Infrared Spectra of 1-5 μm Dust Particles in Plasmonic Mesh

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By

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Abstract

Some types of dust, such as powdered quartz and coal dust, can enter the lungs and cause serious health problems. It is known that an increase in concentration of particulate matter will correlate to an increase in death rate. These particles and particulate matter in general, are under EPA regulation. Particles less than ~5 µm can be inhaled into the human lungs and can cause diseases, while larger particles are filtered by the human nose and throat. The characterization of the size and chemical composition of respirable dust will be important in future health studies. It is difficult to obtain good infrared spectra of particles that are the same size as the wavelength of light. Spectra of such particles are dominated by scattering rather than absorption. This affects the ability to identify the chemical composition of the particles. This project solves the scattering problem by capturing single dust particles in the holes of infrared plasmonic mesh. “Scatter-free” infrared spectra were recorded to determine the chemical composition of respirable dust particles in the 1-5 µm critical size region.
Acknowledgments

I acknowledge Dr. Coe and my group members for being helpful and understanding for all the time I had spent on the data and writing my thesis.
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Major Field: Chemistry

Minor Field: Japanese
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1.1 Why does dust even matter?

It is often easy to forget that dust is highly integrated into our everyday life and can have a profound impact on human health. There are numerous possible sources of dust such as pollen, viruses, fibers, bacteria, diatoms, skin flakes and much more. Some of these types of dust particles are highly monitored and studied. Other dust particles, that are harder to quantify, are the dusts from modern inputs such as radioactive dust from nuclear disasters, pesticides, asbestos and other poisonous smokes\(^\text{[1]}\). Dust generally in small amounts does not affect the state of the human health and the human lungs are well adapted to filtering dust. However, inhaling large quantities of dust can have a detrimental effect on human health. One example of a mass of dust particles caused by a natural event is a dust storm.

Dust storms are an example of an over abundance of particulate matter. They can have a global production between 1060 and 1070 Tg per year with very high spatial and temporal variability\(^\text{[2]}\). North Africa accounts for 70% of this total dust emission. The dust storms have an ability to not only affect those involved in or around the storms, but can also affect those far away on other continents. One of the places that have frequent dust storms is Inner Mongolia from an increase in soil erosion\(^\text{[2]}\). When mass amounts of dust become localized, it turns into a dust storm. These dust storms are natural
geological processes that move and deposit up to 1 mm by strong winds in one storm under different transport modes and these storms often affect areas that are far away from the original source. These dust storms can be caused by wind erosion in desert and steppes, but in places where the top soil is deteriorating such as China, dust storms can be derived from grasslands, loose soils and lake sediments. Dust storms can have a considerable effect on visibility, air quality, human health, and even the climate system. A dust storm in Inner Mongolia of category DM 1, the lowest level for a dust storm, can have density level of PM$_{10}$ of 241µg/m$^3$. On average, there are roughly 30 µg/m$^3$ of urban dust density in the air on a normal day. This is approximately 5x the amount over the density of a healthy air quality (≤-54 µm/m$^3$ of PM$_{10}$) and would be categorized as the color “Orange” in air quality standards set by the EPA$^3$. These dust storms that occur in Mongolia can affect those in North America. This was observed by satellite during a large dust storm that produced a huge atmospheric dust cloud traveling across the Pacific Ocean to the Pacific Coast of North America$^4$. Large dust storms have the potential to affect the PM levels across the United States. Dust particles can contribute to cardiovascular or heart disease, and affect those with asthma$^5$. The metal components in the dust storms have the potential to lower children’s pulmonary function$^5$. The amount of dust in the air is not just a local problem; it can be a world-wide problem that can affect millions.

1.2 1-5 µm dust can enter the human pulmonary system

The human lung is an organ adapted to breathing large quantities of air at any given time. The lungs are capable of taking in 14,000 quarts of air each day, which passes
through the walls of 500 million alveoli \cite{1}. Lungs can capture and expel dust particles quite efficiently, but this is not applicable to over exposure of dust particles. The dust that enters into the lungs can be dissolved and others dispersed as it is ejected as phlegm, but miniature rocks such as sandstone will accumulate in the lungs. These accumulations of miniature rocks can cause diseases and restrict lung function.

Not all dust particles can enter deep into the human lungs. Spherical dust particles larger than 10 µm cannot enter the human lungs because they are too large and are caught by the nose and throat. However, dust particles from the size of 6 to 10 µm can enter deeper into the thorax. Dust particles smaller than 5 µm can enter into the human lungs and eventually into the human alveoli. Dust particles with the approximate size of 1 µm are the largest that can enter into the deeper parts of the lungs. These dust particles are potentially the most dangerous dust particles because they can carry most of the mass. Thus, it is important to have an understanding of the impact that dust particles can have on the pulmonary system especially the particles in the range of 1 to 5 µm.

1.3 Increase death rate from dust

The Environmental Protection Agency (EPA) regulates other chemicals such as carbon monoxide, lead, nitrogen dioxide, and ozone. Due to the increasing known risk associated with fine particulate matter, dust particles that are smaller than 10 µm are also regulated and monitored by the EPA. There are two categories of dust under 10 µm: coarse particulate matter (PM\textsubscript{10-2.5}) which ranges from 10-2.5 µm and fine particulate matter (PM\textsubscript{2.5}), any particles less than 2.5 µm. The EPA recommends a 24-hour exposure limit of 70 µg/m\textsuperscript{3} for PM\textsubscript{10} dust particles. A rise in 10 µg/m\textsuperscript{3} in dust will raise the
mortality rate by 0.25% \[6\]. EPA regulates these particles because particulate matter has been associated with increased respiratory symptoms, decreased lung function, aggravated asthma, development of chronic bronchitis, irregular heartbeats, nonfatal heart attacks, and premature death with people with heart or lung disease\[3\]. Thus, the EPA takes daily dust readings usually categorized as the Air Quality Index (AQI), ranging from 0 (good) to 500 (hazardous) by the density of the particulate matter in the air.

