The Dust Library: Enhanced Infrared Spectra of Individual Respirable Dust Particles

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Nomenclature

IR	=	infrared
FTIR	=	Fourier transform infrared spectrometer
μm	=	10^{-6} meters, microns
MCT	=	Mercury Cadmium Telluride detector of IR radiation
$\tilde{\nu}$	=	wavenumber of IR light in units of cm^{-1}
$m^*(\tilde{\nu})$	=	complex index of refraction of a material as a function of wavenumber
$\varepsilon(\tilde{\nu})$	=	permittivity of a material as a function of wavenumber
ε_0	=	constant value of permittivity
A_j	=	intensity of vibrational transition *j* in permittivity of material
$\tilde{\nu}_{0,j}$	=	wavenumber position of vibrational transition *j* in permittivity of material
Γ_j	=	width of vibrational transition *j* in permittivity of material
f_i	=	volume fraction of a component in a dust sample mixture
ε_i	=	permittivity of a pure component in dust
ε_{eff}	=	effective permittivity of a mixture of components

The Coe Group has used plasmonic metal films with arrays of microholes to capture particles and record scatter-free infrared absorption spectra of individual dust particles of a specific size and narrow size distribution using imaging infrared Fourier transform microscopy. The spectra are scatter-free in spite of the fact that these particles are smaller than the probing wavelengths of light. Dust particles of ~4 μm size have been collected from different environments, including data from our laboratory air, a household filter, the World Trade Center 9/11/2001 event, and the International Space Station. Particles of this size are among the largest that are inhaled into people's lungs, so there is much interest in the chemical composition of these particles considering that increasing particulate concentrations are known to be correlated with deterioration of human health. In addition to samples from various environments, the dust library now includes the spectra of single particles of calibrants, i.e. pure components known to be in the dust which enables the development of quantitative analytical models for composition.

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I. Infrared Spectra of Individual Respirable Particles

PARTICULATE matter abounds in space, our atmosphere, our houses, water, and soil. Airborne particles are mostly natural, but around 6-23% are anthropogenic[1] and therefore diagnostic for human effects on the environment[2]. Particles in the size range 2.5-10 μm are called inhalable coarse particles. They get past the filtering of the nose and throat making it into the lungs; i.e., they are respirable[3]. Since the airborne lifetime of particles decreases as the particle diameter increases, particles in this size range can be expected to be more reflective of the local environment. Clearly much more work is needed on inhalable coarse particles[4]. While there is illuminating work on fine particulate matter correlating elemental analysis with disease rates in regions[4, 5], it is also important to know the molecular/chemical identity and quantity of dust components as might be obtained with infrared (IR) spectroscopy[6]. The IR work described herein enables a preliminary model of dust component fractions that may be useful in characterizing the amounts and chemical components of inhalable coarse particles.

The Coe Group has developed methods[7-11] to record scatter-free infrared (IR) spectra of individual particles smaller than the probing wavelength using plasmonic mesh and an imaging Fourier transform IR microscope. This is accomplished by placing the particles in the holes of a plasmonic metal mesh, i.e. thin Ni films with square arrays of holes as shown on the left side of Figure 1. The square hole size of this mesh tends to trap particles with an effective diameter of ~4 μm with a much narrower distribution than most filters. Particles can be trapped by pumping air through the mesh or by applying powdered samples while air is pumped through the mesh.

