The Impact of Chromatic Aberration on the Infrared Microspectral Analysis of Trace Evidence

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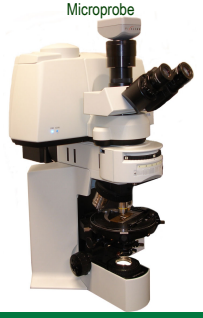
Abstract

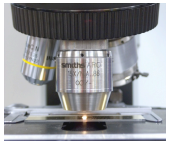
Infrared (IR) microspectroscopy is used for the identification of a plethora of trace evidence, including but not limited to suspicious white powders, fibers, paint, polymers, and drugs of abuse. Analysis with IR microprobes often requires use of a window such as those made from KBr, NaCl, or BaF_2. However, there is little regard for the interaction of both visible and IR radiation with these windows. When visible and IR radiation passes through a window, it is refracted. In addition, there is dispersion of both the visible and IR radiation causing chromatic aberration. Using windows always introduces optical dispersion. This results in an unfocused IR beam when the visible image is in sharp focus, and an unfocused visible image when the IR beam is sharply focused. This presentation demonstrates the effects of optical dispersion on the IR microprobe analyses; trace amounts of suspected bioterrorism hoax powders in a sealed cell were used as examples to illustrate this effect. Sealed cells consist of an IR-reflective microscope slide with a BaF_2 cover slip attached to the slide with an impermeable adhesive, thus enabling the analyst to remain isolated and safe from the sample during IR microprobe analysis. The use of BaF_2 as the cover slip is the best choice of material because of its resistance to chemicals, insolubility in water, and transparency in both the visible and mid-IR regions of the spectrum. However, the refractive indices of BaF_2 for visible and mid-IR radiation are different and it is important to understand the impact of these differences to maximize analytical results. While the use of a cover slip introduces dispersion effects that are unavoidable, it is possible to adjust instrument settings when analyzing in the reflection-absorption mode of an IR microprobe to compensate for dispersion and minimize its impact on the quality of the sample spectrum. This presentation provides information about the interaction of light with BaF_2 in both the visible and mid-IR spectral regions, describes an optimal experimental methodology for collecting quality mid-IR spectra of microscopic trace evidence when using windows, and illustrates the impact of optical dispersion on spectral analyses.

FT-IR Analysis of Suspicious White Powders

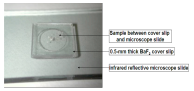
The IlluminatIR™ IR Microprobe



The All-Reflecting Objective (ARO)



The Sealed Cell



Pure Samples and Hoax Powders

Pure Samples:

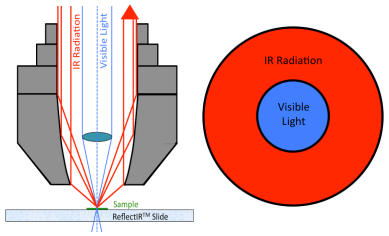
Polystyrene, TNT, Caffeine, Phenacetin, and Benzocaine.

Hoax Powders:

Albumin, Baking Soda, Chalk, Dairy Creamer, Dipel, Dry Milk, Flour, Foot Powder, Kaolin, Non-Dairy Creamer, Powdered Cleaner, Powdered Sugar, Spackling Powder, Talcum Powder, and Yeast.

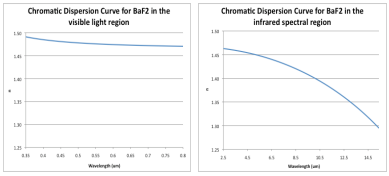
The Path of IR and Visible Radiation

Cross Sections of the ARO:



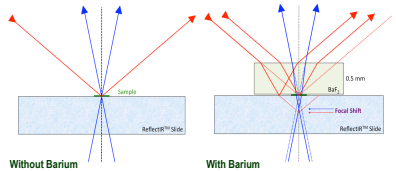
It is important to understand the interaction of light with BaF_2 in both the visible and IR spectral regions in order to optimize IR analysis when a sealed cell is used. IR and visible radiation are refracted differently when entering and exiting BaF_2. These refraction differences are due to the dispersion of BaF_2. Dispersion is the phenomenon in which a wave's velocity varies with its wavelength (or frequency). As a result, different wavelengths of electromagnetic radiation refract at different angles. A plot of the refractive index as a function of wavelength is called a dispersion curve. The IR and visible dispersion curves for BaF_2 are shown below.