Occupational risks also consist of dust hazards with a wide range of associated illnesses and diseases. Masonry workers exposed to quartz can develop acute silicosis \[1\]. Coal miners can eventually develop a black lung disease after years of working at a coal mine. The fine mineral dusts closely associated with these occupations can be deadly, but the existence of harmful dust is not limited to rock minerals. Natural sources of dust can also affect human health such as cotton dust. Cotton dust causes a disease known as brown lung because the dust is a mixture of plant parts, dirt, and bacteria\[1\]. Working with wood can also cause diseases such as sequoiosis and paper-mill-worker’s lung. Biological sources of dust such as wood and cotton often contain fungal dust or bacteria which are the harmful portions of dust. Not all dust directly causes diseases, but minuscule things that are associated with dust can also cause diseases.

In December of 1952, London experienced an unprecedented day known as the London Smog Event. Due to the over combustion of coal, sulfur dioxide and particulate matter accumulated in the air forming a heavy dense fog. This fog is believed to have PM$_{10}$ concentration between 3,000 and 14,000 µg/m$^3$. This event well exceeds the “green” category for PM$_{10}$ categorized by the EPA between 0 to 54 µg/m$^3$. This
unhealthy concentration of particulate matter had dire consequences to the London population with at least 4,000 and as much as 12,000 mortalities. It can be clearly seen that there is a direct correlation between dust and health.

1.4 Purpose of the investigation

As seen in the earlier paragraphs, dust particles or particulate matter is an important part of our everyday health. The chemical identity of these particles is not well known in terms of its effect on the human body. The project will determine the chemical composition and size distributions of micron-scale particles. IR spectra of single dust particles in mesh will provide chemical analysis needed to categorize the particles and correlate to size. The data assembled from this project can be used to identify the possible harmful dust particles that are present within that range.
CHAPTER 2

COLLECTING DUST

2.1 How to collect dust on filters

In order to physically classify dust particles by their relative size, dust was collected onto polycarbonate filters using a SKC pump AirChek®XR5000 which can pump air at the speed of 1 to 5 L/min. The polycarbonate filters are circular filters that are 25 mm in diameter with a filter threshold of 0.8 µm. They are no hydroscopic which enables µg amounts to be weighted. The filter has two sides, rough and smooth. The smooth side of the filter is useful for microscopic observations the dust particles and was used to collect dust in Evans Lab Room 0055 for this section of the chapter. The polycarbonate filter was placed inside a 25 mm in-line Derlin Filter Holder made by SKC Inc. This filter holder has a length of 2 cm, diameter of 3.5 cm, and an effective filtration area of 3.7 cm². This filter holder can be attached from a hose barb adaptor that has an outer diameter of 6.4 mm and an inside diameter of 4 mm to a vacuum line from the fumehood under constriction. Since the air pump was the used at this time, the speed of the air flow was not measured. The air was filtered for 18 hours and 25 minutes over a period of two days. The filter was then weighed on a CAHN GRAM Electrobalance Model G with a total dust accumulation of 0.188 mg. The dusty polycarbonate filter was then analyzed under the optical microscope (Olympus B40) with a 50x objective and pictures were taken from a computer.
2.2 Separation of dust by size

The images taken in the previous section were analyzed using a program called ImageJ, a NIH freeware. First, the dust particles were identified and differentiated from the polycarbonate filter. The dust particles were identified as small specks on the white polycarbonate filter. Lines were drawn around the dust particle using a function called “free hand selection” on ImageJ. From here, by clicking on the “Measure” function, the effective dust pixel area was measured. In order to determine the area of the dust particle in µm, a reference picture of Ni-Mesh (12.6 µm lattice parameter) was taken. The conversion unit between the image pixel and the actual size in µm was established to be 28.44 pixel/12.6 µm. In order to determine an effective diameter, the area obtained from each dust particles were set equal to the area of a circle, \[ A = \frac{\pi}{4} d^2. \] The effective pixel areas of dust particles were converted into µm². These effective diameters of the dust were then assembled into a histogram shown in the figure below.
Figure 2.1: Size and volume distribution of dust. The dust was collected on 7/16/2009 and 543 dust particles were measured placed into 23 bins that are \( \sim 0.65 \) \( \mu \)m in width.

As seen in the figure above, the dust particle distributions peak at the effective diameters of 1.7 \( \mu \)m, 6.3 \( \mu \)m, and 9.5 \( \mu \)m. This indicates that there are at least three distributions in the graph, which suggests (at least) three possible sources of these dusts.
The dark line that goes through the dots in the figure is the sum of the three lognormal terms with three parameters each.

\[
N(d) = a_1 \cdot e^{-0.5\left(\frac{\ln(d) - \mu_1}{\sigma_1}\right)^2} + a_2 \cdot e^{-0.5\left(\frac{\ln(d) - \mu_2}{\sigma_2}\right)^2} + a_3 \cdot e^{-0.5\left(\frac{\ln(d) - \mu_3}{\sigma_3}\right)^2}
\] (1),

where \(N(d)\) is the number of particles/bin, \(d\) is the diameter (µm), \(a\) is a count, \(\mu\) is the mean [in units of \(\ln(d)\) in µm] at a max in a log plot, and the \(\sigma\) is the variance [in units of \(\ln(d)\) in µm]. This equation represents the lognormal distribution with three parameters seen in the top half of Figure 2.1. The fitted values of \(a_1, a_2,\) and \(a_3\) are 135, 15, and 5 respectively. The fitted values for \(\mu_1, \mu_2,\) and \(\mu_3\) are 0.55, 1.82, and 2.25 respectively. The filled values used for \(\sigma_1, \sigma_2,\) and \(\sigma_3\) are 0.45, 0.14, and 0.05, respectively.