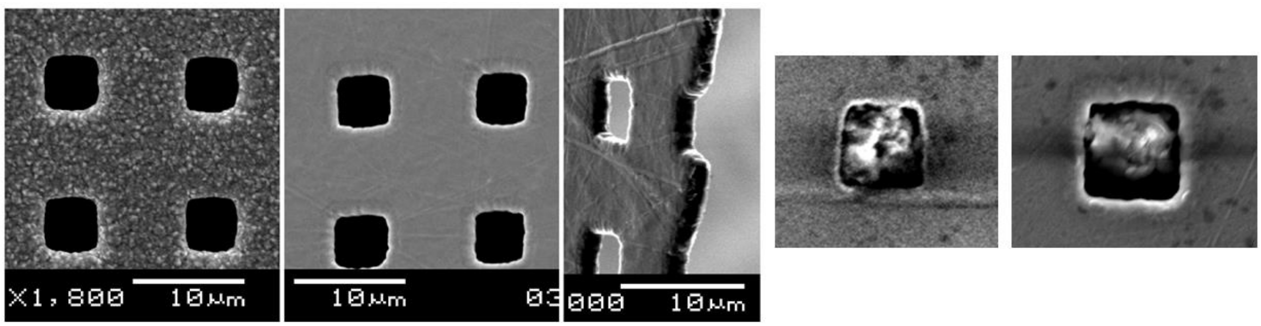


Figure 1. Scanning electron microscope images of plasmonic Ni mesh. *The mesh is produced by Precision Eforming (<u>www.precisioneforming.com</u>) and has a lattice parameter of 12.7 μm, a square hole width of ~5 μm, and a thickness of ~2 μm. When air is pumped through the mesh, dust particles of a specific size are trapped in the mesh holes as shown on the right-hand side. Scatter-free IR absorption spectra can be recorded of individual particles trapped in this manner because IR light runs along the metal surface rather than going directly through the holes.*

The method of obtaining IR spectra of individual particles has been described in detail elsewhere[7-11]. By placing the particles in a plasmonic mesh hole, one avoids the dominant scattering effects normally seen with spectra of particles of similar size to the probing wavelength. One important distinguishing characteristic of the method relative to other IR work is that the spectra can be treated quantitatively. Individual dust particle spectra have been, and continue to be, collected from different environments as described in Section II. In addition, IR spectra of individual pure components, known to be in the dust, have also been collected as described in Section III. An initial model, called a Mie-Bruggeman model, has been devised to obtain volume fractions of the components by analyzing the average single particle spectrum of a collection (Section IV). Finally, initial dust results from the International Space Station are described (Section V).

II. Dust Library

The Coe Group is in the process of publishing the library of spectral IR data in Figure 2. So far, only the lab air dust results have been published[9] and those digital spectra are available in supplemental materials for anyone to analyze. The house filter and World Trade Center 9/11/2001 event results currently exist as a draft to be submitted, while the International Space Station results are just beginning to be analyzed, i.e. will require more calibrants. We are in the process of making the whole library available to the public in the coming year. Each IR spectrum in the library was recorded at 4 cm^{-1} resolution, from 700-4000 cm^{-1}, with a 16 detector, liquid nitrogen cooled MCT array, using a Perkin Elmer Spotlight 300 imaging FTIR instrument. It currently requires about 30 min to record the spectrum of one particle under the best of circumstances, so currently the technique cannot realistically be applied in the field. The dust library currently includes ~246 dust particles and 94 calibrant particles[12].

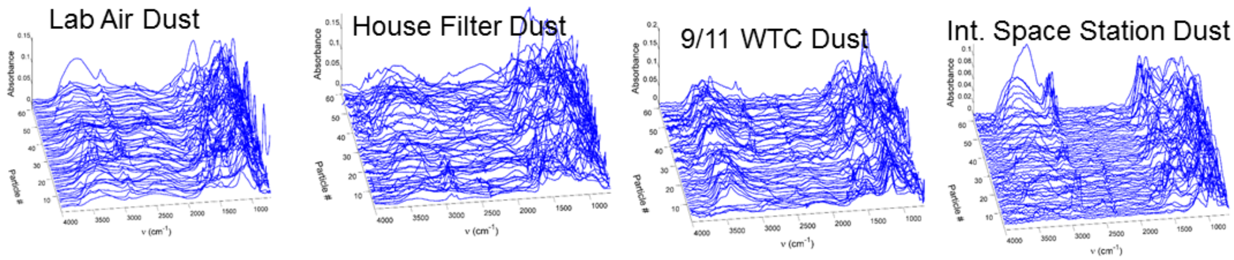


Figure 2. Dust library. *Collections of individual dust particle spectra from our laboratory air, a house filter, the World Trade Center 9/11/2001 event, and the International Space Station. Each collection comprises of ~60 spectra of single particles. Also in the library are single particle IR spectra of pure materials that we have found in respirable dust samples.*