Dispersion Curves for Barium Fluoride:



IR microspectrophotometers are designed so that the IR and visible light are parfocal in air, but the dispersion through the BaF_2 window compromises this parfocality and requires that the detector be aligned to either optimal focus for the visible ray or optimal focus for the IR ray.

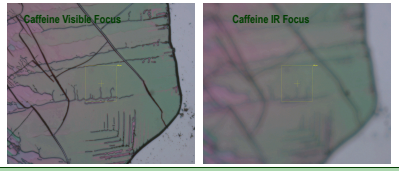
Ray Diagrams:



Without Barium Fluoride Cover Slip **With Barium Fluoride Cover Slip**

The distance between the visible focus and IR focus is called the focal shift. Experiments performed as described in this research were designed to evaluate these dispersion effects and determine whether the visible or IR should be optimized when using the sealed cell.

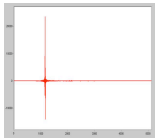
Photomicrograph in Visible Focus and IR Focus:



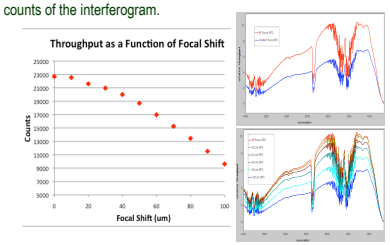
Experiment #1: Throughput

Visible focus was defined as when the image of the sample is in optimal focus and IR focus was defined as when the interferogram signal is at its maximum. By maximizing the interferogram signal, throughput is maximized.

Interferogram:



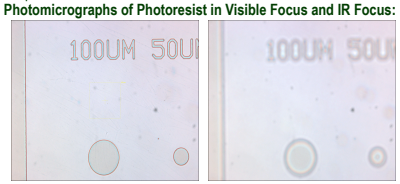
The microscope stage is raised or lowered to obtain IR or visible focus, and also to shift between the two. The decrease of throughput when the focus is shifted from IR focus to visible focus can be seen both on the intensity of the background spectrum in the decrease in counts of the interferogram.



Experiment #2: Focal Shift

The magnitude of the focal shift was both experimentally measured and theoretically calculated. The focal shift was measured using a photoresist slide (in triplicate by two scientists) and equaled 91.5 +/- 0.5 µm.

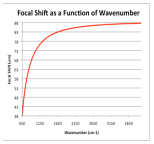
Photomicrographs of Photoresist in Visible Focus and IR Focus:

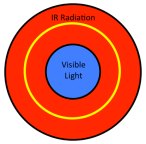


The focal shift was calculated using geometry, trigonometry, and Snell's Law ($n_1 \sin\theta_1 = n_2 \sin\theta_2$). In addition, the dispersion of IR and visible radiation causes the focal shift to be wavenumber (or wavelength) dependant.

$$Focal\ Shift = thickness_{win} \times \left| \frac{\tan\theta_{vis} - \tan\left[\sin^{-1}\left(\frac{n_{air} \times \sin\theta_{vis}}{n_{win}}\right)\right]}{\tan\theta_{vis}} \right| - \left| \frac{\tan\theta_{IR} - \tan\left[\sin^{-1}\left(\frac{n_{air} \times \sin\theta_{IR}}{n_{win}}\right)\right]}{\tan\theta_{IR}} \right|$$

The numerical aperture (NA) of the visible-light lens in the ARO is 0.22 (θ = 12.7°) and the NA of the IR radiation through the ARO is 0.88 (θ = 61.6°). Thus, the incident angle of visible light (θ_{Vis}) is 12.7°, and the incident angle of IR radiation (θ_{IR}, which is the area and intensity average) is 52.8°.