For the line in the volume plot, the number of dust in each bin was multiplied by the volume of each particle as a sphere, \(\frac{1}{6} \pi \cdot d^3\). Although the greatest numbers of particles occur at the effective diameter of ~1.7 µm, the diameters that contribute the largest volume are the peaks with the respective diameters of 6.3 and 9.5µm. This is important because the largest volume usually contains the most mass, which can fuel more reactions.

2.3 Collecting dust on mesh

In order to analyze the chemical composition of dust, single particles of dust needed to be trapped into the 5 µm holes of a plasmonic mesh. Our mesh is a plasmonic film of Ni metal with an array of holes that are ~5 µm width, 12.6 µm apart from each other, with 2 µm thickness as shown in Figure 2.2 (a).
Next, a 5 mm hole was cut out of the polycarbonate filter using a fine metal point and a piece of mesh was cut to cover the hole. The mesh completely covered the hole and was taped onto the filter using scotch-tape. This mesh-modified polycarbonate filter was then placed into a filter holder and fitted onto the air pump flowing at a rate of 1 L/min. Dust was collected on this filter for 4.8 days accumulating 0.008 mg of dust on the mesh. Due to the higher conductance of air through the mesh, rather than the polycarbonate, dust accumulated on the mesh rather than on the polycarbonate filter.

Next, the infrared (IR) spectra of dusty mesh were recorded with a Perkin Elmer IR Elmer Spectrum Spotlight 300 IR imaging microscope. It is equipped with an array of 16 N₂ (l) cooled Mercury Cadmium Telluride (MCT) detectors. It has an imaging
resolution of 6.25 \(\mu\text{m}\) and a wavenumber range of 720-7800 \(\text{cm}^{-1}\). Light incident on the sample comes in a cone with a range of angles from 17\(^{\circ}\) to 37\(^{\circ}\) due to Cassegrain optical system of the microspectrometer.

Two types of scans were used with the instrument. A point mode scan and an image mode scan. Point mode scans a large general area and produces a spectrum for the whole area. Seven point mode scans of 200 \(\mu\text{m}\) x 200 \(\mu\text{m}\) with 512 scans/pixel were taken over different regions on the dusty mesh. Each scan took \(~10\) minutes and the seven scans were averaged to get a good bulk spectrum for the sample. The image mode scanned over a region of 120 \(\mu\text{m}\) x 120 \(\mu\text{m}\) with 4 \(\text{cm}^{-1}\) resolution, 256 scans/pixel, 141 minutes scan time, on the region shown in Figure 2.3. This data was used to see the individual spectrum of the 62 dust particles.
Figure 2.3: Dust 08709 with the assigned hole numbers. There was a total of 0.008 mg of dust accumulated on the mesh.

From here on, the dust particles numbers are assigned by the hole number given in Figure 2.3. Thus, dust # 40 is a dust particle that is in hole 40. The dotted lines defined a 120 μm x 120 μm region to be scanned by the instrument. However, the instrument is never aligned perfectly, so the actual scan region is defined by the solid box outline. The horizontal axis is offset by 11 μm and the vertical axis is offset by 16 μm.
CHAPTER 3

CHEMICAL IDENTITY OF DUST

3.1 Difficulties in taking an IR spectra of micro-sized particles

Chemical analysis of dust particles must be done to determine their chemical composition. However, there are many problems associated with taking IR spectra of micro-sized particles. One of the problems arises from Mie scattering. The light scatters more efficiently in this case rather than being absorbed and this results in an IR spectrum dominated by scattering rather than absorption.

Figure 3.1: IR spectra of polystyrene on ZnSe and in mesh hole[7]

![IR spectra graph with labels and images showing isolated on surface and in metal mesh hole conditions.](image)
There are two IR spectra in Figure 3.1 which are very different from one another. The broad spectrum is a result of one single 5 μm latex sphere on ZnSe and is dominated by scattering. The other spectrum with sharp peaks is due to 5 μm latex sphere inside a mesh hole and is dominated by absorption. There are fundamental differences between the graphs that are dominated by absorption and scattering. The first difference is that the absorption peaks of a 5 μm latex sphere on ZnSe appear as derivatives (Christianson Effect) making the peaks hard to distinguish in the scattered background [7]. However, when the dust particles are placed into mesh holes, absorption dominates rather than scattering. Strong peaks are apparent throughout the spectrum and clearly visible against the background. This indicates the importance of the use of mesh when taking IR spectra of μm-sized dust particles. The mesh acts as a metal belt around the particle which reduces the scattering of light and highlights the vibrational features [7]. The largest component of the scattering background will either bounce off the surface of the metal or bounce back to the particle to be absorbed or transmitted. Thus, the mesh is employed in the experiment to record undistorted, “scatter-free” spectra that can be analyzed with Beer’s Law and standard chemistry techniques.

3.2 Bulk spectra of dust

Dust was separated into three distributions in the previous chapter. However, the chemical identity of the dust is still unknown. To know the identity of the general or the common components in dust, the average spectrum of dust particles need to be analyzed. The average spectrum of 62 individual dust particles was compared against the average of 7 spectra taken over different large sections of dusty mesh.
Figure 3.2: Average IR spectra of 62 individual dust particles and 7 scans over large regions of mesh.

