Measurement of Low-Level Infrared Reflectance

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Outline

I. Introduction – Infrared Spectrophotometry at NIST

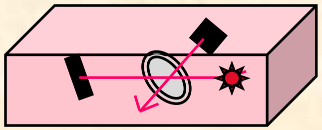
II. Infrared Integrating Sphere Reflectometer

III. Low Level Reflectance; Materials, Detectors, and Cavities

IV. Conclusions

NIST Infrared Spectrophotometry Program Overview

FT-IR Spectrometers



IR Lasers

Measurement Methodologies

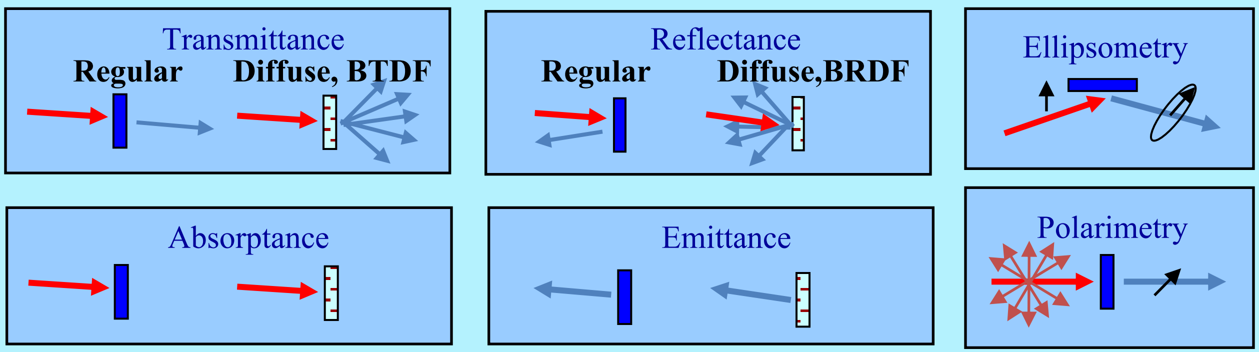
- Modeling Instruments & Methods
- Error Sources Evaluation
- Absolute Methods ρ, τ, α, ε

Specialized Accessories

- Integrating Spheres
- Goniometer & BRDF
- Cryostats & Heaters
- Radiance Comparator
- Cavity Reflectometer

Materials, Coatings, Optical Components, Cavities & Detectors

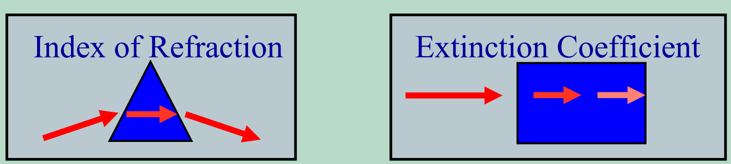
Direct Measurements & Properties



Support Mechanisms

Calibration Service
Physical Standards
Inter-Comparisons
Reference Data
Short Courses

Additional Quantities



Support Communities

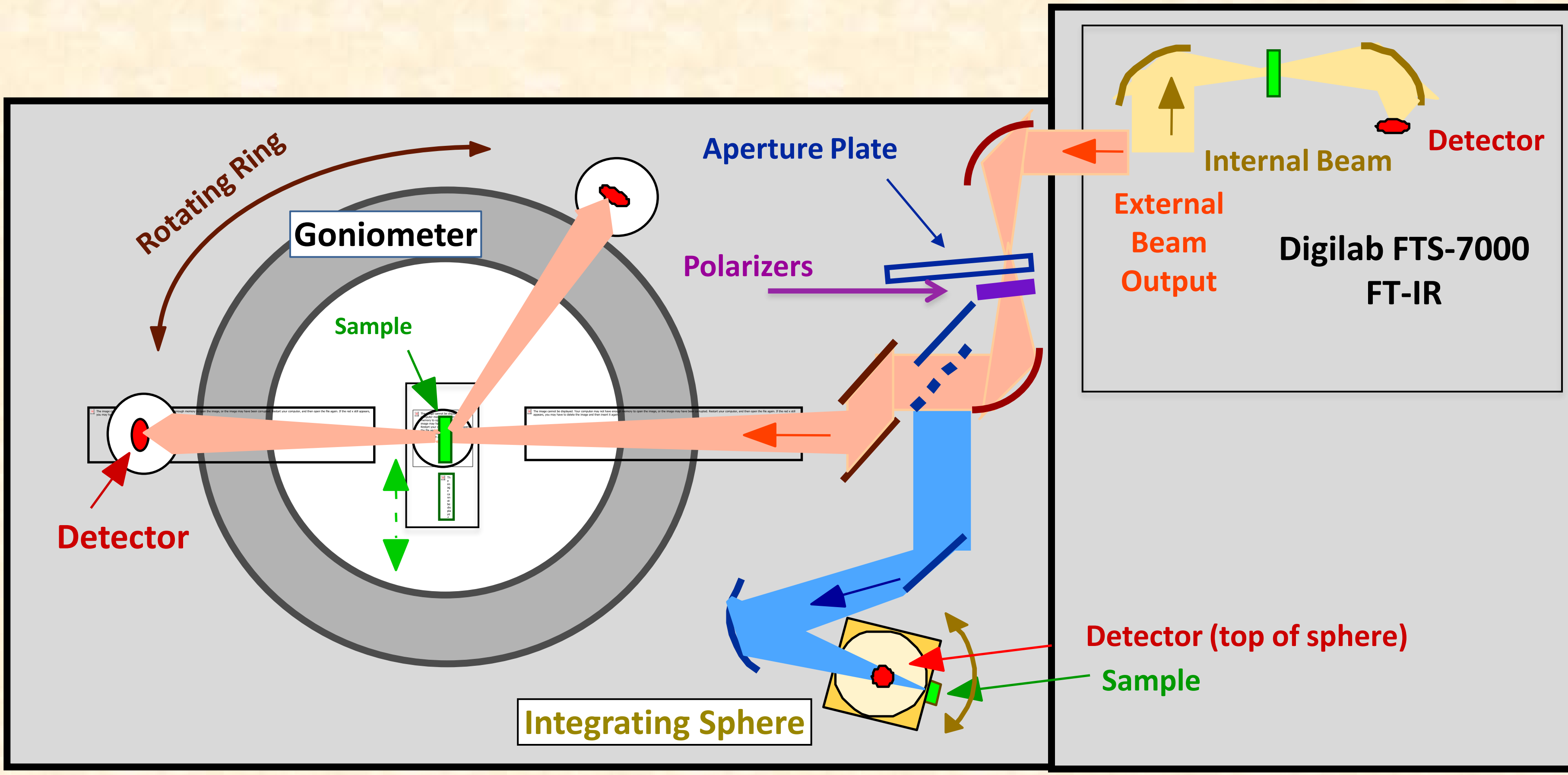
External:	**Internal:**
Industry	Detectors
Government	Sources
Academia	Materials

Applications Requiring Low-level Reflectance

- **Blackbody and Radiometer Cavity Coatings**
  - **Improve to ideal behavior: Planck Radiator - 100% absorbing absorber**
  - **Also reduce/eliminate reflection effects: e.g. ambient background reflection for BB**
- **Detectors Coatings**
  - **Provides greater efficiency**
  - **Reduces errors related to detector reflection**
  - **Is required for detectors used in absolute mode and as standards***
- **Baffling**
  - **Required for elimination of stray light effects**
  - **Diffuse /specular behavior is design factor**
- **Blackbody and Radiometer Cavities**
  - **Very low level (10^{-3} to 10^{-5})**
  - **Alternative to measuring emissivity**
  - **Requires modifications to standard sample measurement device**

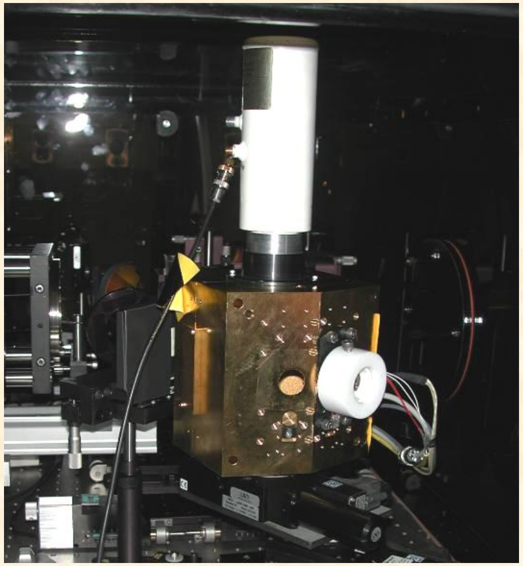
** "A Very Black Infrared Detector from Vertically Aligned Carbon Nanotubes and Electric-field Poling of Lithium Tantalate," J. Lehman, A. Sanders, L Hanssen, B. Wilthan, J. Zeng, C. Jensen, accepted for publication in Nano Letters*

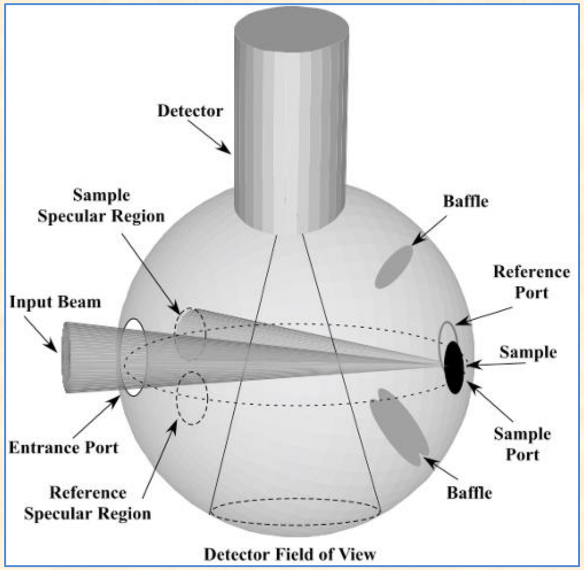
IR Spectrophotomtry System with Goniometer and Integrating Sphere

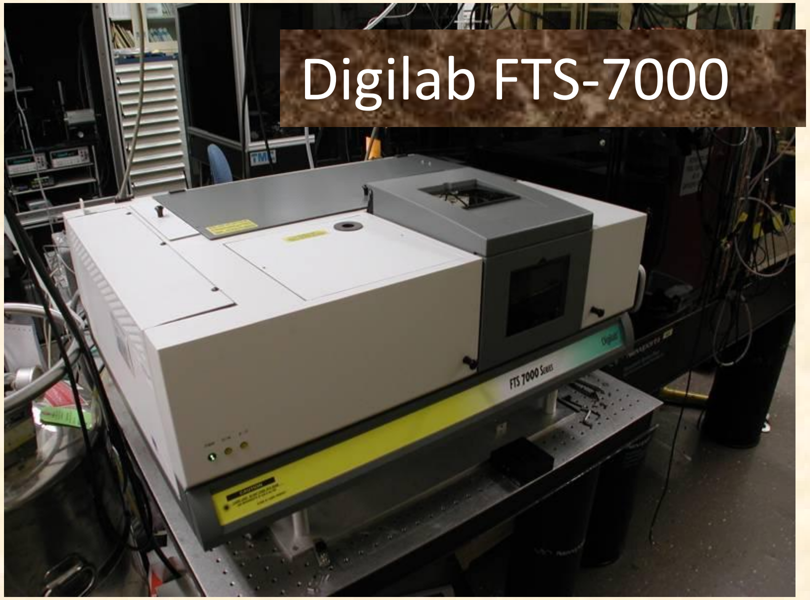


Optical Tables w/ Purged Enclosures

Infrared Reference Integrating Sphere (IRIS) System







FTIR/System Specifications

- λ range: 0.8 - 50 μm
- highest resolution: 0.5 cm^{-1}
- purge for FT and all instrumentation
- high stability and repeatability
- external beam to multiple instruments
- step-scan mode for specialized operation

Sphere Specifications

- λ range: 1.0 – 18.5 μm
- 6 inch diameter
- Gold-plated plasma-sprayed metal coating
- MCT detector w/ concentrator optics
- Spot size 2 - 10 mm
- 8° incidence angle

System Capabilities

- Reflectance, Transmittance, Absorptance & Emittance
- Temperatures 15 - 200 °C
- absolute & relative, specular & diffuse
  - R & T direct
  - A & E indirect
- uncertainties (2σ):
  - specular: ≤ 0.3%
  - diffuse: 1.5 - 3.5%
  - larger for angle dependent structure
- can measure R of transparent samples
- can sort out scatter from total R & T