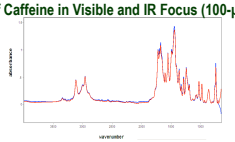


The focal shift was calculated to be an average of 82 µm, with a focal shift of 88 µm for 4000 cm^{-1} (2.5 µm) & 38 µm for 650 cm^{-1} (15.4 µm).

Experiment #3: Spectral Analysis

It was difficult to visually differentiate visible-focus spectra from IR-focus spectra. Noise at the lowest wavenumbers is the most significant observable difference. The increased noise is caused by the absorbance of BaF_2 combined with low throughput in this spectral region.

IR Spectra of Caffeine in Visible and IR Focus (100-µm aperture):



RMS Noise:

	No BaF_2	IR Focus	Visible Focus
100-µm aperture	6.3×10^{-5}	7.1×10^{-5}	1.2×10^{-4}
50-µm aperture	1.3×10^{-4}	1.6×10^{-4}	3.1×10^{-4}
25-µm aperture	4.4×10^{-4}	5.9×10^{-4}	1.2×10^{-3}

The ultimate goal of this study was to determine whether, when using a sealed cell with a BaF_2 cover slip, analysis in IR focus or analysis in visible focus would generate better results. "Better results" was defined as the data set that generated the best hit quality index (HQI) when compared with a library spectrum of the same compound. Both correlation and 1st derivative correlation algorithms were used for the library searches.

Library Search Results (Pure Samples):

Correlation Search	HQI – No-BaF_2 Library	HQI – IR-Focus Library	HQI – Vis-Focus Library
Benzocaine in IR Focus	0.0548	0.0074	0.0100
Benzocaine in Vis Focus	0.0631	0.0091	0.0072
Phenacetin in IR Focus	0.0617	0.0267	0.0475
Phenacetin in Vis Focus	0.0880	0.0465	0.0309

No-BaF_2 Library	HQI – Correlation Algorithm	HQI Difference	Percent HQI Difference
Benzocaine in IR Focus	0.0548	0.083	15.1%
Benzocaine in Vis Focus	0.0631		
Polystyrene in IR Focus	0.0968	0.0351	36.3%
Polystyrene in Vis Focus	0.1319		

Library Search Results (Hoax Powders):

No-BaF_2 Library	HQI – Correlation Algorithm	HQI Difference	Percent HQI Difference
Chalk in IR Focus	0.175	0.058	33.1%
Chalk in Vis Focus	0.233		
Dipel in IR Focus	0.148	0.025	16.9%
Dipel in Vis Focus	0.173		

For the pure samples, when using the No-BaF_2 library, there was a 20% and 7.7% improvement in HQI for IR focus over visible focus for the correlation and 1st derivative searches. When the IR-Focus (library and analysis) was compared to the No-BaF_2 libraries (IR-focus analysis), there was a 1111% improvement in HQI (0.0823) for the IR-focus library and correlation searches, and 1049% improvement in HQI (0.218) for the 1st derivative searches. For the hoax powders, when using the No-BaF_2 library, there was a 17% and 30% improvement in HQI for IR focus over visible focus for the correlation and 1st derivative searches. Ultimately, it was shown that analysis in IR-focus gives the best library search results (lowest HQIs), and libraries should be made using spectra collected in IR focus.

Conclusions

Chromatic aberration of IR and visible radiation through salt windows must be considered when collecting IR spectra with a microprobe:

- There is a significant decrease in throughput when analyzing in visible focus when compared to IR focus.
- The focal shift between IR and visible focus is ~80 - 90 µm (when using a 0.5 mm BaF_2 cover slip and 15-times ARO).
- The RMS noise is roughly twice as large for visible versus IR focus, which becomes more significant with smaller apertures/lower throughput.
- Samples should be analyzed in IR focus to obtain the best HQIs when performing library searches.