The average of 62 individual dust particles is very similar to the average of the 7 spectra over large regions of the dusty mesh. This indicates that the population of dust particles in the 62 individual dust spectra is a good representation of the average bulk dust spectrum.

3.3 Individual spectra of dust

The first question when dealing with dust particles: Are all dust particles the same on a micro-scale level? How are the individual particles different from the average
spectra of dust particles? To address these questions, analysis of individual dust particles was made from the 62 dust spectra.

![Mesasurements of holes filled, empty or close to empty](image)

<table>
<thead>
<tr>
<th>Number of Dust Particles</th>
<th>Hole Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filled Holes</td>
<td>1, 2, 3, 4, 5, 6, 10, 11, 12, 13, 15, 16, 17, 18, 20, 21, 22, 23, 24, 25, 28, 32, 33, 34, 38, 39, 40, 43, 47, 49, 50, 57, 66, 69, 61, 63, 64, 65, 70, 72, 77, 78, 79, 80, 81, 82, 83, 84, 90, 91, 92, 93, 94, 95, 96, 97, 99, 98, 100</td>
</tr>
<tr>
<td>Close to Empty</td>
<td>26, 27, 321, 36, 43, 45, 48, 52, 53, 55, 60, 69, 71, 76, 66, 101</td>
</tr>
<tr>
<td>Empty Holes</td>
<td>23</td>
</tr>
</tbody>
</table>

Figure 3.3: The mesh with the respective hole numbers and a table to the right categorizing the hole as filled, empty or close to empty.

The average spectrum of the 23 empty holes was used as the background for the 62 individual spectra. They were compared against one another and to the average spectrum for similarities and differences. The individual spectra are given in Figure 3.4-3.19.
Figure 3.4: IR spectra of hole 1, 2, 3 and 4. The spectra have a resolution of 4 cm\(^{-1}\) and have 256 scans/pixel.
Figure 3.5: IR spectra of Hole 5, 6, 10, and 11. The spectra have a resolution of 4 cm$^{-1}$ and have 256 scans/pixel.
Figure 3.6: IR spectra of Hole 12, 13, 14, and 15. They have a resolution of 4 cm\(^{-1}\) and have 256 scans/pixel.
Figure 3.7: IR spectra of Hole 16, 17, 18, and 20. The spectra have a resolution of 4 cm\(^{-1}\) and have 256 scans/ pixel.
Figure 3.8: IR spectra of Hole 21, 22, 23, and 24. The spectra have a resolution of 4 cm\(^{-1}\) and have 256 scans/pixel.
Figure 3.9: IR spectra of Hole 25, 28, 32 and 33. The spectra have a resolution of 4 cm\(^{-1}\) and have 256 scans/ pixel.
Figure 3.10: IR spectra of Hole 34, 36, 38, and 39. The spectra have a resolution of 4 cm⁻¹ and have 256 scans/pixel.
Figure 3.11: IR spectra of Hole 40, 46, 48, and 49. The spectra have a resolution of 4 cm$^{-1}$ and have 256 scans/pixel.
Figure 3.12: IR spectra of Hole 50, 57, 58, and 59. The spectra have a resolution of 4 cm$^{-1}$ and have 256 scans/ pixel.
Figure 3.13: IR spectra of Hole 61, 63, 64 and 65. The spectra have a resolution of 4 cm\(^{-1}\) and have 256 scans/pixel.
Figure 3.14: IR spectra of Hole 68, 70, 72, and 77. The spectra have a resolution of 4 cm$^{-1}$ and have 256 scans/ pixel.
Figure 3.15: IR spectra of 78, 79, 80, and 81. The spectra have a resolution of 4 cm\(^{-1}\) and have 256 scans/pixel.
Figure 3.16: IR spectra of hole 82, 83, 84, and 90. The spectra have a resolution of 4 cm\(^{-1}\) and have 256 scans/pixel.
Figure 3.17: IR spectra of Hole 91, 92, 93, and 94. The spectra have a resolution of 4 cm$^{-1}$ and have 256 scans/pixel.
Figure 3.18: IR spectra of Hole 95, 96, 97 and 98. The spectra have a resolution of 4 cm$^{-1}$ and have 256 scans/pixel.
Figure 3.19: IR spectra of Hole 99 and 100. The spectra have a resolution of 4 cm\(^{-1}\) and have 256 scans/pixel.
3.4 Chemical identification of dust particles

The individual spectra of dust particles vary considerably from the average spectrum of the dust particles. Although, they were different from one another, this did not mean that they were pure compounds. There were at least 31 dust particles that contained carbonate, but the identity of the other components that may have been commonly shared in the dust particles are still being analyzed. To better categorize the 62 dust spectra, the spectra were scanned for various common chemical characteristics.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Number of Dust</th>
<th>Total Percentage (%)</th>
<th>Identifying Peak (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate (CO₃²⁻)</td>
<td>31</td>
<td>50</td>
<td>789</td>
</tr>
<tr>
<td>Nitrate</td>
<td>4</td>
<td>6.5</td>
<td>1384</td>
</tr>
<tr>
<td>Quartz</td>
<td>6</td>
<td>9.7</td>
<td>Doublet at ~800</td>
</tr>
<tr>
<td>Organic</td>
<td>24</td>
<td>38.7</td>
<td>2800-3100</td>
</tr>
<tr>
<td>Clay</td>
<td>31</td>
<td>50</td>
<td>~1000</td>
</tr>
<tr>
<td>Total Amount of Dust</td>
<td>62</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 3.1: Table listing how many dust particles consisted of the characteristics