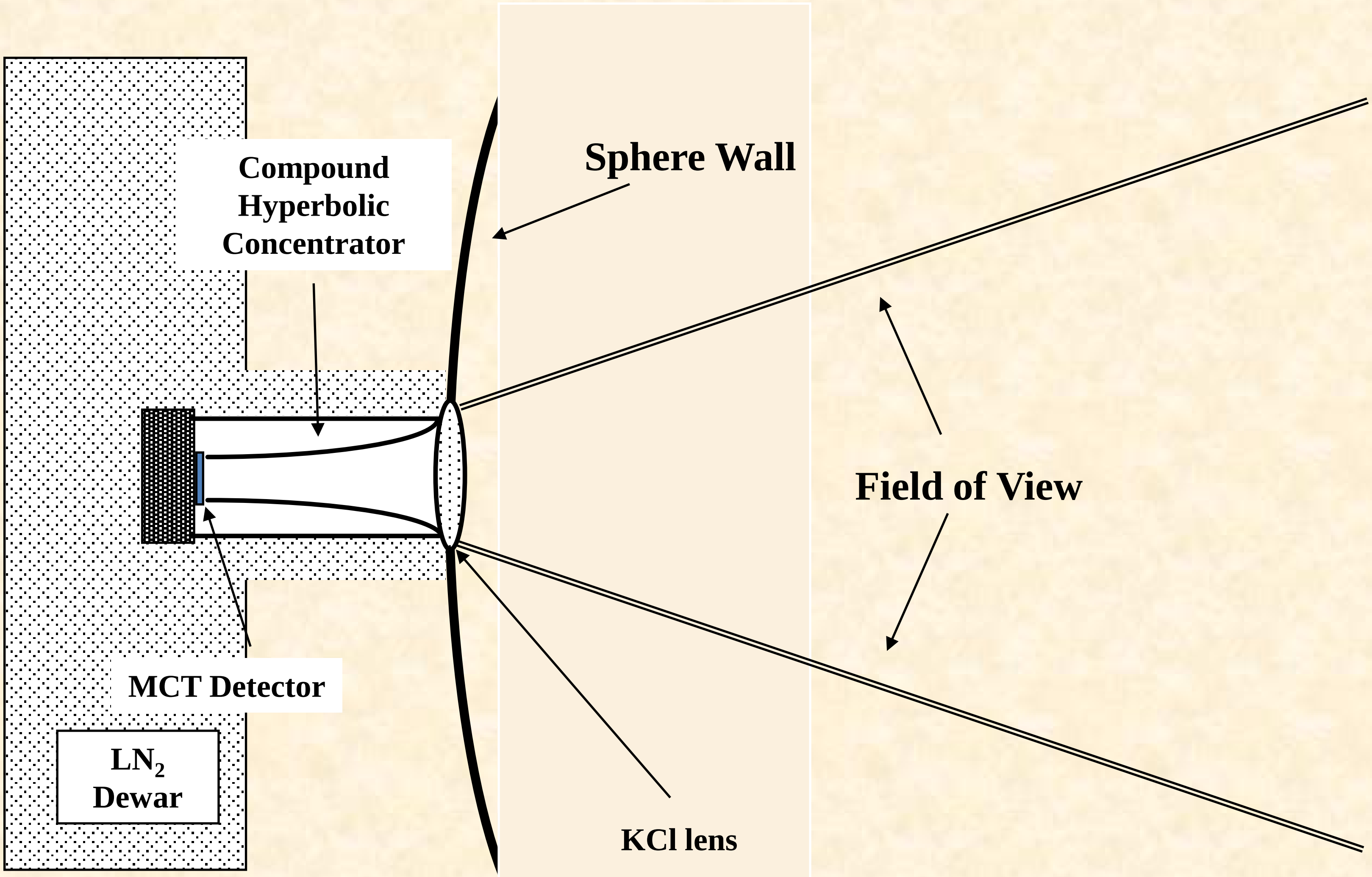
IRIS Features

- Large area MCT Detector with compound hyperbolic concentrator / lens for high throughput
- Gold-coated plasma-sprayed copper sphere coating – close to Lambertian
- Symmetrical design for sample and reference measurements
- Dual rotation stages enables transmittance and reflectance measurements
- Compensating wedge enables separation of diffuse and specular components
- Absolute method developed for “diffuse” reflectance – involves only directly measured results – not theory
- Sample heater allows sample temperatures from 10 °C to 200 °C
- Automated measurement system enables frequent repeats to eliminate drift error and maximum total measurement time (26 – 30 hrs).
- External aperture selection

Important for Accurate Low-level Measurements

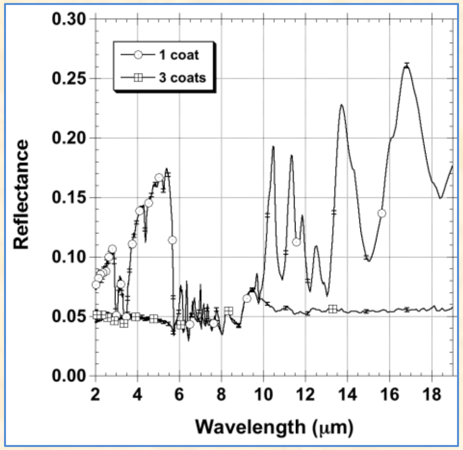
- **Instrumentation:**
  - Optimized throughput to maximize signal
  - Low scatter optics to minimize "dark signal"
  - Spectrometer design features – e.g. FTIR scan not dependent on finding Interferogram Center for sample measurement.
  - Ability to measure over extended time periods – automation
  - Operate non-linear detectors in linear regime; use low R reference
- **Measurement Process:**
  - FTIR: Use "stored" or reference phase spectra to correct sample interferograms
  - Measure port overfill to correct sample measurements

Sphere Detector Arrangement – High Efficiency

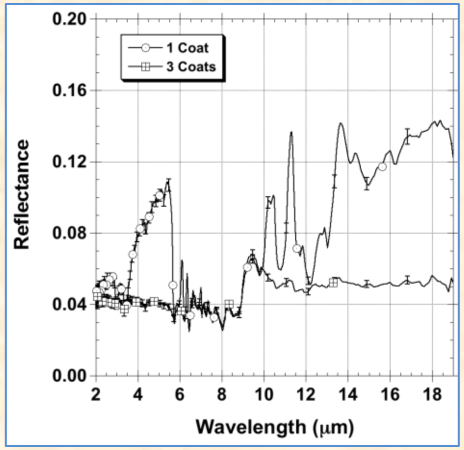


- The non-imaging concentrator enables the detector to obtain signal equivalent to complete hemispherical collection

