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
  - Fixed $\lambda$
  - Tunable $\lambda$

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

**Measurement Methodologies**
- Modeling Instruments & Methods
- Error Sources Evaluation
- Absolute Methods $\rho$, $\tau$, $\alpha$, $\varepsilon$

**Direct Measurements & Properties**
- Transmittance
  - Regular
  - Diffuse, BTDF
- Reflectance
  - Regular
  - Diffuse, BRDF
- Absorptance
- Emittance
- Ellipsometry
- Polarimetry

**Materials, Coatings, Optical Components, Cavities & Detectors**

**Additional Quantities**
- Index of Refraction
- Extinction Coefficient

**Support Mechanisms**
- Calibration Service
- Physical Standards
- Inter-Comparisons
- Reference Data
- Short Courses

**Support Communities**

**External:**
- Industry
- Government
- Academia

**Internal:**
- Detectors
- Sources
- 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 Spectrophotometry 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
• 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

Mid IR Entrance Port Overfill

Mean Value (2 µm - 18 µm) = 0.99999

![Graph showing Port Transmittance and Wavelength (µm)]
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

Reflectance w/ PTFE

Reflectance w/ ESLI Black

x 0.005

x 0.005

Wavelength, µm
Extreme Examples: Black Carbon Samples

Carbon Fiber Sample

Aligned Carbon Nanotube Sample
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.

\[
V_s \quad V_{ep} \quad \frac{ba}{ga} \begin{pmatrix} V_{ea} & V_{ep} \end{pmatrix} \\
F_{diff} \quad V_r
\]
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

\[ R = \frac{V_{sc}}{V_r} \frac{V_{ap}}{V_{back}} R_r \]

\[ E = 1 - R \]

*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**

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

- Detector
- Sample Incident Region
- Sample Reflectance Input Beam
- Entrance Port
- Reference Incident Region
- Reference Input Beam
- Sample
- Empty Reference Port
- Sample Port
- Baffle
- Detector Field of View
NIST Specular – Diffuse Separation Method

Standard Reflectance Measurement

Diffuse Component Measurement

\[
\text{spec} = \frac{V_{\text{Sample}_1}}{V_{\text{Ref}_1}} \quad \text{diff} = \frac{V_{\text{Sample}_2}}{V_{\text{Ref}_2}} \times f_{\text{wedge}}
\]
Complete Hemispherical Laser-Based Reflectometer

- 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

![Graph showing reflectance vs. wavelength with different samples.]

- Empty Port
- Sample 1
- Sample 2

Wavelength, $\mu$m

Reflectance
Absolute Reflectance Evaluation Method*

Reflectance obtained from (4) measured quantities:

1. Ratio of Sample to Reference Measurements in Sphere \( \frac{V_s}{V_r} \)

2. Ratio of Sample Removed to Reference Measurements

3. Relative Sphere Throughput \( \frac{f(\theta_0)}{f_0} \)

4. Relative BRDF \( \frac{f(8^\circ; \theta, \phi)}{f_0} \times \sin(2\theta) \times d \times d \)

Directional-hemispherical Reflectance \( 8^\circ, 2 \)

Integrating Sphere for Specular and Diffuse Samples

Specifications
- \( \lambda \) range: 1.0 - 18 \( \mu m \)
- 6 inch diameter
- gold-electroplated plasma-sprayed metal coating
- MCT detector w/ concentrator optics
- baffling in sphere
- 8° incidence angle

Capabilities
- Reflectance, Transmittance & Absorptance
- absolute & relative specular R, T & A
- absolute & relative diffuse R, T & A
- uncertainties (2\( \sigma \)):
  - 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

\( \eta = 0 \)

\( \eta = 0.5 \)

\( \eta = 1 \)

HDR Designs

“Diffuse” Reflectance

Directional-Hemispherical Reflectance (DHR)
- Single direction illumination
- Hemispherical collection
- $= \frac{\text{Output Flux}}{\text{Input Flux}}$
- Requires uniform collection

Hemispherical-Directional Reflectance Factor (HDR)
- Hemispherical illumination
- Directional collection (small solid angle)
- $= \frac{\text{output flux}}{\text{flux from ideal diffuser}}$
- 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
\((\text{BK-7 Glass, for } R = 0.4)\)

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

## DHR (Diffuse) Reflectance
\((\text{Diffuse Gold, for } R = 0.9)\)

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

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

## Diffuse

<table>
<thead>
<tr>
<th>Uncertainty source (diffuse sample)</th>
<th>Value (unitless)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type B Standard Uncertainty Component</strong></td>
<td></td>
</tr>
<tr>
<td>Inter-reflections</td>
<td>0.00001</td>
</tr>
<tr>
<td>Detector nonlinearity</td>
<td>0.00003</td>
</tr>
<tr>
<td>Atmospheric absorption variation</td>
<td>0.00001</td>
</tr>
<tr>
<td>Beam flip</td>
<td>0.00003</td>
</tr>
<tr>
<td>Inequivalent sample/reference beam alignment</td>
<td>0.00003</td>
</tr>
<tr>
<td>Retro-reflected light lost out entrance port</td>
<td>0.00022</td>
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<tr>
<td><strong>Spatial variation of throughput</strong></td>
<td>0.00083</td>
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<tr>
<td>Errors in sphere mapping</td>
<td>0.00028</td>
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<tr>
<td>Entrance port overfill</td>
<td>0.00001</td>
</tr>
<tr>
<td>Sample port overfill</td>
<td>0.00001</td>
</tr>
<tr>
<td>Beam geometry, polarization</td>
<td>0.00001</td>
</tr>
<tr>
<td>Phase errors</td>
<td>0.00001</td>
</tr>
<tr>
<td><strong>Quadrature sum</strong></td>
<td>0.00091</td>
</tr>
<tr>
<td><strong>Type A Standard Uncertainty Component</strong></td>
<td>0.00015</td>
</tr>
<tr>
<td><strong>Expanded Uncertainty ($k=2$)</strong></td>
<td>0.00184</td>
</tr>
</tbody>
</table>
NIST Specular – Diffuse Separation Method

Standard Reflectance Measurement

\[ \text{spec} = \frac{V_{\text{Sample}_1}}{V_{\text{Ref}_1}} \]

Diffuse Component Measurement

\[ \text{diff} = \frac{V_{\text{Sample}_2}}{V_{\text{Ref}_2}} \times f_{\text{wedge}} \]