



IARPA MORGOTH'S CROWN: Spectral Measurement Procedure

Contents

IARPA MORGOTH'S CROWN: Spectral Measurement Procedure	1
IR Spectroscopy of Solids	1
KBr Pellet Absorption Spectra	6
References	8

IR Spectroscopy of Solids

Pacific Northwest National Laboratory (PNNL) has measured infrared (IR) reflectance spectra of solid materials (substrates, bulk solids, and sieved or airbrushed trace solids) that will be used for the prize challenge. This document details the procedures and protocols used to record these reference spectra. It is well known that for solids the absorption-mode (transmission) spectra can be used for chemical, mineral or material identification and in many cases quantitation. Traditionally, this has meant grinding the solids and dispersing the fine powder and pressing it into a medium such as an IR-transparent potassium bromide (KBr) or sodium chloride (NaCl) pellet for the measurement. For the solids specimens in the SILMARILS program (which uses active laser illumination), and generally in passive hyperspectral imaging, however, all samples are to be interrogated using reflected IR light. The reference spectra thus also need to be recorded in reflectance mode. For both the bulk materials and those samples deposited on a substrate, we have measured the reflectance spectra in the laboratory using an integrating sphere to capture the reflected light. As seen in the sketch of **Figure 1**, sphere measurements provide two sets of spectra for each sample, namely the diffuse-only reflectance spectra and the hemispherical (a.k.a. total) reflectance, which represents the sum of both the specular and diffuse components. For the hemispherical measurements, the scenario at left shows how the light enters the sphere from the right, is reflected off a mirror down to the sample, and all the reflected light scattered into the 2π steradians of the hemisphere is collected. This includes both the specular and diffuse components; the specular ray is shown as a long red arrow, the diffuse components are shown as green arrows of different lengths. For the diffuse-only measurements seen in the right panel, a dome is removed from the upper portion of the sphere, allowing the specular component to escape. The dome size corresponds to the solid angle of the light subtended by the IR-reflected beam.

Total = specular + diffuse
(also called hemispherical)

Diffuse only
(remove specular)

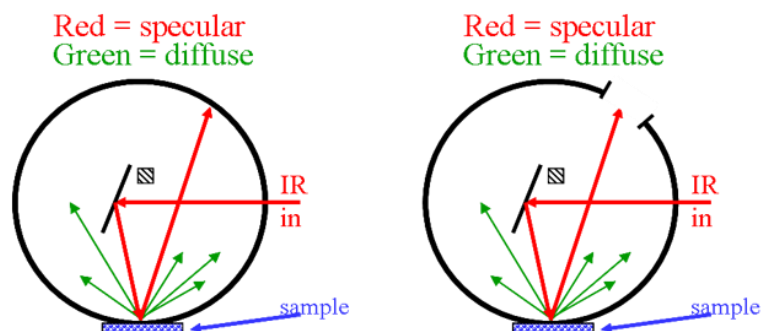


Figure 1. Cartoon Sketch of the Use of the Integrating Sphere in Hemispherical Mode (left) and Diffuse-only Mode with the Top Gold Dome Removed (right). The detector is shown as hatched square on a surface of the sphere into the plane of the paper.

The integrating sphere/spectrometer combination used for these data has previously been described (Blake et al. 2014; Johnson et al. 2015; Rettie et al. 2016). The sphere is the Bruker A562 model, a two-port 75 mm matte-gold-coated sphere with an attached mid-band Mercury cadmium telluride HgCdTe liquid nitrogen-cooled (MCT) detector. The sphere either sits inside the sample compartment of the Tensor 37 as seen in **Figure 2**, or is bolted to a Bruker Optics IR Cube FTIR spectrometer. The Fourier Transform Infrared (FTIR) provides the modulated and focused infrared beam as the input to the sphere. Inside the sphere, a flip mirror reflects the incoming IR beam to either a top port, a bottom sample port, or to another reference point on the sphere's front wall of the sphere as has been described (Su et al. 2014 ; Myers et al. 2015; Rettie et al. 2016). The top port (removable for diffuse-only measurements) is used during the hemispherical reference measurement and has an inner surface curvature to match that of the sphere (Blake et al. 2014).