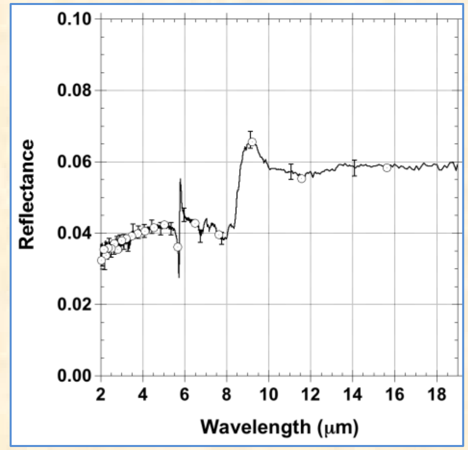
Black Paint Examples



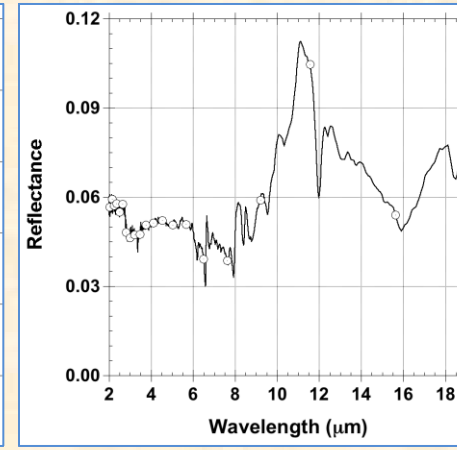
Aeroglaze Z-302



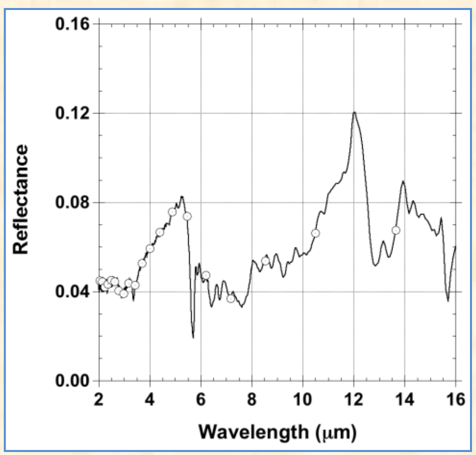
Aeroglaze Z-306



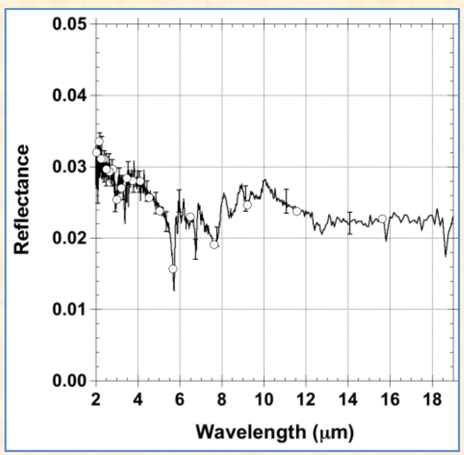
Krylon Black



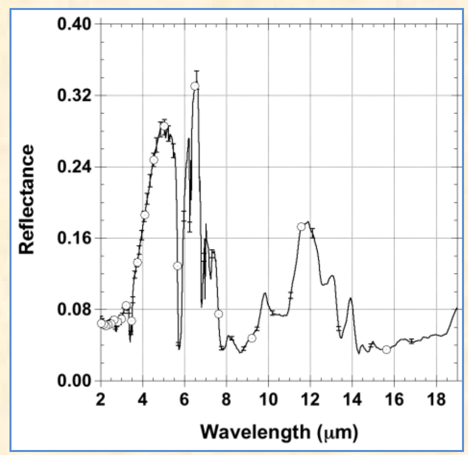
Stycast Epoxy



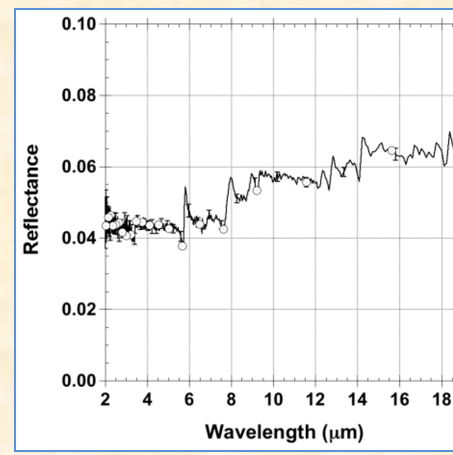
Awlgrip



Senotherm

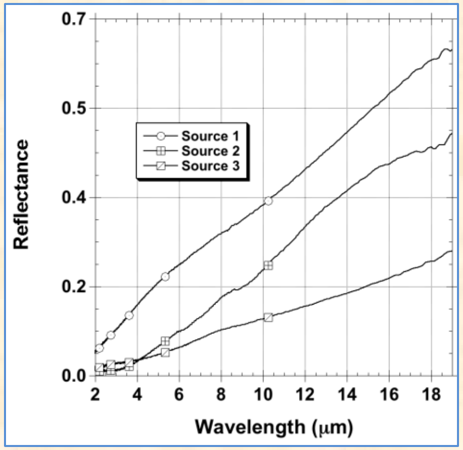


Zynolite

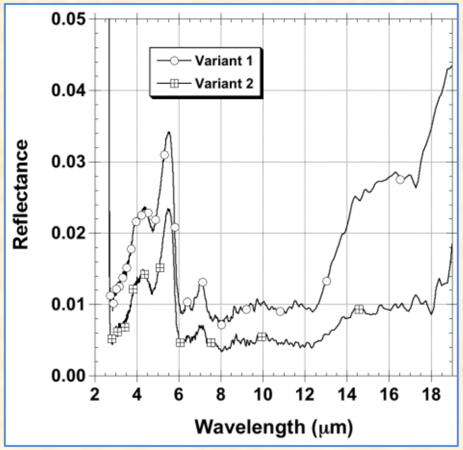


Testors Black

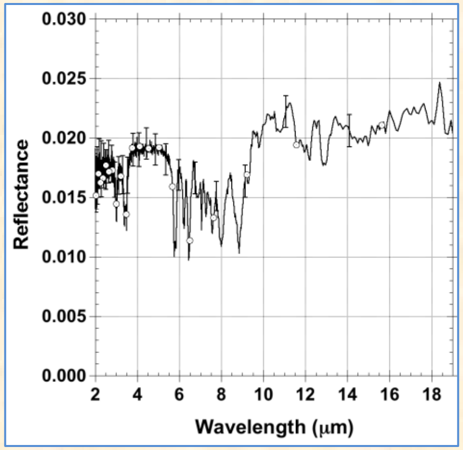
Black Surface Examples



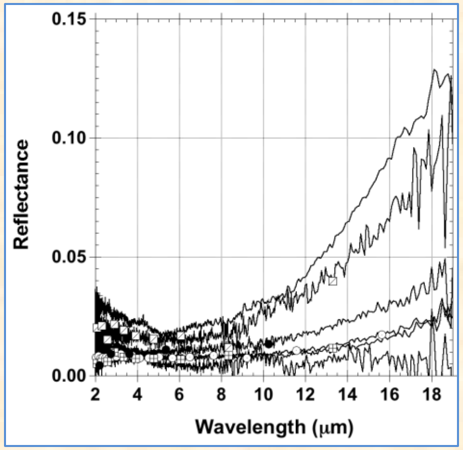
Nickel Phosphorous



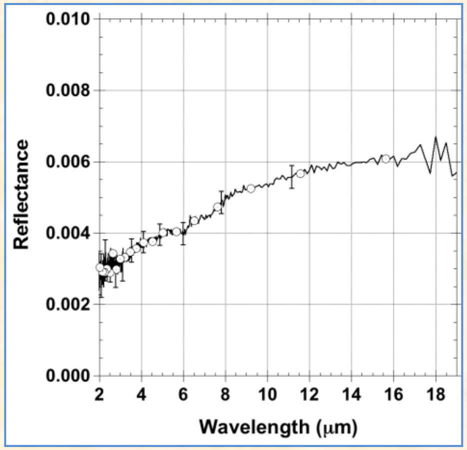
Enhanced Martin Black



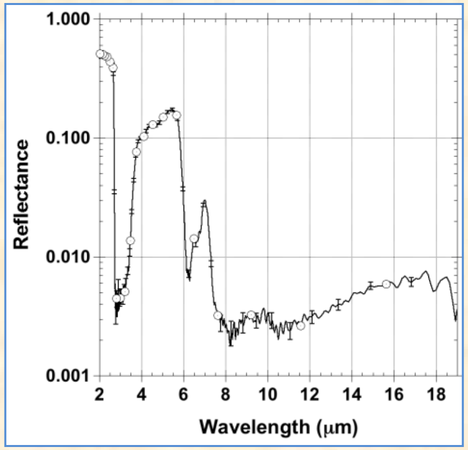
Ultra-Pol Cloth



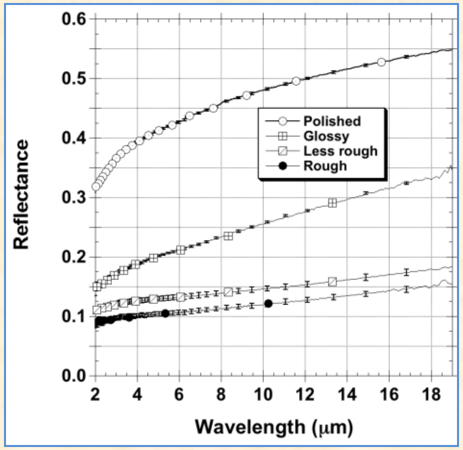
Gold Black Series



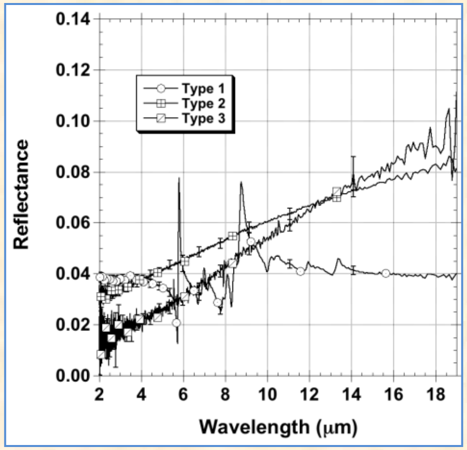
ESLI Vel Black



Deep Sky Black

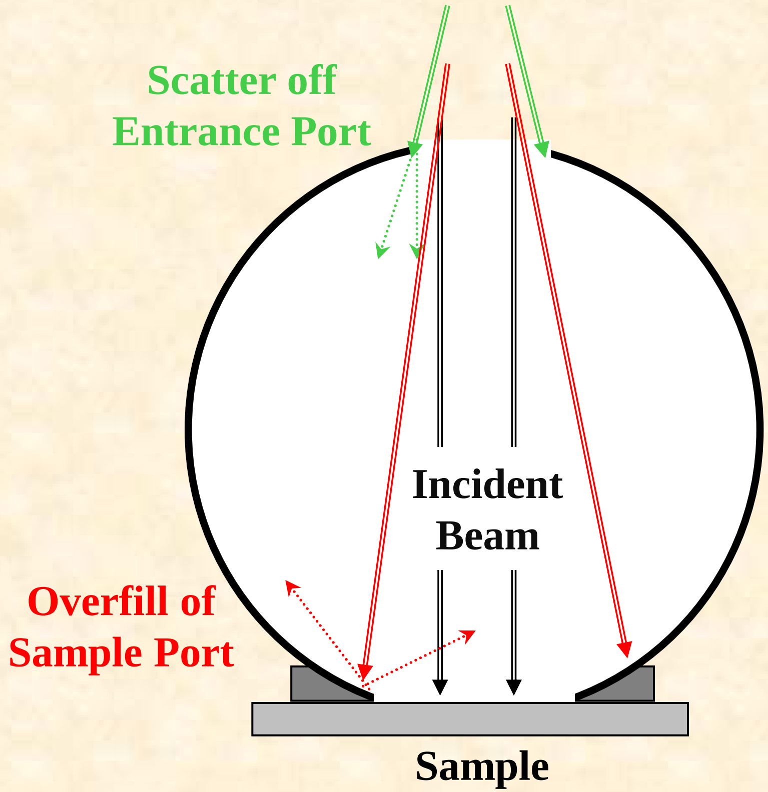


Graphite Series



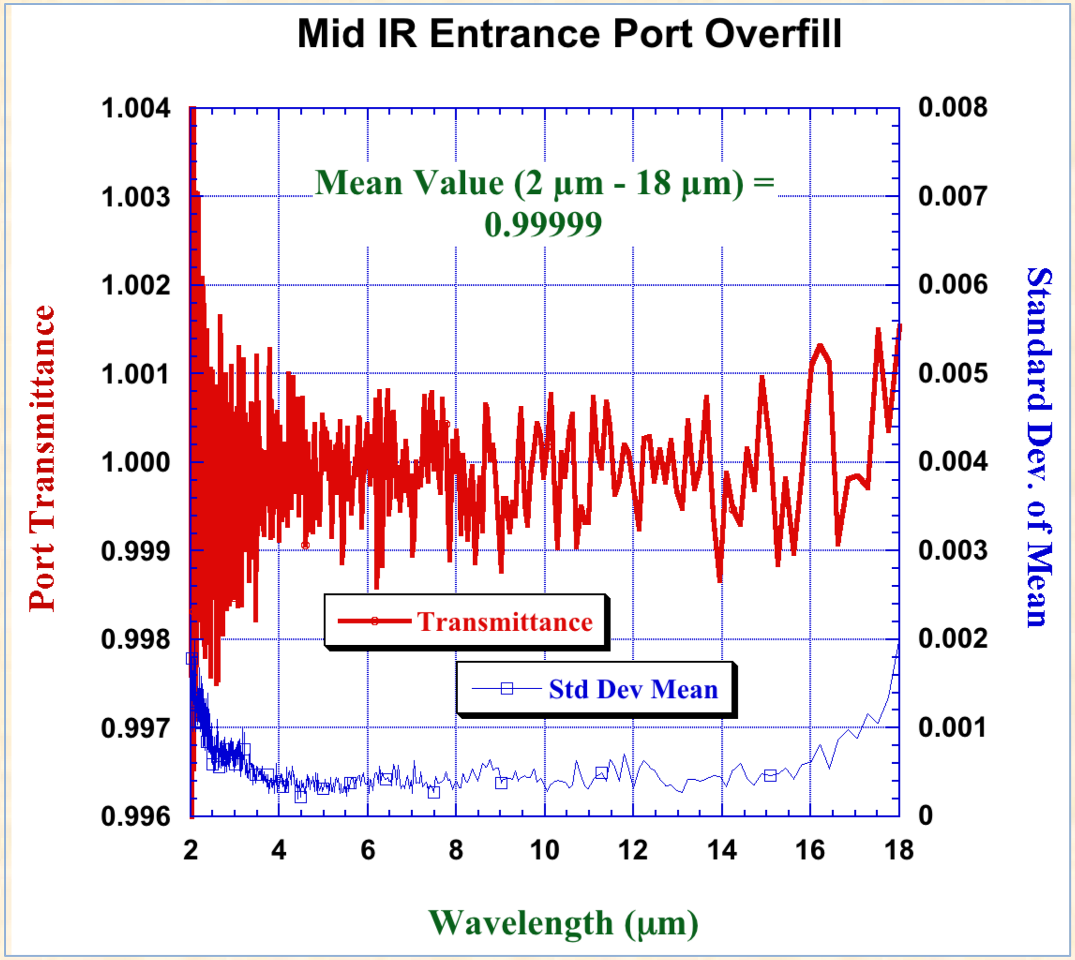
Carbon Nanoparticles

Error Source: Scattered Light in Input Beam

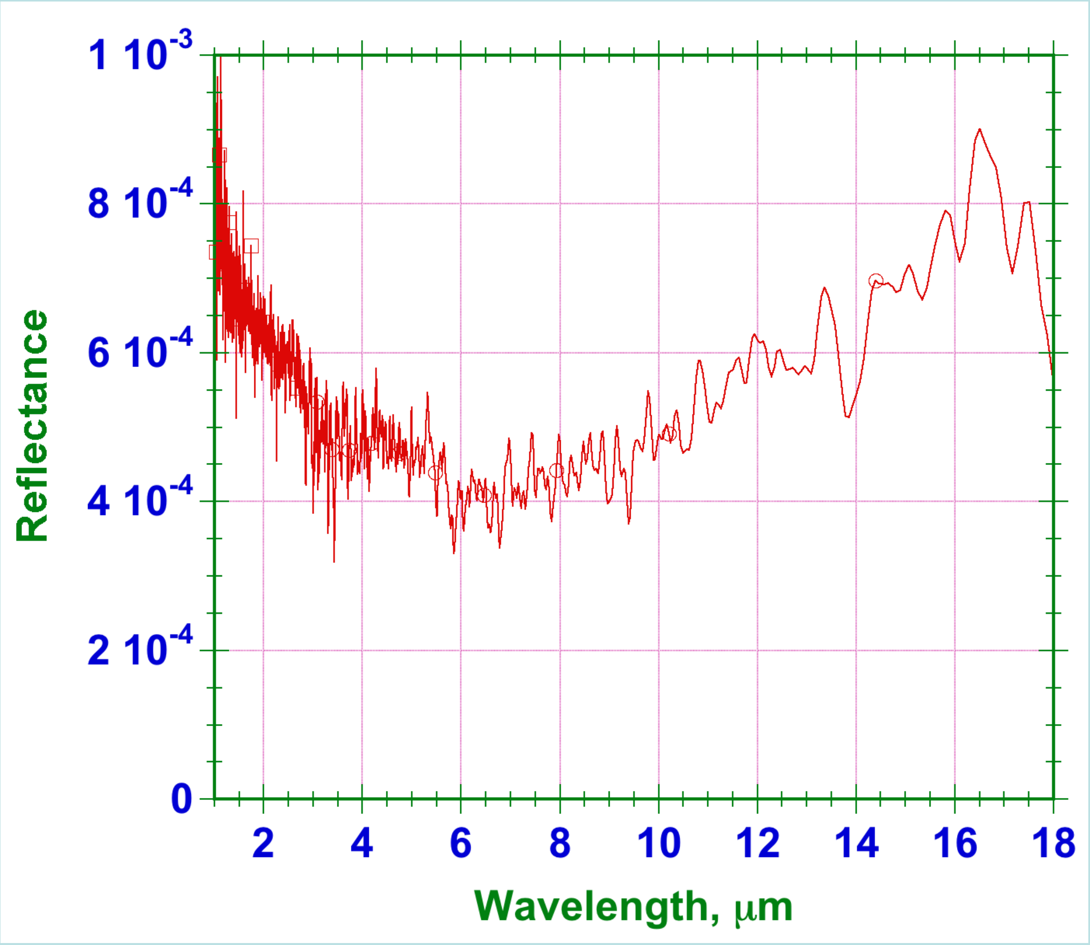


- Scattered light in input beam overfills entrance port; small amount of scattered light may scatter off edge of entrance port & contributes to sample/reference measurement. Measurements performed – negligible < 10^{-4}
- Scattered light in input beam overfills sample/reference port, – contributes to sample/reference measurement.

Error due to Entrance Port Overfill: Transmittance of Aperture Matched to Entrance Port



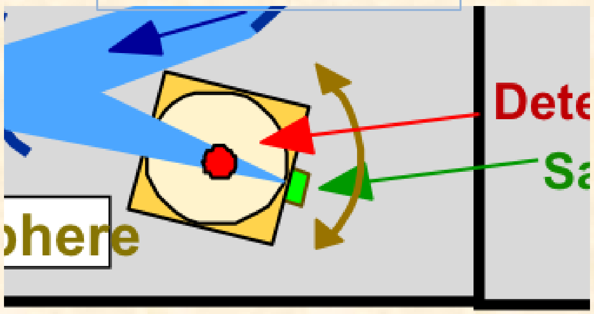
Error due to Sample Overfill: Empty Sample Port 'Reflectance'



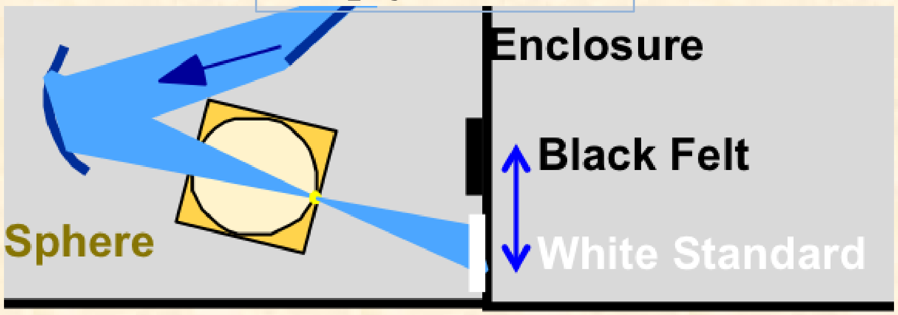
- 16 cm-1 resolution, 24 hr, repeated 24 times