3.4.1 Dolomite vs. calcite

Ohio was once a glaciated area approximately 14,000 years ago during the Pleistocene Era. When the glaciers retreated, sedimentary deposits called till were left behind as remnants [8]. These deposits are often found containing minerals with cations such as, Ti, Zr, Fe, Ca, and K. Glaciers are known to contain dissolved CaCO₃ from the bedrock, which can be released when the glacial deposits melt. Calcite (CaCO₃) can be formed from glaciated deposits when limestone and other calceous materials are exposed to the elements during glacier retreats [9]. As the glaciers melt due to increasing
temperatures, the calceous mineral deposits such as CaCO$_3$ are left behind on the bedrock. Dolomite (CaMg(CO$_3$)$_2$) can form when the Mg minerals intermix with the calcium deposits and crystallizes. There are also variable amount of Mg naturally in shellfish. However, Mg decays on a geologically time scale eventually only leaving Ca deposits behind. The glaciated deposits would make the probability of finding carbonate particles higher within the area.

Carbonates (dolomite and calcite) are found to be components of 31 of the 62 dust particles collected on the mesh. The IR spectra of dolomite and calcite are very close to each other. However, there is a characteristic peak for dolomite at 730 cm$^{-1}$ and calcite at 713 cm$^{-1}$\textsuperscript{[10]}. The absorption peak at these two locations, suggests that 14 out of 31 were carbonate-containing dust particle dolomite and 17 out of 31 were calcite.

![Figure 3.20: The top IR spectrum is Hole 49 which greatly resembles the bottom IR spectrum of dolomite\textsuperscript{[11]}.](image)
Hole 49 is likely to be a dust particle that is mostly dolomite [Ca·Mg (CO₃)₂]. Hole 49 exhibits a large CO₃²⁻ peak at 1445 cm⁻¹ (v₃) and a small peak at 730 cm⁻¹ (v₄), which are both characteristic of dolomite [12]. The large carbonate peak at 1445 cm⁻¹ is a broader peak and can shift over a range of 150 cm⁻¹ from orientation and dispersion effects within the crystal structure [13]. The 879 cm⁻¹ (v₂) peak in dolomite is less dependent on the concentration of Mg inside the mineral [13]. Thus, this peak is not a good reference peak for dolomite and the 713 cm⁻¹ peak is used as reference for calcites (CaCO₃) [10].

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>v₁ (Raman Only)</th>
<th>v₂</th>
<th>v₃</th>
<th>v₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>1096</td>
<td>876</td>
<td>1436</td>
<td>746</td>
</tr>
<tr>
<td>Calcite</td>
<td>1086</td>
<td>872</td>
<td>1407</td>
<td>712</td>
</tr>
</tbody>
</table>

Table 3.2: The vibrational modes of calcite and dolomite [14]

The v₁ is a CO₃²⁻ symmetric stretch, the v₂ is a CO₃²⁻ asymmetric deformation, v₃ is a CO₃²⁻ asymmetric stretch, and v₄ is a CO₃²⁻ symmetric deformation [12]. Minor shifting in the peak location may be from the natural impurities present in the sample [12].
Figure 3.21: The top IR spectrum is from Hole 80 and the bottom is calcite$^{[11]}$. Hole 80 is believed to be calcite (CaCO$_3$) due to the carbonate peaks at 1454 cm$^{-1}$ and the small sharp peak at 713 cm$^{-1}$. Due to the lack of Mg in calcite, the placement of the peaks has shifted from dolomite. The tell-tale marker of carbonate in calcite at the 713 cm$^{-1}$, 876 cm$^{-1}$, and the 1450 cm$^{-1}$ makes calcite the most probable identity for hole 80.
There are also clues that suggest Hole 57 is a mixture of both calcite and dolomite. This possibility is evident with the appearance of two peaks at 714 and 729 cm⁻¹, the peak at 886 cm⁻¹, and the other corresponding carbonate peaks in the spectrum.

### 3.4.2 Silicate and clay dust particles

The next most common form of dust is clay silicate minerals. The three most common clay minerals are illite [(K,H₃O)(Al, Mg, Fe)₂(Si, Al)₄O₁₀[(OH₂), (H₂O)]], kaolinite [Al₂Si₂O₅(OH)₄], and montmorillonite [(Na, Ca)₀.₃₃(Al₆,Mg)₂(Si₄O₁₀)(OH₂)·nH₂O].
Figure 3.23: The top spectrum is Hole 5. The middle spectra is montmorillonite and the bottom is kaolinite\textsuperscript{[11]}. Hole 5 is believed to be a combination of kaolinite and montmorillonite with some carbonate. Due to its lower fraction in kaolinite than montmorillonite, the characteristic peaks at 3638 cm\(^{-1}\) and 3718 cm\(^{-1}\) are not very distinct\textsuperscript{[15]}. The carbonate
peak at 1472 cm⁻¹ and 746 cm⁻¹ are believed to be dolomite with a higher fraction of magnesium.

Figure 3.24: The top is a spectrum of hole 63 and the bottom is a spectrum of Quartz.

Hole 63 is a very good representation of quartz with a vibrational peak at 1091 cm⁻¹. The characteristic doublet at 783 cm⁻¹ and 796 cm⁻¹ for quartz is evident in the spectrum. There is a smaller presence of carbonate with peaks at ~1400 cm⁻¹, 711 cm⁻¹, and 877 cm⁻¹. This carbonate particle may be calcite due to a peak at 711 cm⁻¹.
Hole 72 has very sharp peak at 1385 cm\(^{-1}\) which can be a distinguishing marker for nitrate\(^{[16],[17]}\). This dust particle has carbonate stretches at 1445 cm\(^{-1}\) and 711 cm\(^{-1}\) which may be due to calcite.