The integrating sphere has a purge gas connection to provide a constant dry nitrogen purge during measurement (Johnson et al. 2015). Via the use of a specular exclusion port at the top, two sets of spectra are recorded for each sample: the diffuse-only reflectance spectra and the hemispherical reflectance. All data were collected using either a Bruker Tensor 37 (**Figure 2**) or a Bruker Matrix IR cube. Again, a SiC source and a Ge/KBr broadband beamsplitter were used. The sphere has a dedicated liquid nitrogen-cooled MCT detector, which is a 2×2 mm element with a 60° field of view. In combination, the system covers the 7500 to 600 cm⁻¹ spectral range. The instrument was purged with ultra-high purity (UHP) nitrogen to remove H₂O and CO₂ gas. The interferograms were collected using double-sided, forward-backward acquisition at 4.0 cm⁻¹ resolution, using a Mertz phase correction (Mertz 1967) with a Norton-Beer medium apodization (Lee et al. 2012). Typically, 2048 scans were averaged. Key operational parameters for the FTIR instrument are summarized in **Table 1**.



Figure 2. Photograph of the Gold A562 Integrating Sphere Housed in the Bruker Tensor 37 FTIR Sample Compartment. The MCT detector is seen in the red Dewar housing at back.

Table 1. Experimental Parameters for Bruker Tensor 27/37 FTIR Solids Reflectance Measurements

Infrared source	Glow bar	Phase resolution	16.0 cm ⁻¹
Beamsplitter	Broadband (BB) KBr	Phase correction mode	Mertz
Detector	LN ₂ cooled MCT 2x2 mm	Apodization mode	Blackman-Harris 3-term
Sampling Accessory	A562 Integrating sphere	Zerofilling factor	4
Mirror velocity	40 kHz	Number co-added scans	2048 typical
Aperture	open	High frequency limit	15802.4 cm ⁻¹
Laser wavenumber	15802.4 cm ⁻¹	Low Frequency Limit	0.0 cm ⁻¹
Focal length	69 mm	High pass filter	Open
Wavenumber range	7500 to 600 cm ⁻¹	Low pass filter	Open
Spectral resolution	4.0 cm ⁻¹	Preamplifier gain	Auto
Acquisition mode	Double-sided forward back	Switch Gain	On – factor 8x

In terms of specifics, the A562 sphere has a diameter of 75 mm with a nominally matte-gold interior surface that displays some specular characteristics (Koehl and Forcht 2003). **Figure 1** shows that on a vertical plane centered at the sphere's geometric center is a 2.0 cm diameter entrance port where light from the interferometer enters the sphere. A small flip mirror is positioned inside the sphere so that light entering the sphere can be directed downward to a 1.9 cm diameter sample port at the bottom of the sphere, back out the entrance port, upward to a 3.2 cm diameter specular exclusion port in the top half of the sphere, or to any point on the sphere wall along an arc joining the centers of these three ports. Light from the interferometer comes to a focus at the flip mirror. The specular exclusion port is large enough to account for the beam divergence of the spectrometer's optics. The centers of the sample and specular exclusion ports are in the same vertical plane as the entrance port. On a horizontal plane through the sphere's equator bisecting the entrance port but at 90° to the entrance port, is a 1.0 cm diameter port for the MCT detector. Two diffuse gold-coated baffles (not shown) are positioned near the detector port to prevent first-bounce light from either the bottom sample port or the specular exclusion port from reaching the detector.

The flip mirror is connected to the exterior of the sphere by a thin axle that is connected to a lever arm so that the mirror can be flipped from the “up” position pointing at the specular exclusion dome port or to

the “down” position pointing at the sample port. Two setscrews are used to delimit the travel of the lever at either end of its travel; the left and right screws are adjusted so as to center, in part, the light when it is focused in the top and bottom ports, respectively. With the mirror pointing down, the angle between the incident light on the sample surface and the surface normal is 14.8°. For the data reported here the IR beam points at the diffuse gold dome at the top of the sphere, the dome having the same curvature as the sphere; the sample is in place for both measurements. As the sample port opening is of significant size (19 mm) relative to the total sphere surface, it has been shown that the reflectivity of the sample itself plays a significant factor in the sphere’s overall reflectance, so the sample is thus kept in place for the reference spectrum to maintain a constant sphere albedo (Rettie 2016).