Empty Port "Reflectance" Measurement: Component due to Enclosure Reflection

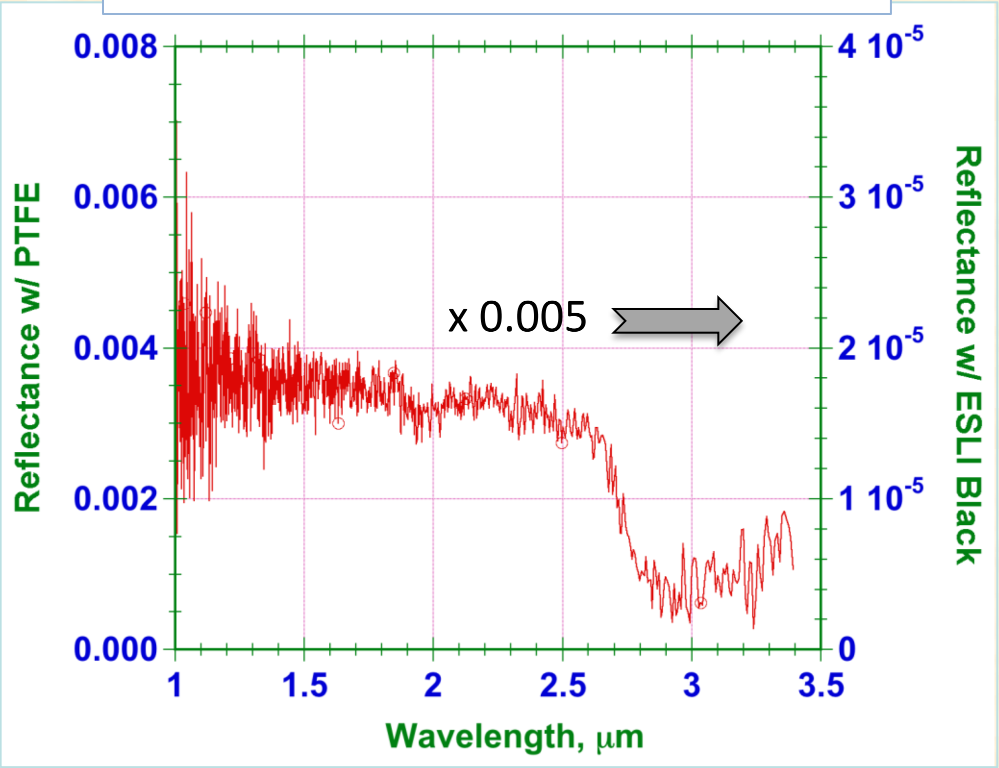
Standard Setup



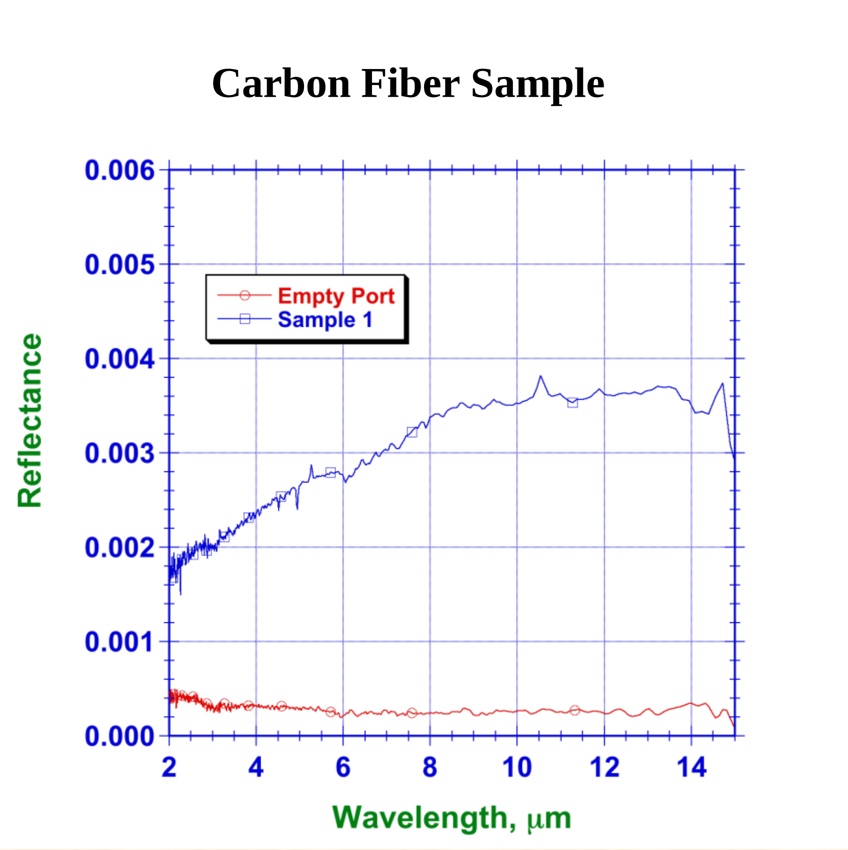
Empty Port Test

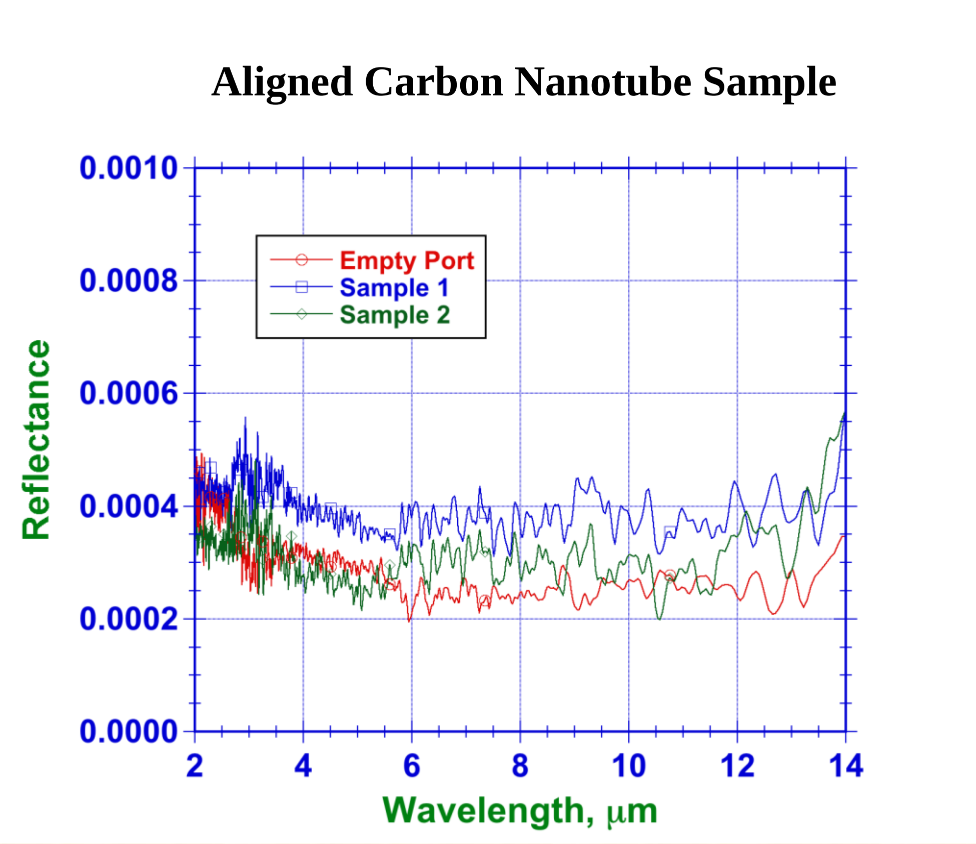


Result with PTFE Standard on Wall

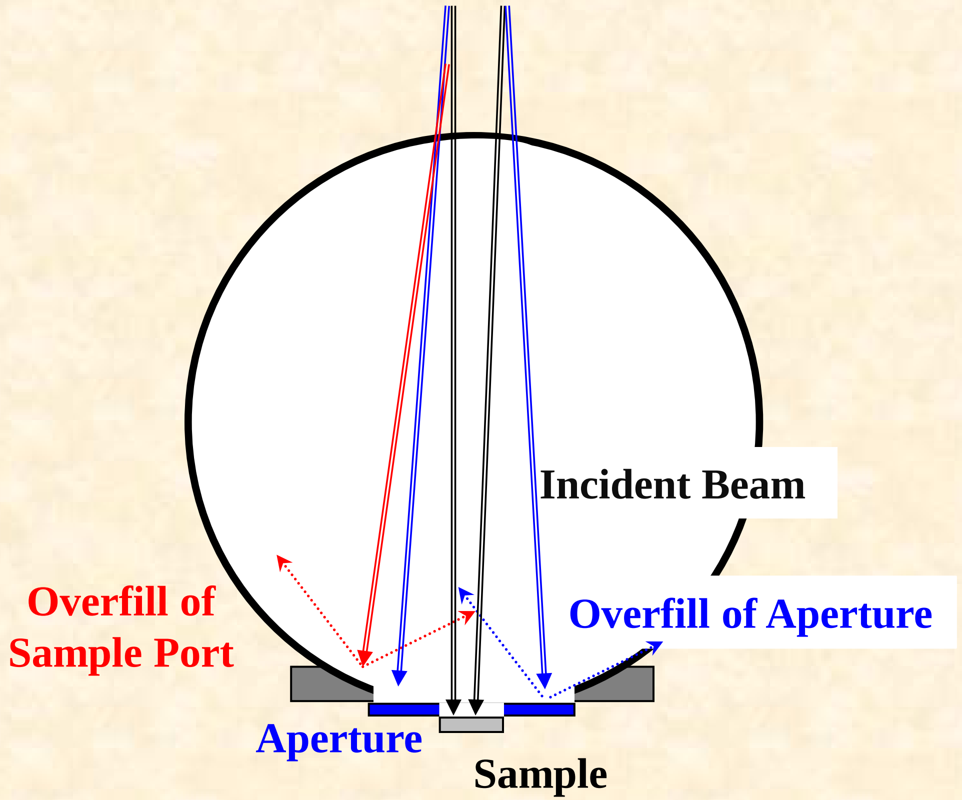


Extreme Examples: Black Carbon Samples





Small Sample (Detector) Case: Use Gold & Black Apertures

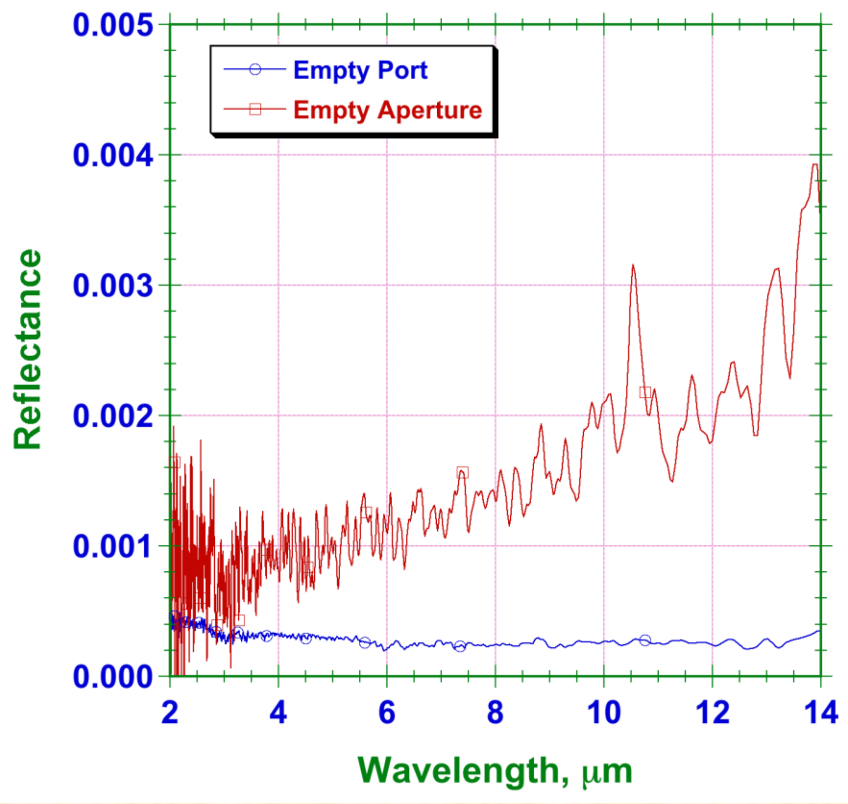


- Gold Aperture to quantify overfill of sample
- Black Aperture in final sample measurement to reduce contribution & residual error.

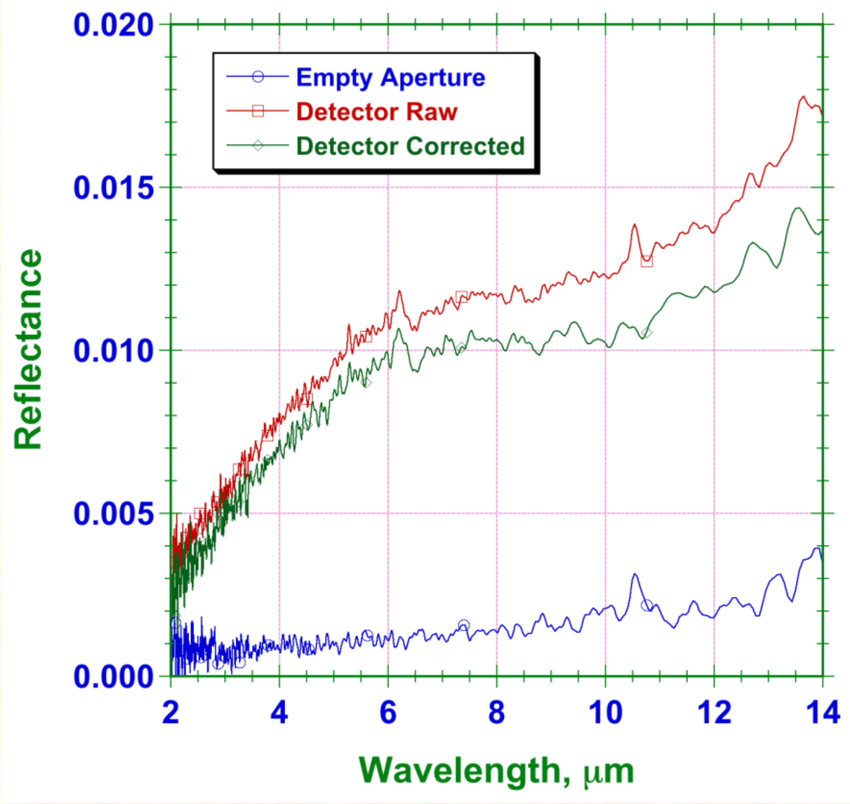
$$r_s = F_{diff} \frac{V_s - V_{ep} - \frac{r_{ba}}{r_{ga}}\left(V_{ea} - V_{ep}\right)}{V_r}$$

Results for Black Detector w/ Carbon Nanotube Coating

Sample Overfill Measurements
(8 mm aperture)



CNT – Coated Pyroelectric Detector



Complete Hemispherical Laser-Based Reflectometer for Cavities – Radiometers and Blackbodies

Cavity Reflectance Measurement Characteristics:

- Low reflectance levels: 10^{-3} to 10^{-6}
- Reflection primarily in near-retro direction – normal to cavity aperture
- Not suitable for typical IR spheres (large entrance aperture) and spectral measurements (low S/N ratio)
- Can be polarization sensitive – for specular trap designs

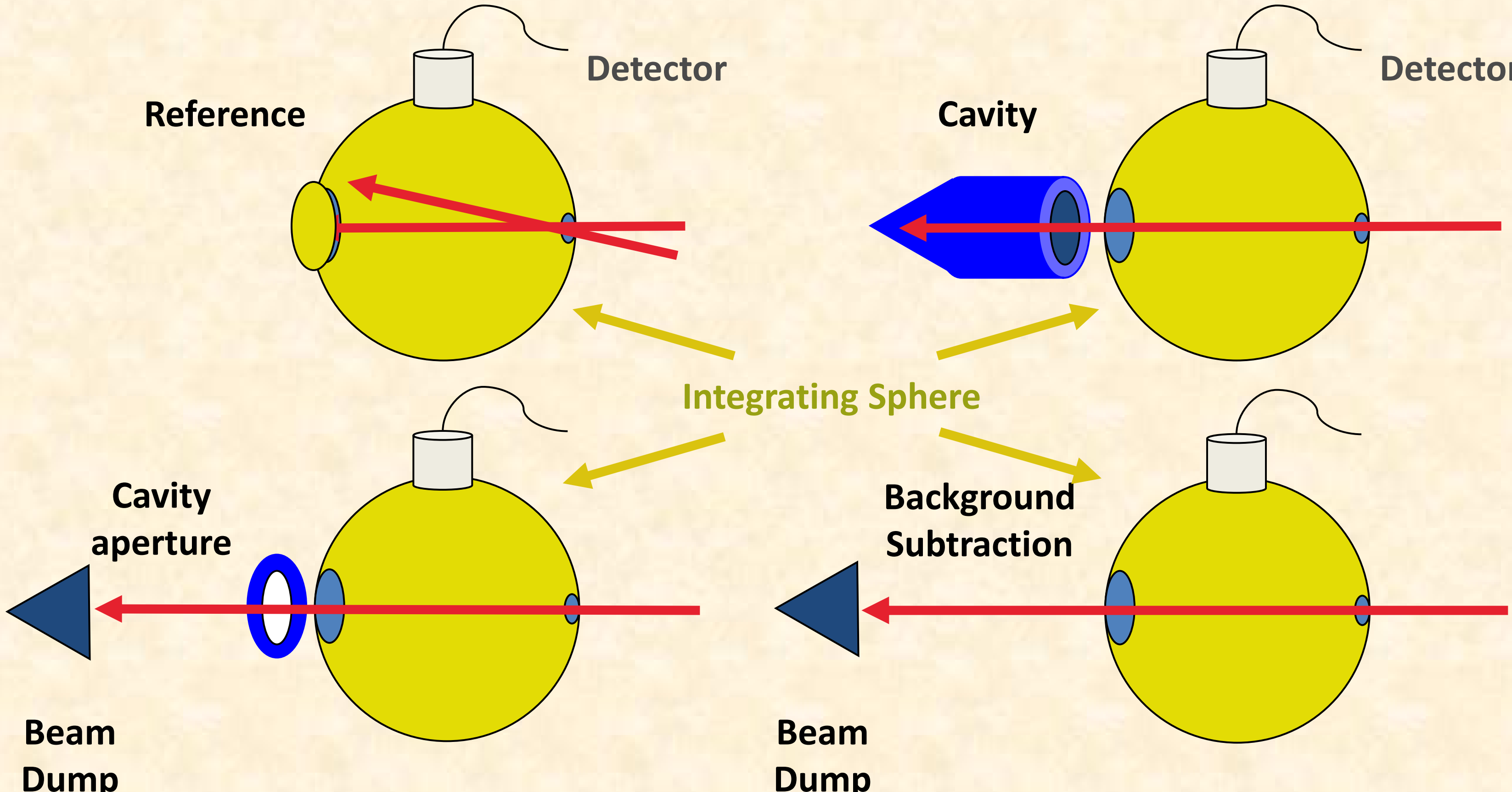
CHILR Special Features:

- Laser sources enable high power for good S/N ratio and small beam (1.5 mm to 2.5 mm)
- Small sphere entrance aperture (6 mm dia. Vs. Sphere 20 cm dia.) => minimal loss of cavity reflectance
- High stability/low drift lasers

CHILR Specifics:

- Laser sources: 10.6 µm, 5 µm, 4 µm, 1.55 µm, and 1.32 µm
- Detectors: MCT, pyroelectric and InGaAs;
- Motorized stages used to manipulate sphere and cavity
- Can map spatial uniformity & angle dependence
- Can measure reflectance down to approx. 10^{-5} (equivalent to emissivity 0.99999)
- Reflectance expanded uncertainties currently 10 - 20% for 10^{-3} to 10^{-5} range

Schematic of CHILR* Measurement Method



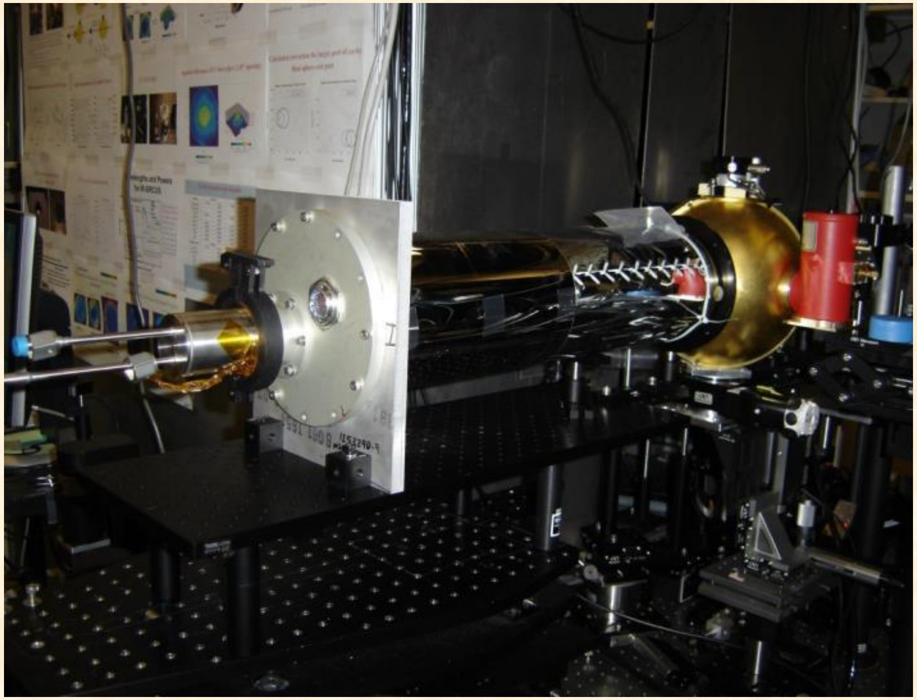
$$R = \frac{V_{sc} - V_{ap}}{V_r - V_{back}} R_r$$

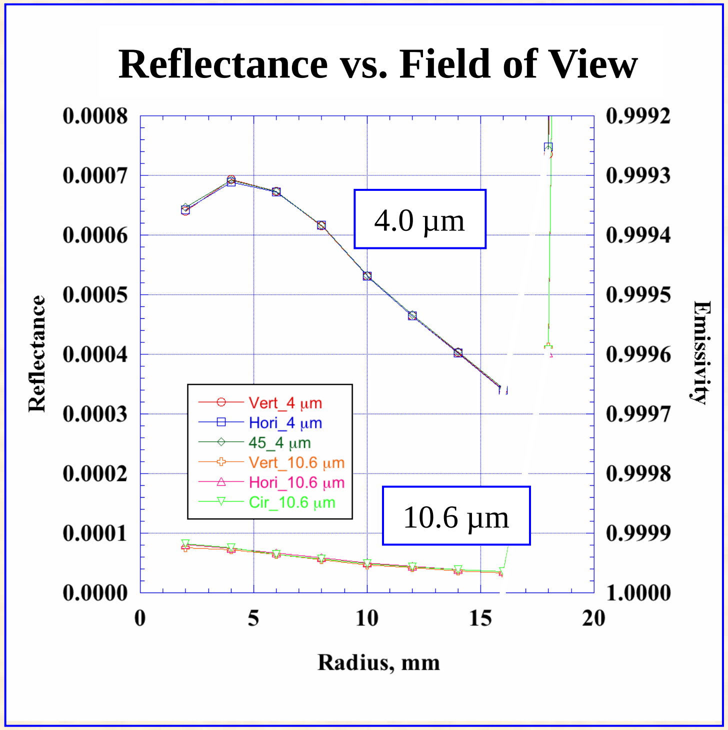
$$E = 1 - R$$

*Complete Hemispherical Infrared Laser Reflectometer

Example: CHILR Reflectance of Inverted Cone Design Blackbody with Z-302 Specular Coating

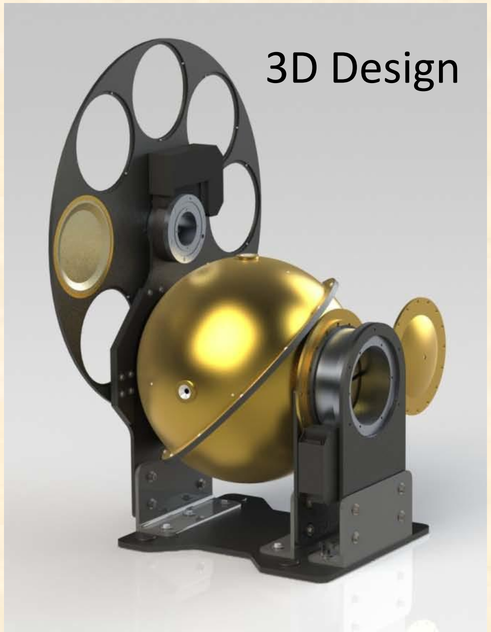
Low Temperature Blackbody Source

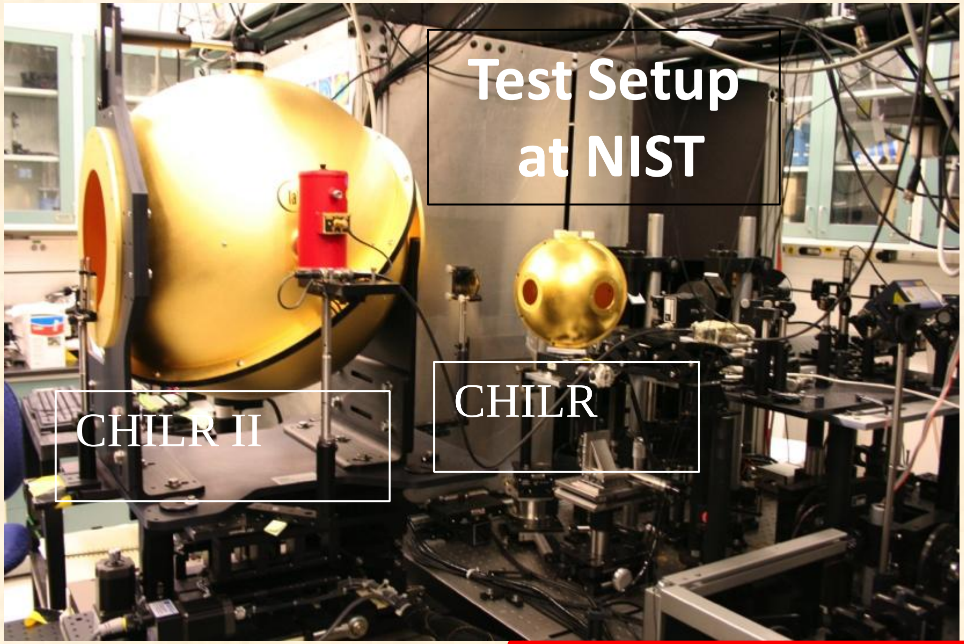




- **Cavity reflectance at 4 µm approx. 10 x that at 10.6 µm**
- **Likely explanation:**
  - **other Z-302 paint samples show increased diffuse component at 4 µm compared to 10.6 µm.**

CHILR* II for Large Aperture Blackbodies





Basic parameter	CHILR I	CHILR II
Sphere diameter	8 in dia.	20 in dia.
Input port	6 mm dia.	10 mm × 4 in slot
Collection port	2 in dia.	8 in dia.
Detector port	0.5 in/2 in dia.	0.5 in/0.5 in dia.
Coating	Infragold – “like”	Diffuse Gold – Good BRDF
Maximum BB Aperture	2 in. (1 in. w/o correction) dia.	8 in. dia.

Conclusions

- **NIST has established capabilities for the accurate measurement of low level infrared spectral reflectance of samples, including detector elements, down to the 10^{-4} level.**

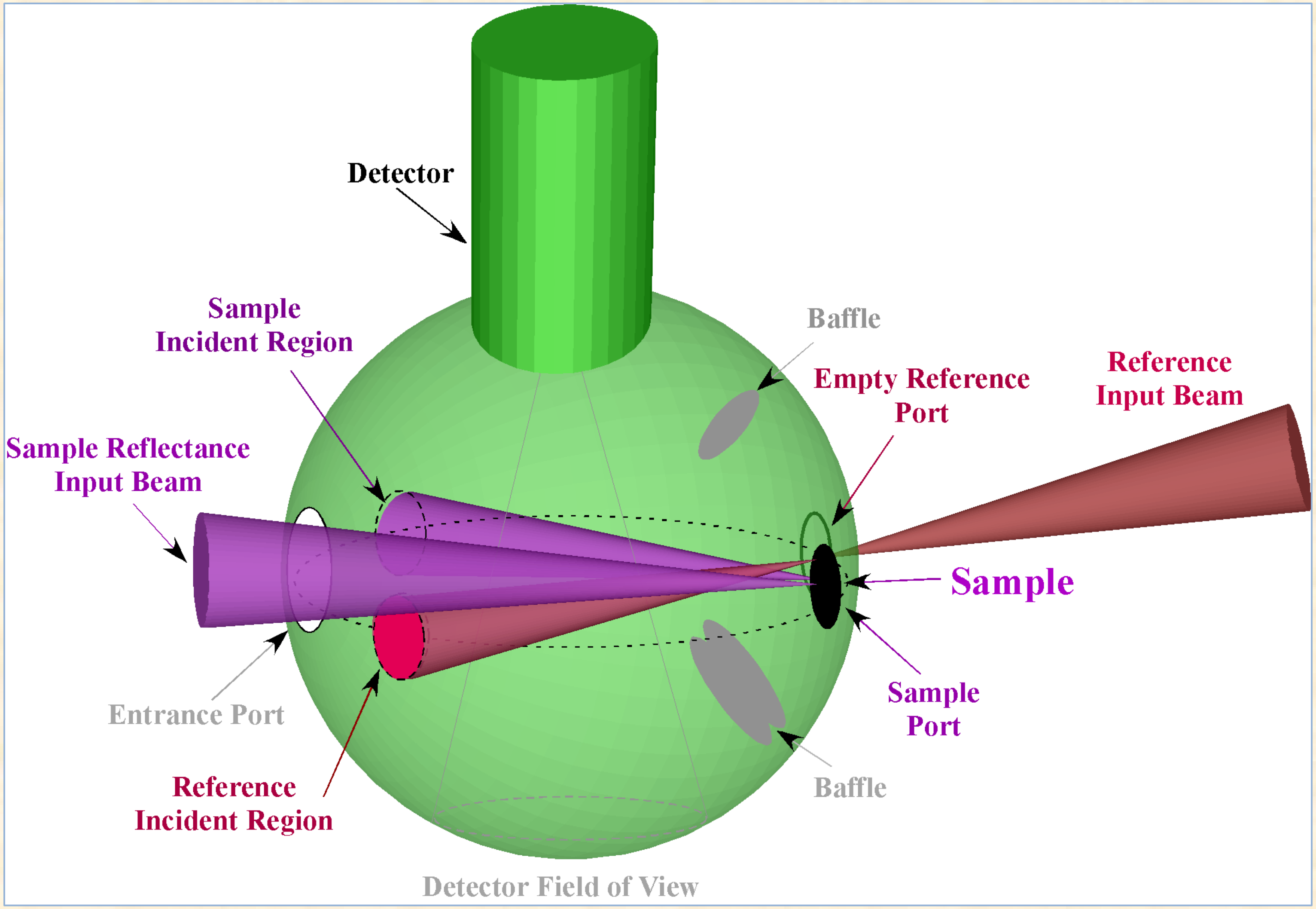
- **NIST has established capabilities for the accurate measurement of low level laser–based infrared reflectance of blackbody and radiometer cavities to the 10^{-5} level.**

- **Sources of error including stray light need to be evaluated and accounted for.**

- **These measurement capabilities help to support the development of improved coatings, as well as the baffling, detectors, blackbodies and radiometers that they are used for.**