### 3.5 The smallest CO\(_3^{2-}\) dust particle that can be detected

In this experiment, dust was sucked into 5 µm holes. The maximum size of the dust particles that can be detected are dust particle that have a diameter of roughly 5 µm. However, what is the smallest dust particle that can be detected? To investigate the smallest size particle that is visible in this experiment, calculations were done using the absorption spectra of the carbonate peaks. Calculations involving the carbonate peak at ~880 cm\(^{-1}\) was used to determine the smallest size dust particle from the list of carbonate spectra. This carbonate peak was used because 31 out of 62 (50 %) of the dust particles collected contained the carbonate peak at ~880 cm\(^{-1}\).
First, to calculate the smallest dust particle that was detected with the IR spectrometer, it was assumed that the largest signal comes from the particle with maximum volume. It was also assumed that the volume of the particle with maximum signal is about the same as the volume of the hole. The mesh hole parameters were 5 x 5 x 2 µm, so the volume of each hole is ~50 µm³. The volume of the particle was used to calculate an effective diameter of the particle if the particle was spherical with the same volume. Using this assumption, the maximum size dust particle will have a radius of 2.3 µm or a diameter of 4.6 µm. The effective diameter (d) of 4.6 µm was used for the following equations. The maximum peak area (I_{max}) correspond to the maximum volume (V_i), serving as a ratio to obtain the effective spherical volumes of CO_3^{2-} in each dust particle from the intensity(I_i) of the IR absorption at 879 cm^{-1}.

\[
\frac{V_i}{V_{max}} = \frac{I_i}{I_{max}} \tag{2}
\]

The basic equation for the volume of the sphere (V), \(V = \frac{1}{6} \pi \cdot d^3\) is used with equation 2 to get, \(d_i = \left(\frac{6 \cdot V_e \cdot I_i}{\pi \cdot I_{max}}\right)^{\frac{1}{3}}\), where d_i is the effective spherical diameter of carbonate for the index species. Since \(V_i = \frac{4}{3} \pi \left(\frac{d_i}{2}\right)^3\), the d_i can be rewritten as:

\[
d_i(\mu m) = 2.8 \cdot \left(\frac{I_i}{I_{max}}\right)^{1/3} \tag{3}
\]

The results are given in Table 3.3.

<table>
<thead>
<tr>
<th>Hole Number</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Peak Area (units)</th>
<th>d_i (diameter in µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>880.6</td>
<td>0.061</td>
<td>1.7</td>
</tr>
<tr>
<td>21</td>
<td>878.3</td>
<td>0.546</td>
<td>3.6</td>
</tr>
<tr>
<td>22</td>
<td>88.13</td>
<td>0.278</td>
<td>2.8</td>
</tr>
<tr>
<td>28</td>
<td>877.9</td>
<td>0.213</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>32</td>
<td>880</td>
<td>0.913</td>
<td>4.2</td>
</tr>
<tr>
<td>33</td>
<td>880.1</td>
<td>0.914</td>
<td>4.2</td>
</tr>
<tr>
<td>38</td>
<td>876.5</td>
<td>0.48</td>
<td>3.4</td>
</tr>
<tr>
<td>39</td>
<td>878.2</td>
<td>0.406</td>
<td>3.2</td>
</tr>
<tr>
<td>40</td>
<td>877.6</td>
<td>0.188</td>
<td>2.5</td>
</tr>
<tr>
<td>46</td>
<td>883.9</td>
<td>0.599</td>
<td>3.7</td>
</tr>
<tr>
<td>47</td>
<td>883.9</td>
<td>0.798</td>
<td>4.0</td>
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<tr>
<td>49</td>
<td>878.9</td>
<td>1.007</td>
<td>4.4</td>
</tr>
<tr>
<td>50</td>
<td>875.3</td>
<td>0.128</td>
<td>2.2</td>
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<tr>
<td>57</td>
<td>886.6</td>
<td>0.324</td>
<td>3.0</td>
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<tr>
<td>58</td>
<td>885.2</td>
<td>0.412</td>
<td>3.2</td>
</tr>
<tr>
<td>59</td>
<td>885.6</td>
<td>0.397</td>
<td>3.2</td>
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<tr>
<td>63</td>
<td>876.1</td>
<td>0.183</td>
<td>2.5</td>
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<td>91</td>
<td>878</td>
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</tr>
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</tr>
<tr>
<td>96</td>
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<td>0.212</td>
<td>2.6</td>
</tr>
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<td>97</td>
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<td>0.387</td>
<td>3.2</td>
</tr>
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<td>98</td>
<td>882</td>
<td>0.304</td>
<td>2.9</td>
</tr>
<tr>
<td>99</td>
<td>886</td>
<td>0.363</td>
<td>3.1</td>
</tr>
<tr>
<td>100</td>
<td>881.9</td>
<td>0.443</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Table 3.3: List of hole number, peak area, peak height and the effective radius for dust particles with carbonate.