The detector and its preamp are bolted to the sphere. The sample or sample cup is pressed tightly against the bottom of the sphere avoiding artificially low reflectance values that can arise from optical standoff, even from distances < 1 mm (Baribeau and Zwinkels 2012; Thiede and Melsheimer 2002; Weidner et al. 1985). The radiant flux L inside the sphere, when illuminated by IR light from the interferometer, is given by (Labsphere 2015)

$$L = \frac{\Phi}{\pi A_s} \cdot \frac{\rho}{1-\rho(1-f)} \quad (1) \quad (2)$$

where Φ is the incident power (typically between 0.030 and 0.040 W), A_s is the sphere’s surface area, $1.767 \times 10^{-2} \text{ m}^2$, ρ is the reflectance of the matte gold surface of the sphere, and f is the exchange fraction, which is the ratio of the surface area of the open ports to the sphere’s total surface area. Using a similar spectrometer we have measured an incident power Φ of 0.036 W. When the cap is in the specular exclusion port, $f = 0.0227$ and $L = 8.7 \text{ W}/(\text{m}^2 \text{ sr})$ and with the cap removed $f = 0.0677$ and $L = 5.39 \text{ W}/(\text{m}^2 \text{ sr})$. The second term on the right side of equation (1) is referred to as the sphere multiplier and scales the radiance of the sphere due to multiple reflections as a function of sphere reflectance and port fraction.

Myriad samples and samples types were used for the MORGOTH’S CROWN prize challenge samples. As seen in **Figure 1**, two requirements needed for successful measurement of the solids are a) that the sample be able to sit horizontally, with a relatively level surface, and b) that its uppermost surface be pressed tightly against the bottom port of the integrating sphere. Different configurations were required to achieve this goal. As seen in **Figure 3**, the samples had to be prepared differently. For solid powders and granules, the samples were simply loaded into a sample cup of at least 3.5 mm depth and leveled with a laboratory spatula, as seen for the cup in panel A) at left.

Several of the samples for the prize challenge have an analyte coated onto a substrate. In those cases, the entire substrate was placed atop an inverted sample cup and pressed up against the bottom of the integrating sphere. This is seen in panel B) the sample was then placed atop an inverted black sample cup and pressed against the bottom of the sphere. In some cases the substrate was glass, which is transparent at frequencies above $\sim 3,000 \text{ cm}^{-1}$. For this reason, the sample cup was used below the sample coupon as the cup is made of Delrin® which has been tested and is known to have minimal reflectance at IR wavelengths. Lastly, for some of the samples, especially those coated onto aluminum as seen in frame C), the samples were quite relatively delicate and care was taken so as to avoid scraping or smudging the analyte off the substrate.

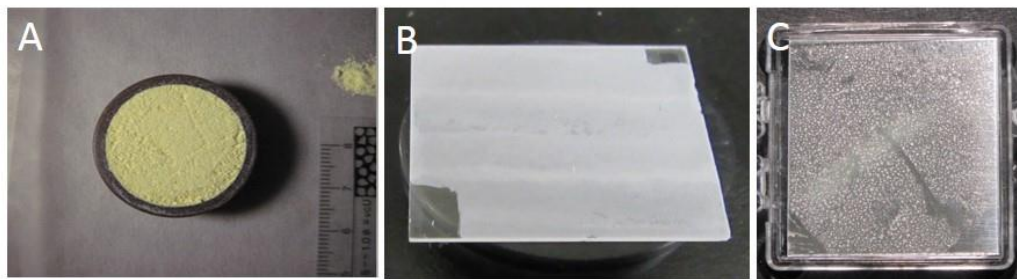


Figure 3. Photograph of the Three Different Types of Solid Samples Measured by the Integrating Sphere for the Prize Challenge

KBr Pellet Absorption Spectra

Infrared absorption spectra of solids have long been used for chemical and material identification, especially in the “fingerprint region” between 1,500 and 500 cm^{-1} spectral domain. The method is usually more time-consuming in terms of sample preparation, but the technique offers a more distinct physical insight as it is measuring only the absorption coefficient, proportional to the optical constant k in the refractive index.