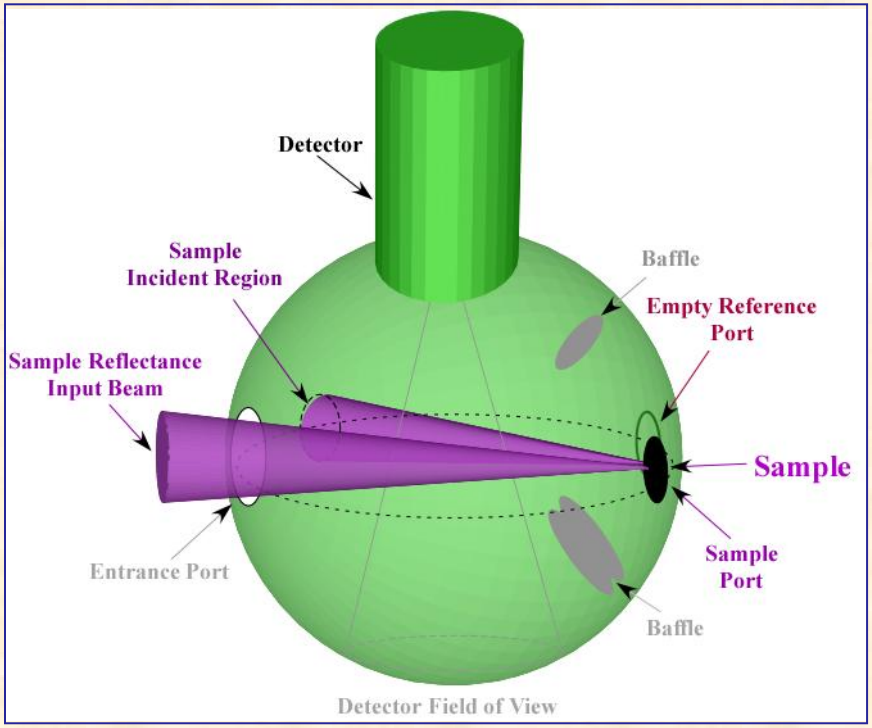
Back Up Slides

Reflectance Measurement Geometry



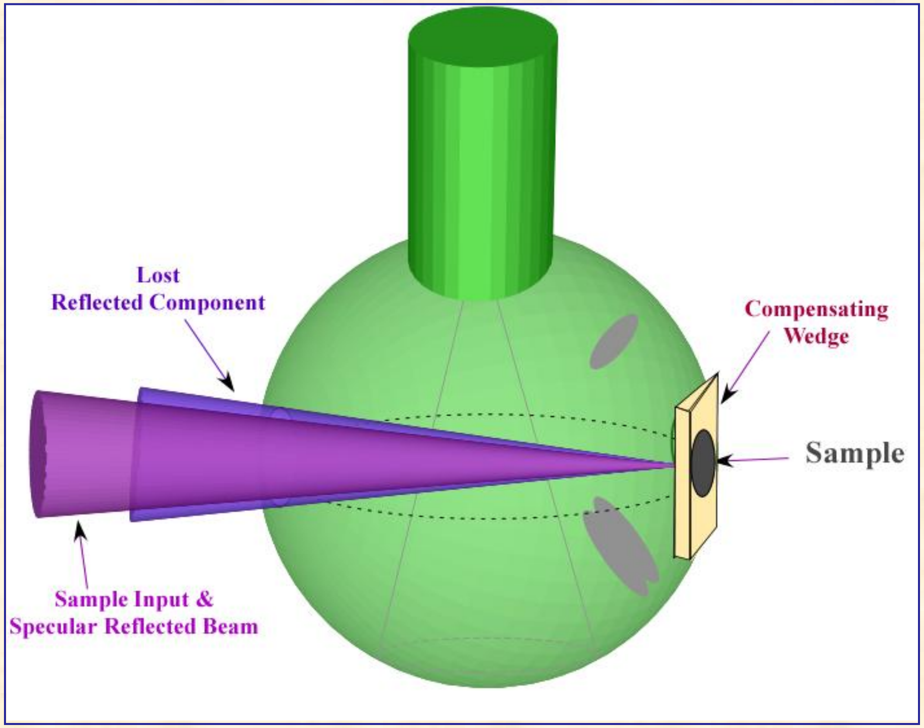
NIST Specular – Diffuse Separation Method

Standard Reflectance Measurement



$$r_{spec} = \frac{V_{Sample_1}}{V_{Ref_1}} - r_{diff}$$

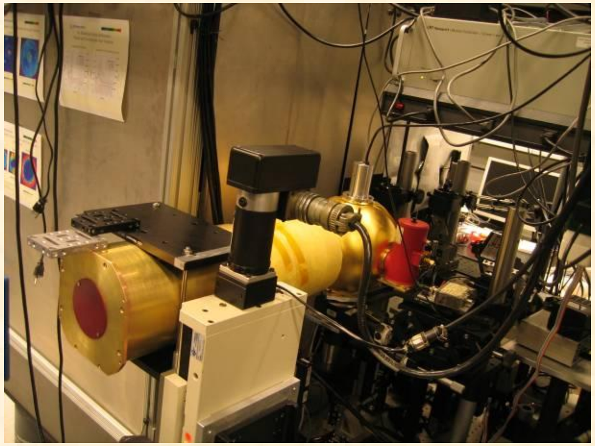
Diffuse Component Measurement



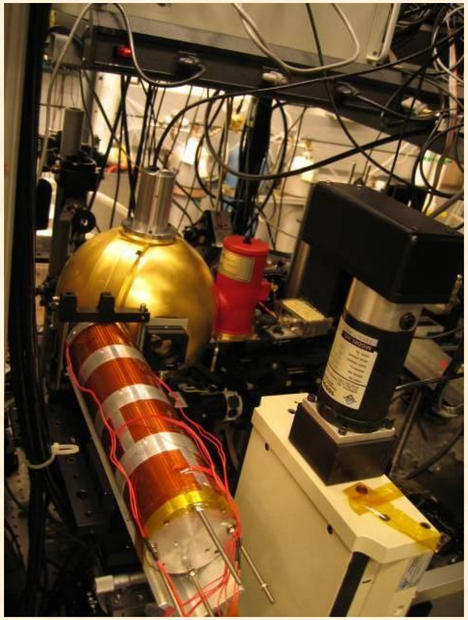
$$r_{diff} = \frac{V_{Sample_2}}{V_{Ref_2}} \times f_{wedge}$$

Complete Hemispherical Laser-Based Reflectometer

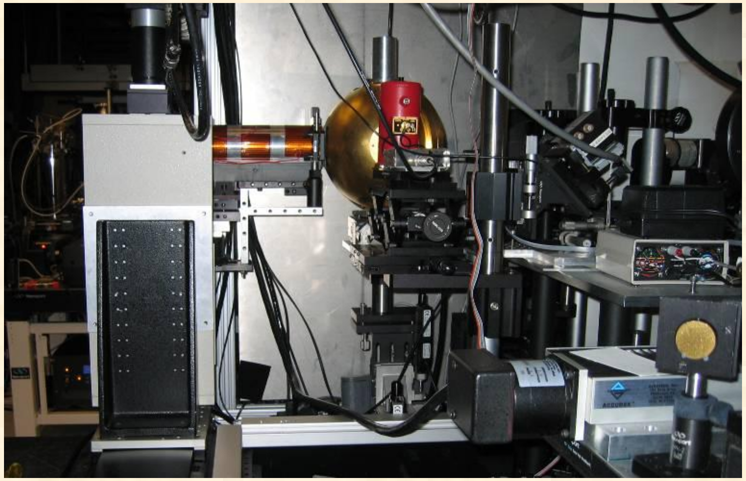
View of Setup w/AERI BB



Top View of Setup w/HU BB

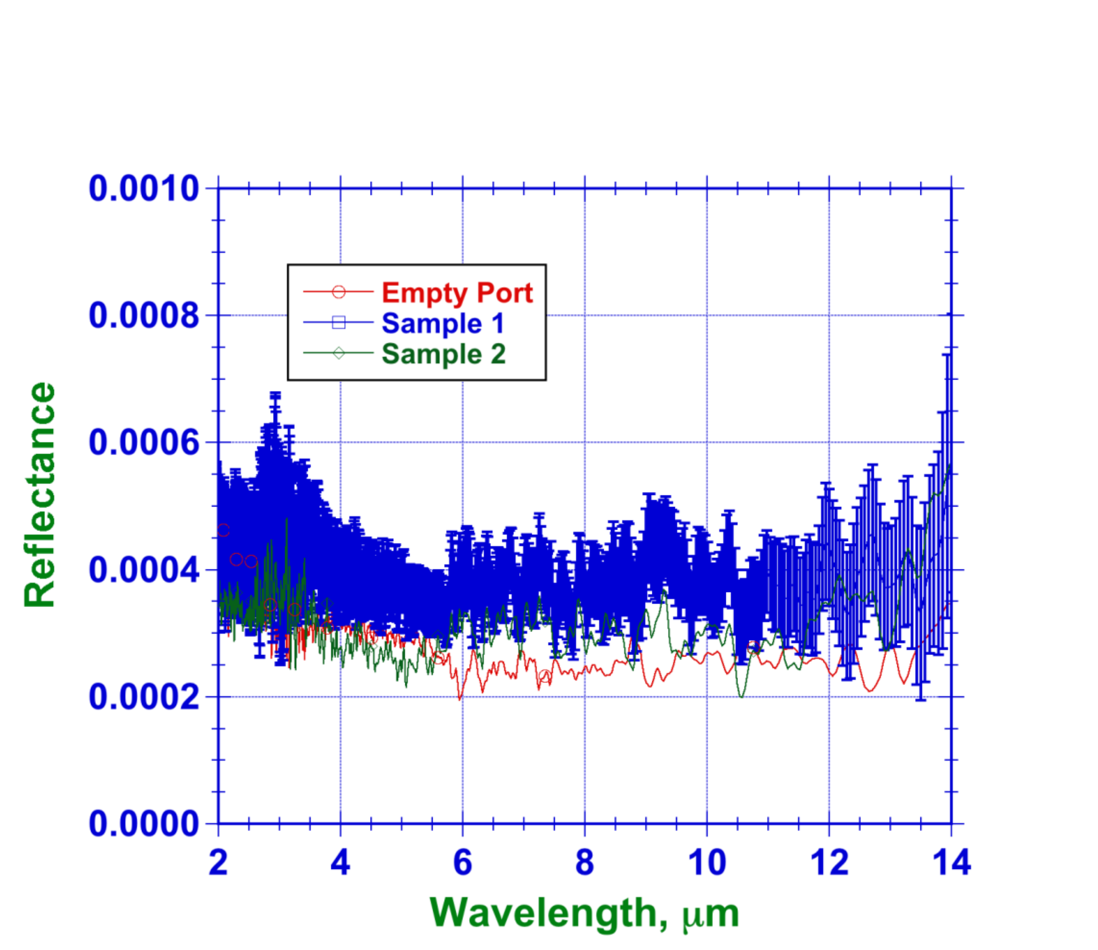


Side View of Setup w/HU BB



- Designed for complete hemispherical reflectance measurement using 20 cm gold integrating sphere with 6 mm entrance aperture (1/2 angle = 1°) and 50 mm sample port
- Laser sources: 10.6 µm, 1.32 µm (3.39 µm, 1 - 5 µm available, 6 - 10 µm potential)
- Detectors: MCT, pyroelectric and InGaAs; array, quadrant detectors for beam alignment and profiling
- Motorized stages used to manipulate sphere and cavity
- Map spatial uniformity & angle dependence
- Can measure reflectance down to approx. 10^{-5} (equivalent to emissivity 0.99999)
- Reflectance expanded uncertainties previously estimated 15 - 20% for 10^{-3} to 10^{-5} range, black sample R=0.0022 within .0002 of spectral DHR

Example Uncertainties



Absolute Reflectance Evaluation Method*

Reflectance obtained from (4) measured quantities:

1. Ratio of Sample to Reference Measurements in Sphere V_s / V_r

4. Relative BRDF $f(8°;\theta,\phi)/f_0$

Directional-hemispherical Reflectance

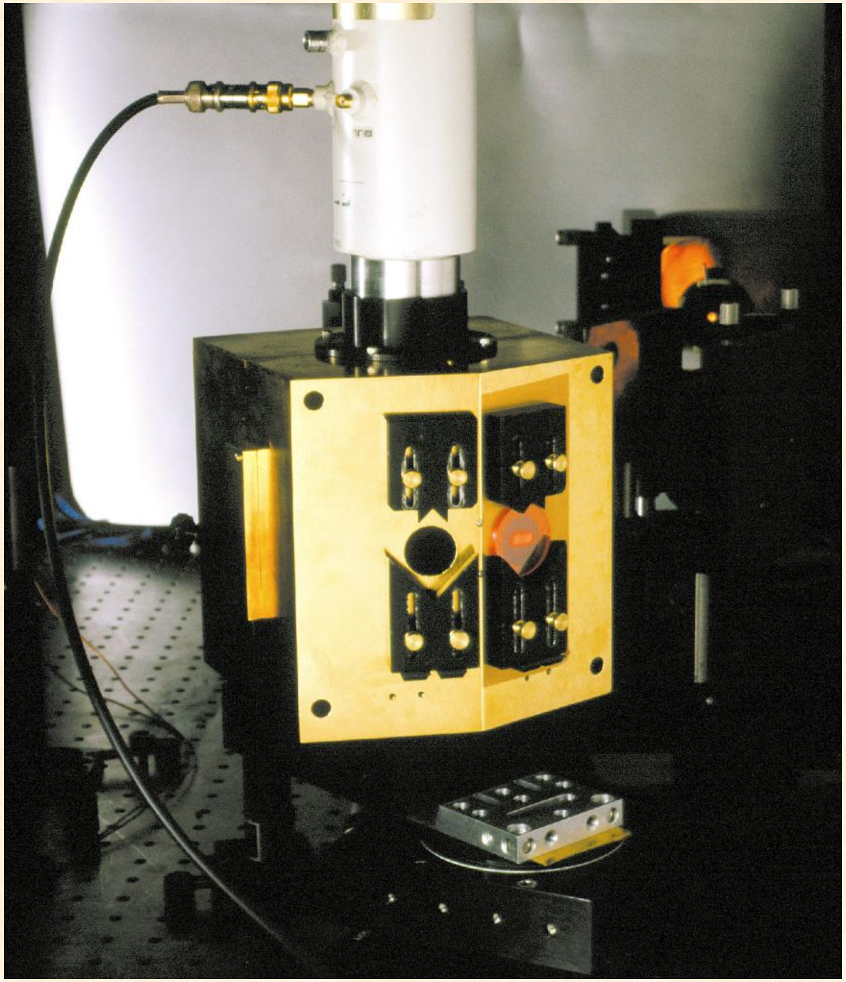
$$\rho_{8°,2\pi} = \frac{V_s}{V_r}\frac{V_{r_0}}{V_{s_0}}\left[\frac{\int_0^{2\pi}\int_0^{\pi/2} f(8°;\theta,\phi)/f_0 \cdot \sin(2\theta)\cdot d\theta \cdot d\phi}{\int_0^{2\pi}\int_0^{\pi/2} f(8°;\theta,\phi)/f_0 \cdot \tau(8°;\theta,\phi)/\tau_0 \cdot \sin(2\theta)\cdot d\theta\cdot d\phi}\right]$$

2. Ratio of Sample Removed to Reference Measurements

3. Relative Sphere Throughput $\tau(\theta,\phi)/\tau_0$

L M Hanssen and K A Snail, "Integrating Spheres for Mid- and Near Infrared Reflection Spectroscopy", in Handbook of Vibrational Spectroscopy, J.M. Chalmers and P.R. Griffiths (Eds), John Wiley & Sons, Ltd, Volume 2, pp. 1175 - 1192 (2002).