III. Calibrants

Spectra of ~4 μm individual particles of pure materials known to be in dust samples have been recorded for quartz, calcite, dolomite, gypsum, three types of clay, yeast cells, polyethylene, and humic acid[12]. The average spectra of a group of individual spectra from each material (excepting humic acid) is given in Figure 3. Since individual dust particles show many crystalline spectral effects, these spectra were averaged to account for particle orientation. Each average spectrum was fit with a Mie model which requires an index of refraction of the particle as a function of wavenumber:

$$m^*(\tilde{\nu}) = \sqrt{\varepsilon(\tilde{\nu})} = \sqrt{\varepsilon_0 + \sum_j \frac{A_j \tilde{\nu}_{0,j}^2}{\tilde{\nu}_{0,j}^2 - \tilde{\nu}^2 - i\Gamma_j \tilde{\nu}}} \quad , \quad (1)$$

where the index of refraction, *m*, is the square root of the permittivity, ε, and the vibrational parameters of the material are given by $A_j, \tilde{\nu}_{0,j}, \Gamma_j$ for the intensity, position, and width of each vibration, *j*. Given a complex permittivity, one can predict an orientationally-averaged IR absorption, scattering, or extinction spectrum of a particle using Mie theory. The details of this process have recently been published[12] and the permittivities have been tabulated for all[12] calibrants (as shown in Figure 3) except humic acid/salt which will soon follow. There are many interesting spectroscopic lineshape effects when particles are about the same size as the probing light[7], so it is important to have a calibration of particles of the same size as the sample collections. The results can of course be applied to any particle sizes of interest in order to predict extinction, scattering, or absorption spectra for particles of different size than those measured in this work. The resulting permittivities can be combined to create models to treat particles of mixed composition which is typical of respirable dust. Our first of such models is presented in the next section.

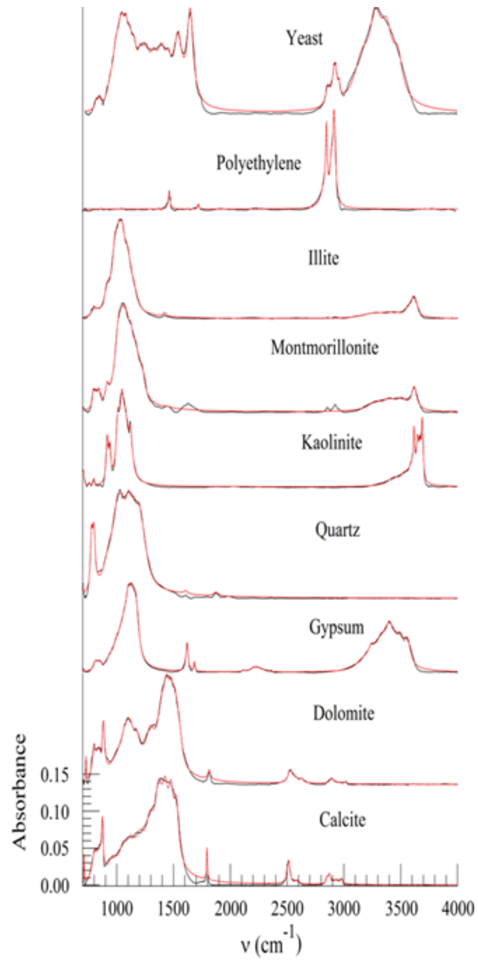


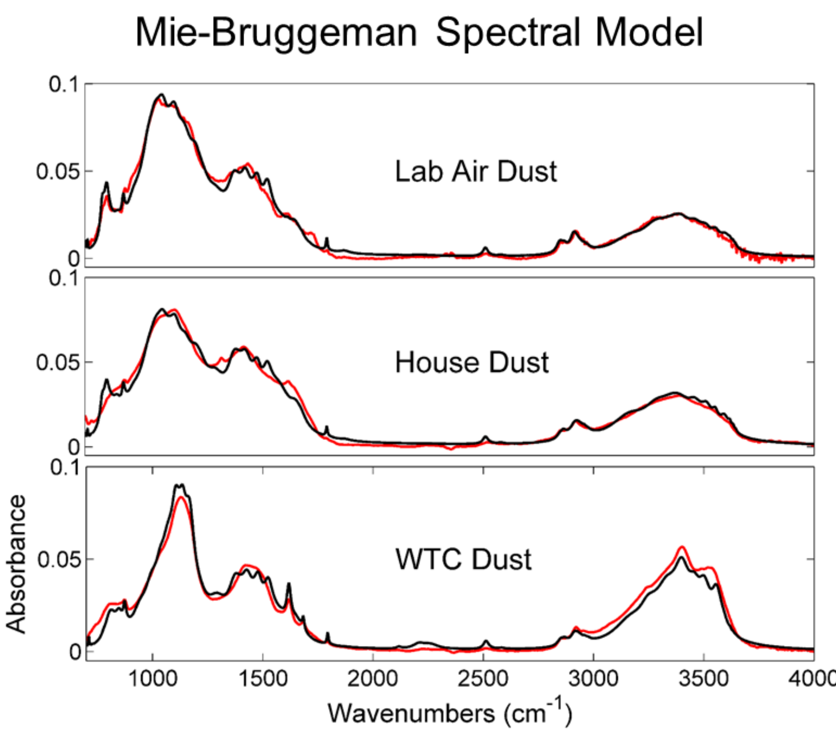
Figure 3. Average IR spectra of calibrant particles. *Spectra of individual calibrant particles were averaged and fit to the permittivity defined by a damped harmonic oscillator model .*