All the solids transmission spectra were measured using a Tensor 37 spectrometer (**Figure 2**).

The measurement parameters for the solids transmission measurements are summarized below in **Table 2**.

Table 2. Experimental Parameters for Bruker Tensor 37 Solids KBr Transmission Measurements

IR source	Glow bar	Phase resolution	16.0 cm^{-1}
Beamsplitter	Broadband (BB) KBr	Phase correction mode	Mertz
Detector	DTGS	Apodization mode	Blackman-Harris 3 term
Sampling Accessory	Solid 12.5 mm sample holder	Zerofilling factor	4
Mirror velocity	10 kHz	Number co-added scans	512
Aperture	3 mm	High frequency limit	15802.4 cm^{-1}
Laser wavenumber	15802.4 cm^{-1}	Low Frequency Limit	0.0 cm^{-1}
Focal length	100 mm – Tensor 37	High pass filter	None
Wavenumber range	7800 to 400 cm^{-1}	Low pass filter	10 kHz
Spectral resolution	2.0 cm^{-1}	Preamplifier gain	Auto
Acquisition mode	Double-sided forward back	Switch Gain	On – factor 8x

The transmission spectra were recorded using the standard KBr pellet method. In each cases this meant grinding the solid powder and dispersing the fine powder and pressing it into the IR-transparent KBr for each measurement. This includes the four samples: acetaminophen, warfarin, caffeine, and potassium nitrate (KNO_3). In all cases a KBr pellet (12.7 mm diameter) was pressed for transmission measurements. The analyte was mixed, typically at ca. 1.0% by mass in KBr and pressed via a Carver Laboratory Press Model C, 12 Ton capacity in the pellet form.

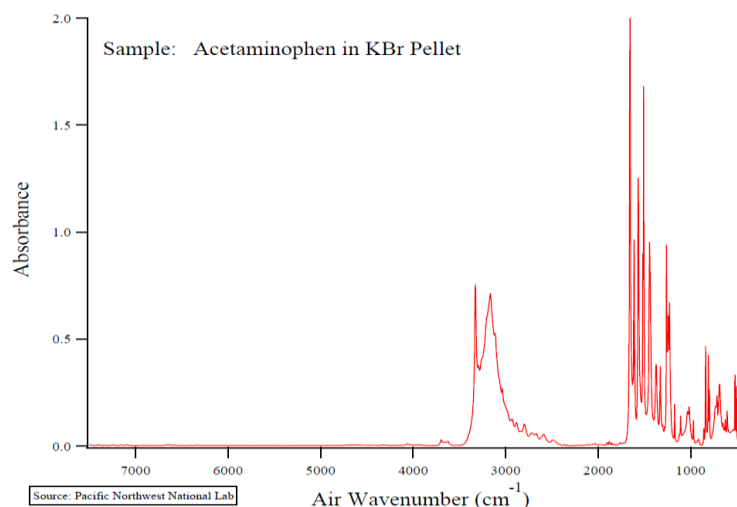


Figure 4. Plot of the IR absorption spectrum of acetaminophen powder embedded (ca. 1% by mass) in a KBr pellet and recorded using the protocols described above.

In the case of the KBr pellets, especially since they were measured at 2.0 cm⁻¹ resolution, the number of interferograms averaged was increased to 512 scans. In addition, several spectra were measured and averaged together to improve signal-to-noise. For the data processing of such spectra, a “blank” KBr reference spectrum has been subtracted from the analyte spectrum to remove any signatures associated with impurities in the KBr. The spectrum has also been baseline-corrected to account for stray light scattering. After baseline correction, the spectrum was normalized from 0 to 2.0 ABS units.

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