Integrating Sphere for Specular and Diffuse Samples



Specifications

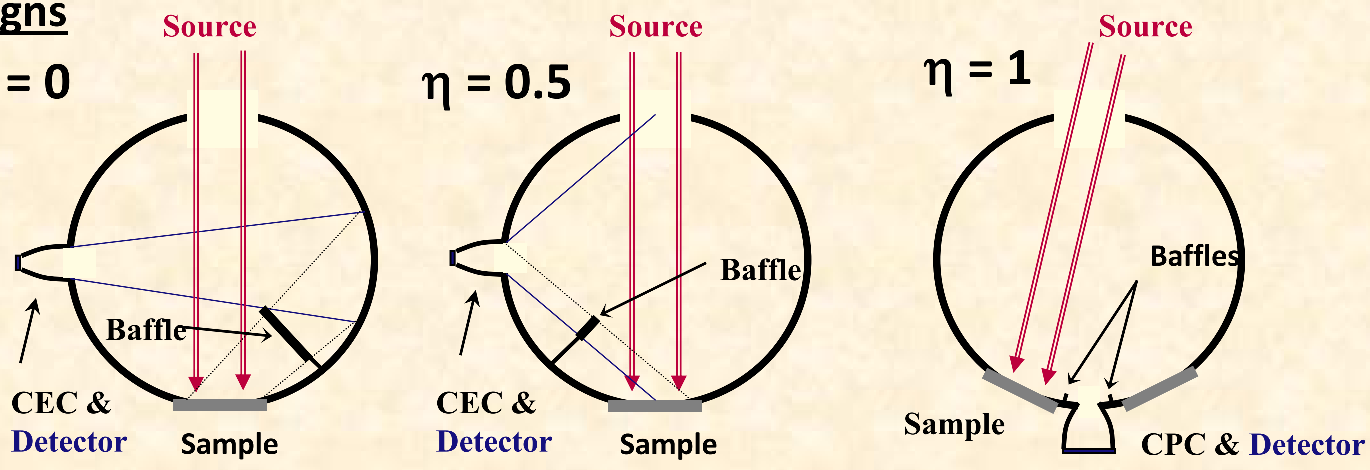
- λ range: 1.0 - 18 μm
- 6 inch diameter
- gold-electroplated plasma-sprayed metal coating
- MCT detector w/ concentrator optics
- baffling in sphere
- 8° incidence angle

Capabilities

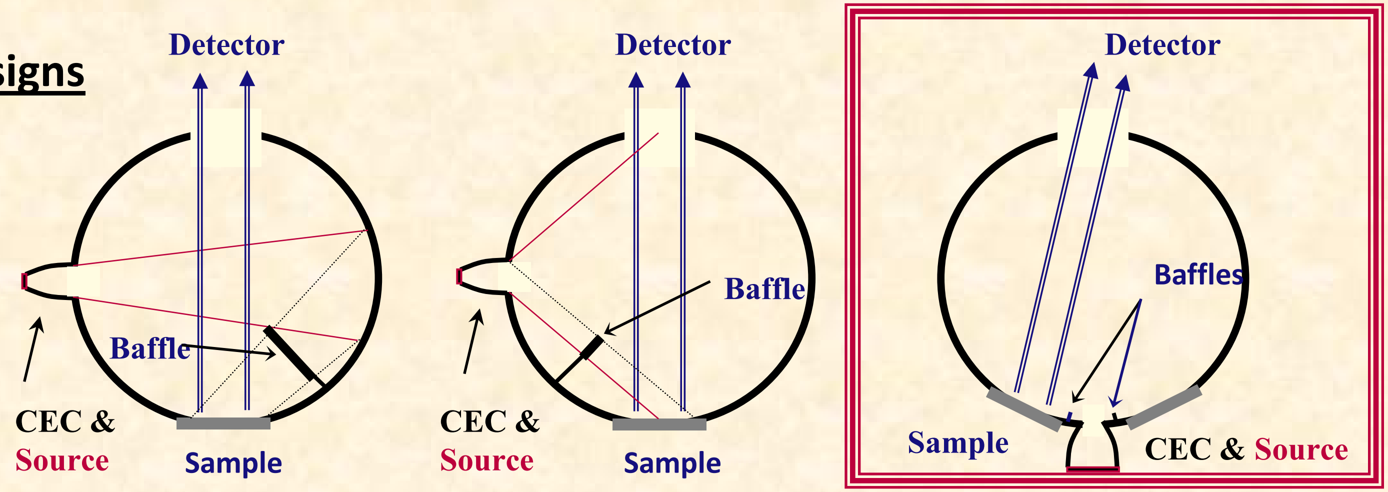
- Reflectance, Transmittance & Absorptanc
- absolute & relative specular R, T & A
- absolute & relative diffuse R, T & A
- uncertainties (2σ):
  - specular: $\leq$ 0.3%
  - diffuse: 1.5 - 3%
  - larger for angle dependent structure
- can measure R of transmissive samples
- can sort out scatter from total R & T

Isotropic Sphere Designs

DHR Designs

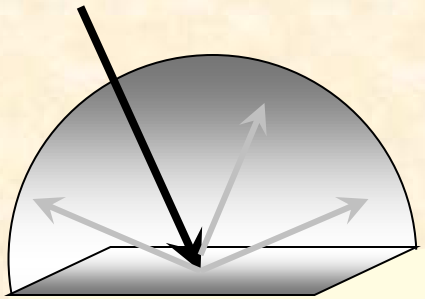


HDR Designs



K. A. Snail and L. M. Hanssen, "Integrating sphere designs with isotropic throughput", Applied Optics* ***28* *no. 10, 1793 (1989).*

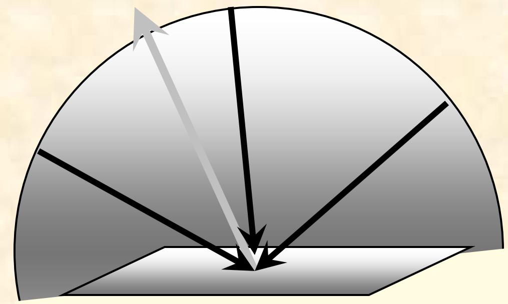
"Diffuse" Reflectance



Directional-Hemipsherical Reflectance

DHR

- Single direction illumination
- Hemispherical collection
- = Output Flux/Input Flux
- Requires uniform collection



Hemispherical-Directional Reflectance Factor

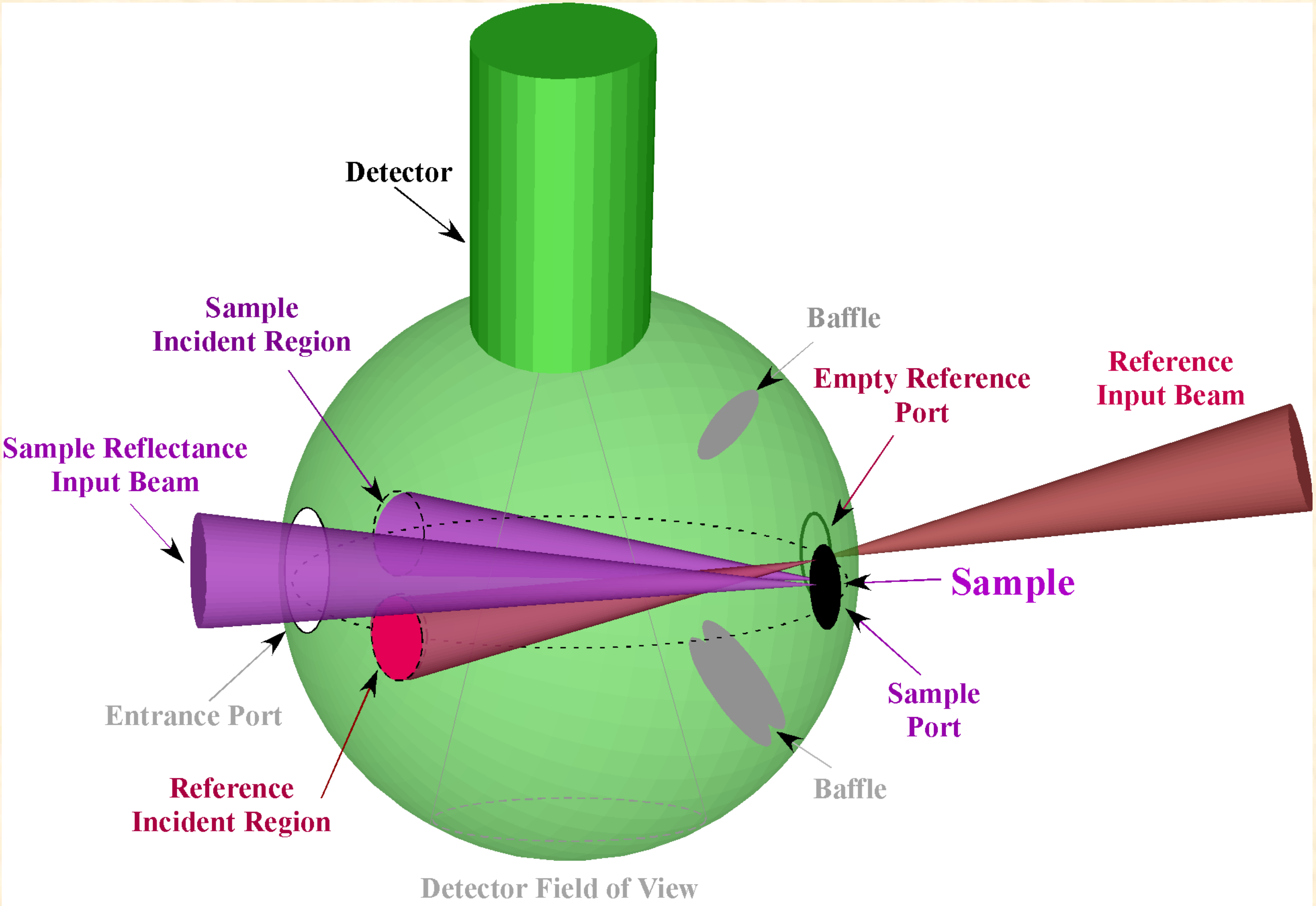
HDR

- Hemispherical illumination
- Directional collection (small solid angle)
- = output flux/flux from ideal diffuser
  output flux/(input flux*proj. solid angle)
- Requires uniform radiance illumination

Approach to Absolute Infrared Diffuse Reflectance

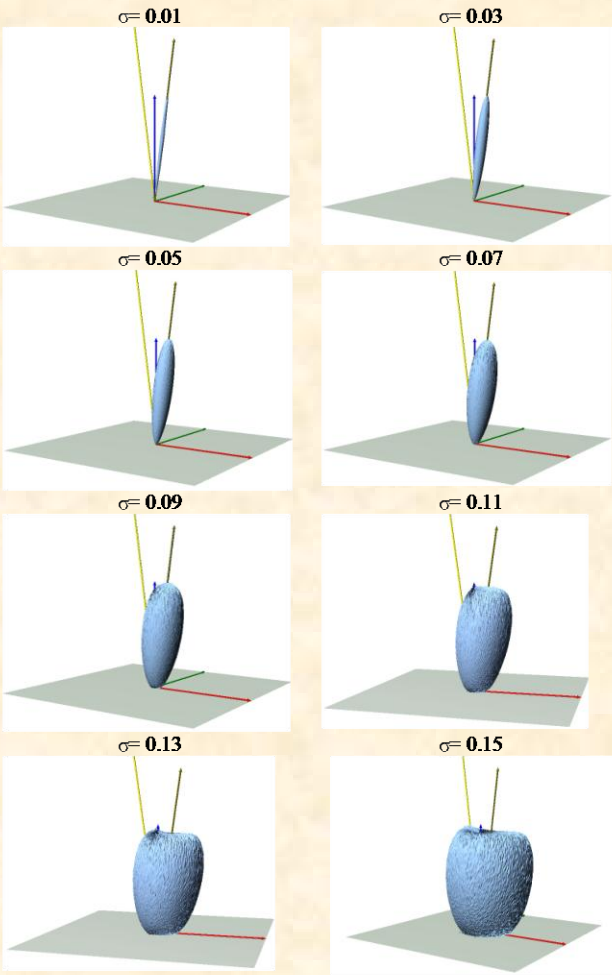
- Absolute method issues
  - Absolute sphere instruments at National Measurement Institutes (NMIs) are UV-VIS-NIR, require ideal sphere / sample behavior
  - Infrared spheres considerably less ideal than UV-VIS-NIR versions
  - (NPL uses integrated UV-VIS-NIR BRDF & IR hemi-ellipsoid system)
- Need method for uncertainty determination & analysis
  - Error from use of standard sphere theory potentially very large
  - Direct sphere characterization required
- New method developed to account for non-ideal spheres
  - Method consists of direct measurements only
  - No assumptions of ideal sphere or coating behavior
  - No reliance on sphere theory

Reflectance Measurement Geometry (Absolute for Specular Samples)

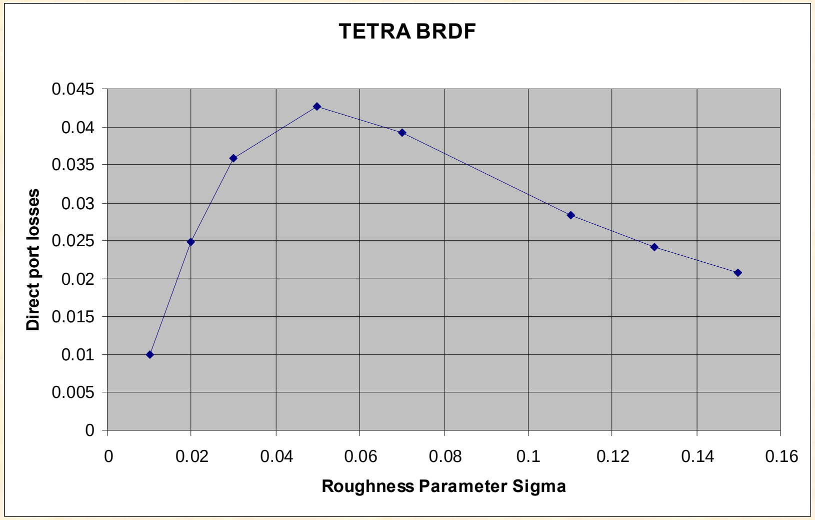


Sphere Error Analysis: BRDF Model I

TETRA (NIST)