IV. Mie-Bruggeman Model

A Mie-Bruggeman model has been developed to analyze the average spectrum of a dust particle collection in order to obtain volume fractions of the components[12]. Bruggeman theory is a simple effective medium theory that provides an effective permittivity, ε_{eff}, of a mixture based on component volume fractions, f_i, and the pure permittivities of the components, ε_i. Our model uses a numerical iterative approach starting with an initial guess of the volume fractions which is used to obtain an initial guess of the effective permittivity. Then the following relation is used interatively to refine the guess

$$\varepsilon_{eff,k} = \frac{\sum_{i=0}^{n-1} \frac{f_i \varepsilon_i}{\varepsilon_i + 2\varepsilon_{eff,k-1}}}{\sum_{i=0}^{n-1} \frac{f_i}{\varepsilon_i + 2\varepsilon_{eff,k-1}}} \quad . \tag{2}$$

The expression has been used with mixtures of up to 10 components. The effective permittivity of the mixture is used with Mie theory to predict an orientationally-averaged IR spectrum of an average particle of the mixed sample, then the volume fractions are varied in a nonlinear least squares approach while comparing to the experimental



Volume Fractions

Calibrant	Lab Air %	House Dust %	WTC %
quartz	24	15	2
carbonate	12	12	11
clay	24	18	0
gypsum	5	1	50
organics	34	53	36

Figure 4. Mie-Bruggeman model fits. *Mixture model fits of the average IR spectra from single particle collections of lab air, house dust from a filter, and the World Trade Center 9/11/2001 event.*

average spectrum in order to find the best fit. Figure 4 shows the best fits for lab air dust, house dust, and the World Trade Center 9/11/2001 event. Our group has developed both Fortran and MATLAB programs which are based on Bohren and Huffman's Mie theory code[13] (appendix of 1987 edition gives Fortran code, other options are available at https://code.google.com/p/scatterlib/wiki/Spheres, used without modification). The nonlinear least squares fitting used grid-search method[14] with constraints to keep the volume fractions positive. The Mie-Bruggeman model is preliminary. Work on known single particle mixtures that we have synthesized is underway to address fit stability and convergence, as well as the possibility of multi-value composition solutions.

V. International Space Station

Vacuum cleaner bag debris from the International Space Station (ISS), expedition 31, was provided to us by NASA. Most of what is currently known about the composition of ISS dust comes from studies featuring scanning electron microscopy with energy dispersive X-ray spectrometry (SEM EDS)[15]. The EDS work gives mass % of elements which is quite important, but one would need information about the chemical formulas of possible component materials to estimate mass fractions of components, i.e. a model of possible components. The FTIR technique gives

