard	Material	Range/Comment
• Diffuse Reflectance	SRM 2019x SRM 2021	White Tile Black Enamel on Steel	400-2500 nm. 250-2500 nm. (questions on accuracy >2200)
• Specular Reflectance	SRM 2003g SRM 20(?)	First surface aluminum mirror Second surface aluminum	250-2500 nm. 250-2500 nm.
• Color Reflectance	BCRA Series II	Colored enamel on steel	Produced by British Ceramic Research Association. Calibrated by N.P.L. (England). Contains 8 colors, 3 neutrals, and a difference green pair.
• Transmittance (photometric scale)	SRM 930x SRM 1930x	Neutral Density Filters	Only available up to 1 Å; SRM 930 contains 30%, 40%, and 50% T. Calibrated at five discrete wavelengths in visible region.
• Transmittance (wavelength scale)	SRM 2034y	Holmium Oxide Glass	Calibrated for 10 peaks between 240-830 nm.

x - not currently available - last available series was series e

y - not currently available, equivalent is Hoya HV-1

SECONDARY STANDARDS

Calibrated by Secondary Laboratories Using National Lab Primary Standards

Type	Standard	Material	Range/Comment
• Diffuse Reflectance	Labsphere SRS	Proprietary Thermoplastic	250-2500 nm - Available as white and Grey Scale
	Tiles	Ceramic or Ceramic on Metal	Generally Visible(color) range only
	Russian Opal	Diffuse White Opal Glass	Visible (color range)
• Specular Reflectance	Labsphere SRS	First surface aluminum mirror	300-2200 nm NRCC traceable
		First or second surface mirrors	Calibrated Mirrors(customer provided) calibrated by NRCC, NIST(formerly)
• Color Reflectance	BCRA Series II	Colored enamel on steel	Produced by British Ceramic Research Association Calibrated by secondary lab such as Hemmendinger Color Labs or Labsphere. Range 360-830 nm.
	Labsphere CSS	Pigmented Thermoplastic	Range 360-830 nm. Highly diffuse (non-glossy) Set contains 7 colors, 3 neutrals, and a wavelength calibration standard.
	Erie Ceramics	Enamel on Steel	As calibrated- Glossy - Similar to BCRA's without cachet of National lab approval.
• Reflectance	Labsphere WCS	Rare Earth Oxide Doped Spectralon	250-2500 nm Erbium,holmium, or dysprosium oxide in Spectralon
• Transmittance (photometric scale)	Neutral Density Filters		Colored Glass for Visible Range; Metal on glass or quartz for VIS-NIR or UV-VIS-NIR respectively. Range as calibrated
• Transmittance (wavelength scale)	Holmium Oxide Glass Didymium Glass		Calibrated versus NIST filter As with Holmium Oxide Glass/Broader Peaks

WORKING STANDARDS

Generally calibrated in -house versus primary or secondary standards

<u>Type</u>	<u>Standard</u>	<u>Comments</u>
• Diffuse Reflectance	Labsphere Spectralon	Durable, diffuse, wide spectral range, flat reflectance. Wide range of Reflectance Standards available. Not suitable for use around non-polar solvents or contaminants.
	Packed PTFE Powder	Well characterized, high reflectance over wide spectral range, very diffuse Fragile, reflectance dependent on packing density, manufacturer of resin. Attracts dust through static charge.
	Packed Barium Sulfate	Classic standard, diffuse, fairly stable but fragile. Reflectance extremely dependent on quality of BaSO ₄ . Best is Eastman-Kodak 6091 White reflectance standard.
	Tiles	Durable, glossy, stable, but usually limited range
• Color	Russian Opal	Limited range white standard. Very white but easily (and irreversibly) contaminated. Relatively expensive.
	Munsell Papers	Limited range but wide variety of reflectances. Easily damaged but quite inexpensive. Translucency a negative.
	Labsphere Spectralon CSS Color standards	Same advantages as Spectralon reflectance standards. Less thermochromic than tiles, enamels, plastic plates. Not as spatially uniform when very small areas ($\leq 4 \text{ mm}^2$).
	Colored Glazed Tiles	Very stable; glossy, thermochromic
	Colored Plastic Tiles	Wide variety of available colors; Translucent, Calibrated at 45°/0° geometry.
	Munsell Papers	Wide variety available as both glossy and matte. Have problems inherent with paper standards - sensitive to moisture, bending, creasing, translucent. Don't age well unless very well cared for.

Comments

First surface aluminum or Gold on glass (for IR) are easily scratched, Second surface mirrors present some geometry problems.

Useful for calibration of spectrophotometer wavelength scale in reflectance mode. Consist of rare earth oxides (erbium, holmium, or dysprosium oxide in Spectralon.

Colored glass for visible range; Metal on glass or quartz for VIS-NIR or UV-VIS-NIR respectively.

Hoya HY-1 filter for spectrophotometer wavelength scale calibration in transmittance

As with Holmium Oxide Glass/Broader Peaks

Standard

Calibrated Mirrors

Labsphere WCS Rare Earth Oxide Doped Spectralon

Neutral Density Filters

Holmium Oxide Glass

Didymium Glass

Type

• Specular Reflectance

• Reflectance (wavelength scale)

• Transmittance (photometric scale)

• Transmittance (wavelength scale)

Instrument or Method Standards

Materials of known reflectance or transmittance that are physically/environmentally stable can be used to check instrument accuracy for a particular measurement or technique. These can range from anything from "standard" paper to standard solutions to a standard culture plate. If it is reproducible, it can be used as a standard.



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