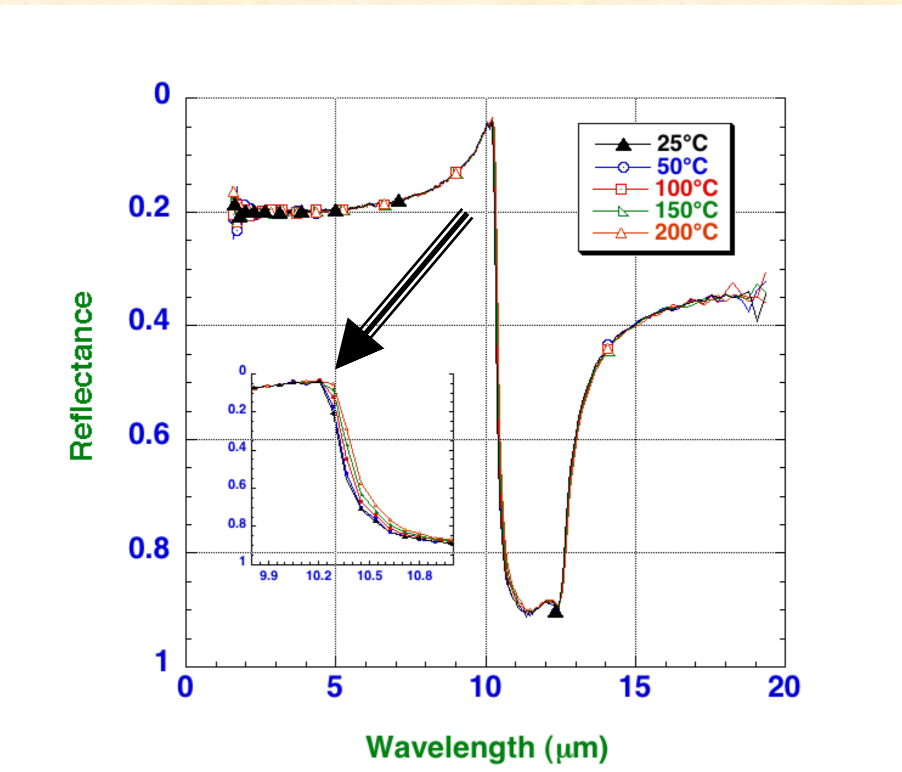
Entrance Port Loss



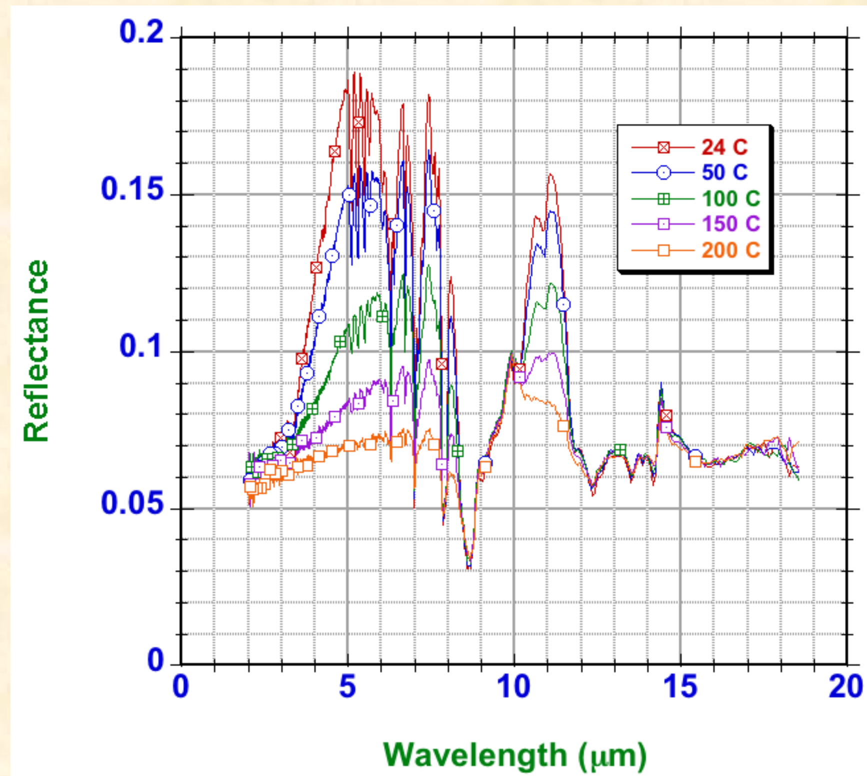
- Entrance port lost (retro-reflection) unavoidable component of error
- BRDF now only at 10.6 μm
- Plan to set up direct measurement

Temperature Dependent Reflectance Examples

SiC polished



Black Paint (diffuse)



NIST Uncertainty Budget Examples

Regular (Specular) Reflectance

(BK-7 Glass, for R = 0.4)

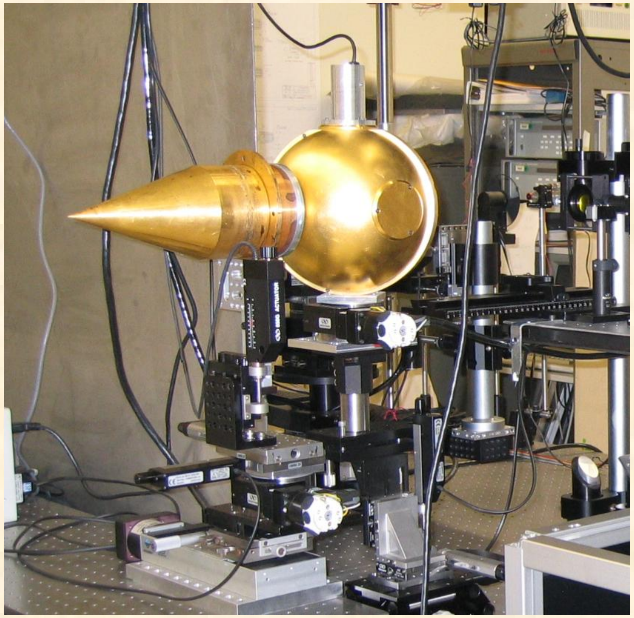
Uncertainty source	Value (unitless)
Type B Standard Uncertainty Component	
Inter-reflections	0.00013
Detector nonlinearity	0.00011
Atmospheric absorption variation	0.00004
Beam flip	0.00010
Inequivalent sample/reference beam alignment	0.00030
Retro-reflected light lost out entrance port	0.00012
Entrance port overfill	0.00005
Sample port overfill	0.00004
Beam geometry, polarization	0.00020
Phase errors	0.00006
Quadrature sum	**0.00044**
Type A Standard Uncertainty Component	0.00015
Expanded Uncertainty (k=2)	**0.00093**

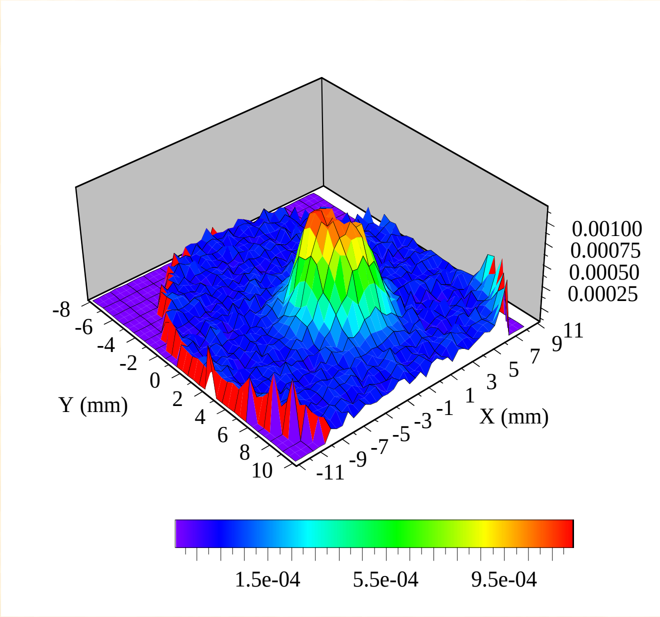
DHR (Diffuse) Reflectance

(Diffuse Gold, for R = 0.9)

Uncertainty source	Value (unitless)
Type B Standard Uncertainty Component	
Inter-reflections	0.0002
Detector nonlinearity	0.0006
Atmospheric absorption variation	0.0001
Beam flip	0.0005
Inequivalent sample/reference beam alignment	0.0005
Retro-reflected light lost out entrance port	0.004
Spatial variation of throughput	**0.015**
Errors in sphere mapping	0.005
Entrance port overfill	0.0001
Sample port overfill	0.0002
Beam geometry, polarization	0.0002
Phase errors	0.0002
Quadrature sum	**0.016**
Type A Standard Uncertainty Component	0.0002
Expanded Uncertainty (k=2)	**0.033**

Complete Hemispherical Reflectometer Instrument





- Designed for variable angle incidence up to normal; laser input
- Entrance port 1/2 angle = 1˚
- Can measure down to approx. 10^{-5} (equiv to emissivity 0.99999)
- Map spatial uniformity & angle dependence
- Used for Cavity and low reflectance sample measurements

Example Uncertainty Budgets for Black Samples ($\rho = 0.05$)

Specular

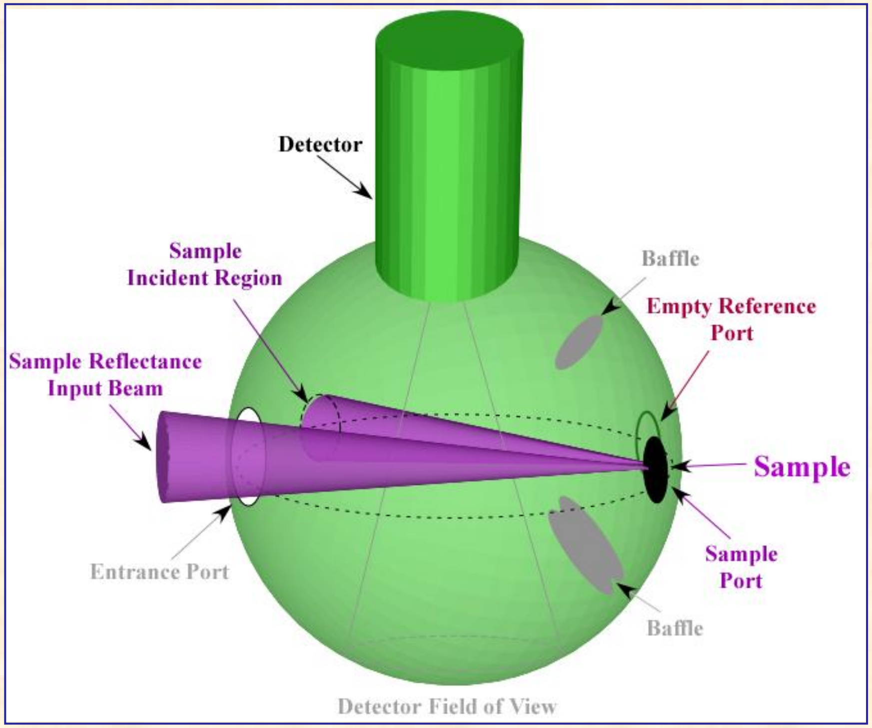
Uncertainty source (specular sample)	Value (unitless)
Type B Standard Uncertainty Component	
Inter-reflections	0.00002
Detector nonlinearity	0.00011
Atmospheric absorption variation	0.00001
Beam flip	0.00001
Inequivalent sample/reference beam alignment	0.00004
Retro-reflected light lost out entrance port	0.00008
Entrance port overfill	0.00001
Sample port overfill	0.00004
Beam geometry, polarization	0.00003
Phase errors	0.00006
Quadrature sum	0.00016
Type A Standard Uncertainty Component	0.00015
Expanded Uncertainty (k=2)	0.00044

Diffuse

Uncertainty source (diffuse sample)	**Value (unitless)**
Type B Standard Uncertainty Component	
Inter-reflections	0.00001
Detector nonlinearity	0.00003
Atmospheric absorption variation	0.00001
Beam flip	0.00003
Inequivalent sample/reference beam alignment	0.00003
Retro-reflected light lost out entrance port	0.00022
Spatial variation of throughput	0.00083
Errors in sphere mapping	0.00028
Entrance port overfill	0.00001
Sample port overfill	0.00001
Beam geometry, polarization	0.00001
Phase errors	0.00001
Quadrature sum	**0.00091**
Type A Standard Uncertainty Component	0.00015
Expanded Uncertainty (k=2)	**0.00184**

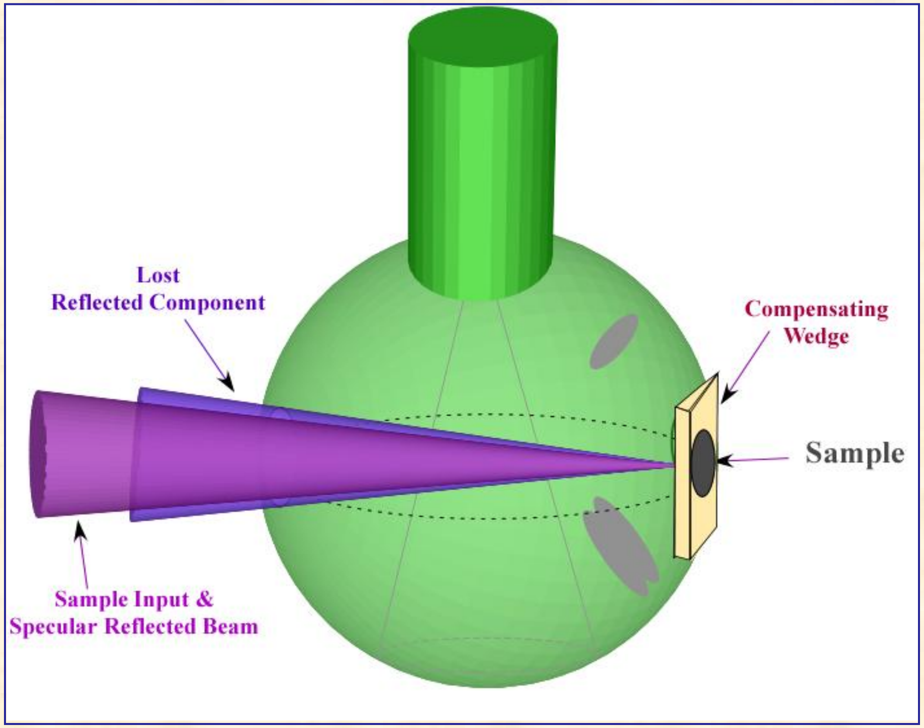
NIST Specular – Diffuse Separation Method

Standard Reflectance Measurement



$$r_{spec} = \frac{V_{Sample_1}}{V_{Ref_1}} - r_{diff}$$

Diffuse Component Measurement



$$r_{diff} = \frac{V_{Sample_2}}{V_{Ref_2}} \times f_{wedge}$$