From the list of particles with carbonate, the smallest size carbonate dust particle that can be seen is < 1.7 μm. To see smaller particles than 1.7 μm, the scanning resolution and the signal to noise ratio must be improved. Instead of scanning with a resolution of 256 scans/pixel, scanning with 512 scans/pixel would improve the quality of the data and the signal-to-noise ratio. This in turn can improve the ability to see particles that are smaller than 1.7 μm.
3.6 Principle component analysis

Principle component analysis (PCA) is a mathematical method used to separate data into groups. This separation of groups is useful for quantifying and categorizing the components in a dataset. This analysis was used on the 62 individual dust particle spectra that were obtained. By separating the dust particles using the PCA, a correlation, in the dust particles may become apparent. In order to do this, several steps must be taken with the 62 individual dust particle IR spectra. First the IR spectra of the 62 dust particles were placed into columns in a large matrix, X.

![Table of matrix X]

Figure 3.26: Matrix X starting from column 0 as Hole 1 with the absorption spectrum of each hole spectra in columns. The average spectra of the 62 dust particles (\( \bar{x} \), as a column) was computed (as shown in Figure 3.26) and subtracted from each of the spectra in columns to form a new matrix, B.
The matrix B is multiplied by its transpose to produce a variance-covariance matrix, C.

\[ C = \frac{1}{\text{Number of spectra}} \cdot B \cdot B^T \]  

The variance-covariance matrix (C) will be used to correlate peaks within the dataset. The variance-covariance matrix is diagonalized to obtain the most important eigenvalues and the eigenvectors of the matrix. The eigenvectors, in this case, are represented as a specific IR spectrum. The eigenvector with the largest eigenvalue is labeled as principle component 1 or PC1, as shown in Figure 3.27. The second most important component will be principle component 2 or PC2, and the process continues as one gets further down into the Ps. When the scores of principle components (Eq. 6) are plotted against one another, the dust particles separate into groups.

\[ Y = W^T \cdot Z \]

where Y is the scores of the principle component, the Z is the Z-score matrix, and \( W^T \) is the transpose of the W matrix, where W is defined as the eigenvectors. The first principle component score (P1) as the y-axis and the second principle component score (P2) as the x-axis were correlated with each other onto a score as shown in Figure 3.28.
Figure 3.27: The top graph is a spectrum of principle component 1 and the bottom is a spectrum of principle component 2.
Figure 3.28: PCA analysis (700 -900 cm\(^{-1}\)) comparing P1 and P2 of the 62 dust particles, where the number indicates the hole of the dust particle.
The calcite (713 cm\(^{-1}\)) is separated from the dolomites (730 cm\(^{-1}\)) in the previous section, also separate on the PCA scores. The dolomite, the upper group, and the calcite the lower group are separated diagonally from each other on the score plot. The numbers seen in the PCA scores corresponds to the hole number of the dust particle. Thus, if a dust particle is in Hole 1 then it is referenced as “1” on the plot. The dust particles that are on the furthest outer edge of the grouping are the strongest representative for the group. For example, Hole 49 is a very strong representative of dolomite, and is on the out edge of the grouping. The dust particles that are around the borderline of the calcite and dolomite along the P1 = 0 line, tends to have both dolomite and calcite peak such as the one seen in Hole 57. The dust particles below the P1 = 0 line then tends to become more calcite-like in the calcite grouping.
Figure 3.29: PCA of P1 vs. P2 showing the correlation between 713 and 730 cm$^{-1}$ of dolomite and calcite
The particles that are further from the intersection point are particles that have stronger composition of Mg\textsubscript{2}CO\textsubscript{3} than Ca\textsubscript{2}CO\textsubscript{3}. As the dolomite particles near the calcite groups, the composition between the Mg and the Ca becomes more even. The particles on the far side of the calcite groups are primarily composed on Ca\textsubscript{2}CO\textsubscript{3}.

### 3.7 Separation into four groups

Using the PCA analysis as seen in Figure 3.30, it can be seen that the 62 dust particles have separated into two other groups other than calcite and dolomite.

![PCA plot (700-900 cm\textsuperscript{-1}) of P1 vs. P2 with all four groups](image)

Figure 3.30: PCA plot (700-900 cm\textsuperscript{-1}) of P1 vs. P2 with all four groups
Figure 3.31: IR spectra of the four groups: calcite, dolomite, group 1 and group 2.
The IR spectra of all four groups with the average spectrum are compared against one another on the same plot. The IR spectra of dolomite and calcite groups are very similar to the average spectrum. However, the two other groups, Group 2 and Group 1 are slightly different from the average. Group 2 have peaks around 1000 cm\(^{-1}\) suggestive of clay minerals that contain silicates such as quartz. The PCA analysis of these spectra shows promise, but the work is not yet complete.
• It is important to recognize the use of plasmonic mesh to obtain the infrared spectra of individual dust particles. The plasmonic mesh allows the light that otherwise would be scattered to interact with the particles, and enhancing the absorption while minimizing the scattering effect. “Scatter-free” spectra of 62 individual 1-5 μm dust particles in the holes of plasmonic mesh were taken in this experiment.

• There were three dust size distributions with maxima at ~1.7 μm, ~6.7μm, and ~9.8μm. The three distributions can be evidence of at least three different sources of the dust particles collected on the polycarbonate filter.

• Within the 62 dust particles trapped in the mesh holes there were possible amounts of: 31 carbonates which contained varying degrees of carbonate or dolomite

• There was presence of: 26 organic: (22/26 alkane stretches and 4/26 aromatic/alkene stretches), 4 nitrates, 31 Si-clay minerals and 6 quartz.