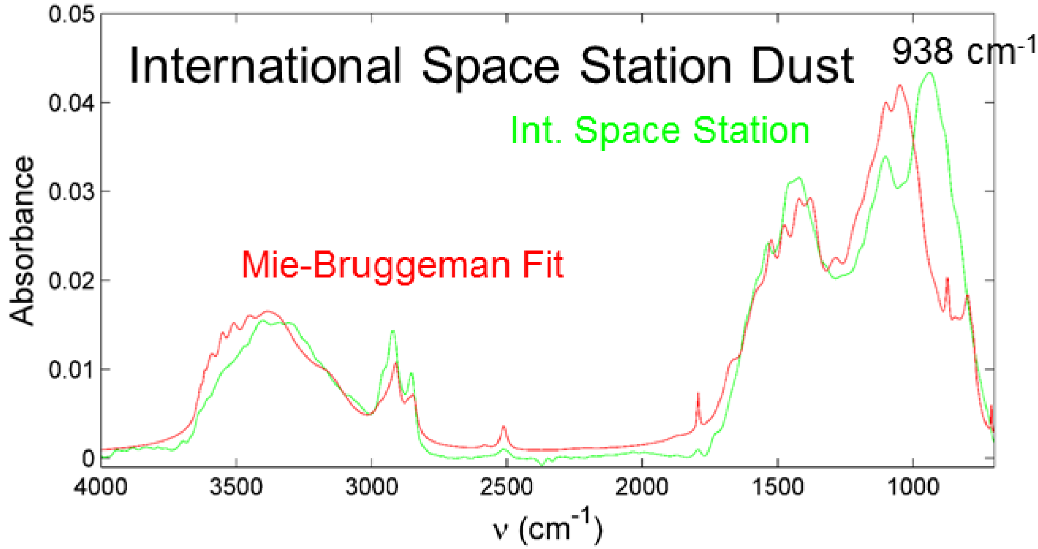


Figure 5. Mie-Bruggeman model fit of International Space Station Dust. *Mixture model fit of the average IR spectra from ISS dust. The volume fractions are not accurate because a material in the dust with a prominent peak at 938 cm^{-1} is not present in the calibration that worked well for the previous dust collections. The fraction of organics was 62%, however this value will change when the missing calibrant is discovered.*

more insight on how elements bond with each other and therefore on the identity of the component materials. This information is different and complimentary to the analysis done by EDS. Our work is focused on individual respirable dust particles in a narrow size range of perhaps ~3.8-4.5 μm. The size range of particles that are trapped in the holes of our plasmonic mesh is fixed by the size of the holes and produces a much narrower distribution compared to common filtering methods. While we measure a very specific particle size, please note that our results can be applied to particles of any size or a distribution of sizes. The chemical composition of respirable particles can be very different than the composition of the bulk dust sample, indeed the categories of components of a bulk study are usually very different than the calibrants of our Mie-Bruggeman model. Our work bears directly on the particles that the astronauts are inhaling.

A small scoop of the finest cut of ISS dust was placed on top of a piece of our plasmonic Ni mesh while air was pumped through from beneath. The spectra of ~60 individual particles are displayed at the right most side of Figure 2. A Mie-Bruggeman fit of the average ISS dust spectrum is given in Figure 5. There is a peak in the experimental average ISS dust spectrum at 938 cm^{-1} which does not fit with the Mie-Bruggeman model, even though the model worked well for lab air, house dust, and the WTC 9/11/2001 event. Accurate volume fractions require that all important materials are in the calibration, so a search is underway for a missing calibrant component with a prominent peak around 938 cm^{-1}. Many dust components and zeolites have prominent peaks at ~1000 cm^{-1} which is a bit higher than the peak of the missing calibrant. Possible candidates for the missing calibrant include borosilicate fibers from the particulate filters, polymer coatings like polyacetal, and zeolites from the carbon dioxide scrubbers. Apparently, NASA currently employs Ca^{2+} LTA (5A Zeolite) for CO_2 removal on board the ISS[15, 16]. Zeolites are aluminosilicates with strong silicate bands at ~1000 cm^{-1}, however the substitution of Ca^{2+} for the more typical Na^{+} of zeolites likely leads to a red shift of the silicate band into a region[17] from ~920 cm^{-1} to 1000 cm^{-1}. For this reason, we think Ca^{2+} LTA it the most likely possibility. This is speculative, but interesting, because the previous SEM EDA study[15] found no definitive evidence for particles from the zeolites of the carbon dioxide removal assembly. Clearly, zeolites, particularly Ca^{2+} substituted zeolites, need to be included in our list of calibrants, as well as other possible matches such as borosilicates and polyacetals. Work recording single particle spectra of these and other candidate components continues on this project.

VI. Conclusion

Single particle, scatter-free IR absorption spectra can be recorded of subwavlength particles using plasmonic metal mesh and an imaging Fourier transform IR microscope. Collections of single particle IR spectra have been recorded from lab air, dust from a house filter, the World Trade Center 9/11/2001 event, and the International Space Station. A dust library is being compiled including the collections of dust particles from different environments and pure materials that are known components of dust. A Mie-Bruggeman model which predicts the IR spectra of mixtures of components has been successfully applied to the former three collections, however more work on calibrant components is required to discover a missing major component of respirable dust particles on the International Space Station.

Acknowledgments

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