11. RRUFF, *Database for Raman, X-ray, Infrared and Chemistry*.


APPENDIX A

Histogram distribution of the size of the dust particles

Input Dust Particle Radii in Microns

<table>
<thead>
<tr>
<th>Polycarbonate filter</th>
<th>wetlab microscope used</th>
</tr>
</thead>
<tbody>
<tr>
<td>n1 := READPRN(&quot;dust716radius.txt&quot;)</td>
<td>n1 := rows(a)</td>
</tr>
<tr>
<td>n1 := 543</td>
<td>ii := 0..n1 - 1</td>
</tr>
<tr>
<td>convert to diameter</td>
<td>a := a_ii \cdot 2</td>
</tr>
</tbody>
</table>

Make a Histogram

<table>
<thead>
<tr>
<th>number of bins</th>
<th>n := 23</th>
</tr>
</thead>
<tbody>
<tr>
<td>range of histogram in microns</td>
<td>rmax := 15</td>
</tr>
</tbody>
</table>

index for no. of edges

j1 := 0..n

define bin edges

x_{j1} := 0.0 + \frac{j1}{n} \cdot \max

shift to center of bin

y := hist(x, a)

x_{j1} := x_{j1} + \frac{\max}{n \cdot 2}

index for no. of bins and points of fit

i := 0..n - 1

Fit Histogram to a Set of Lognormal Distributions

define fitting function

\begin{align*}
\text{fln}(x, a, \mu, \sigma, a2, \mu2, \sigma2, a3, \mu3, \sigma3) & := a \cdot e^{-\frac{\ln(x) - \mu}{\sigma}} + a2 \cdot e^{-\frac{\ln(x) - \mu2}{\sigma2}} + a3 \cdot e^{-\frac{\ln(x) - \mu3}{\sigma3}} \\
\text{standard deviation} & := \sqrt{\sum_{i=1}^{n} (y_i - \text{fln}(x_i, a1, \mu1, \sigma1, a2, \mu2, \sigma2, a3, \mu3, \sigma3))^2} \\
\text{initial guesses} & := a1 := 135, \mu1 := 0.55, \sigma1 := 0.45, a2 := 15, \mu2 := 1.82, \sigma2 := 0.14, a3 := 5, \mu3 := 2.25, \sigma3 := 0.05 \\
\text{constraints} & := \text{Minerr}(a1, \mu1, \sigma1, a2, \mu2, \sigma2, a3, \mu3, \sigma3) = 0, a2 > 0, \sigma2 > 0, a3 > 0, \sigma3 > 0 \\
\text{final std. dev.} & := \text{SSE}(a1, \mu1, \sigma1, a2, \mu2, \sigma2, a3, \mu3, \sigma3) = 6.576 \\
\text{plotting range} & := x2 := 0.01..rmax
\end{align*}
Volume Distribution

volume for a particle of diam x at each bin

\[ V_i = \frac{4}{3} \pi \left( \frac{x_i^3}{2} \cdot 10^{-6} \right) \cdot 100^3 \]

continuous variable for volume for a particle of diam x

\[ V2(x2) := \frac{4}{3} \pi \left( \frac{x^3}{2} \cdot 10^{-6} \right) \cdot 100^3 \]
APPENDIX B

PCA of the 62 dust particles

Prinicipal Component Analysis of Infrared Spectra

INPUT
Input spectra in the form of text files stripped of the extra information at the beginning

\[
\begin{align*}
\text{a1} & := \text{READPRN}("h\_all\_nu.txt") \quad \text{m} := \text{rows}(\text{a1}) \quad m = 1.651 \times 10^3 \quad i := 0..m-1 \quad v_i := a_{1,0} \\
\text{X} & := \text{READPRN}("h\_all\_10.txt") \quad \text{spectra are in columns}
\end{align*}
\]

number of spectra \( n := \text{cols}(\text{X}) \quad n = 62 \quad j := 0..n-1 \)

index of the columns, one for each spectrum

\[
\begin{align*}
\text{calculate the average} \\
\text{spectrum for substraction} \\
\text{from each spectra} \\
\sum_{j} X_{i,j} \\
u_i := \frac{\text{\sum_{j} X_{i,j}}}{n}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{cccccccc}
0.2 & 0.1 & 0.0 & -0.1 \\
X_{1,0} & X_{1,1} & X_{1,9} & u_i \\
\end{array}
\end{align*}
\]

subtract the mean spectrum from each spectra (PCA is analysis of variations from the mean)

vector of all ones in the spectra direction \( h_{0,j} := 1 \quad B := X - u \cdot h \)

\[
\begin{align*}
\text{calculate the variance-covariance matrix} \\
C := \frac{1}{n} B \cdot B^T \\
\text{(need this to get the eigenvectors and scores later)}
\end{align*}
\]

57
subtract the mean spectrum from each spectra (PCA is analysis of variations from the mean)
vector of all ones in the spectra direction $h_{0,j} := 1$ $B := X - u \cdot h$

calculate the variance-covariance matrix $C := \frac{1}{n} \cdot B \cdot B^T$ (need this to get the eigenvectors and scores later)

find the most important eigenvectors using the expectation method

pick the number of desired components and make an index $L := 14$ $q := 0..L - 1$

initialize the principal eigenvector matrix $W_{i,j} := \frac{1}{n}$

pick the accuracy index $k := 10$

$W :=$

\[
\begin{align*}
&\text{for } q \in 0..L - 1 \\
&t \leftarrow B \cdot \left( B^T \cdot B \right)^k \cdot B^T \cdot W^q \\
&W^q \leftarrow \frac{t}{\sqrt{t-t}} \\
&B \leftarrow B - W^q \cdot \left( B^T \cdot W^q \right)^T
\end{align*}
\]

find the corresponding eigenvalue $D_q := \left( W^T \cdot C \cdot W \right)_{q,q}$

<table>
<thead>
<tr>
<th>$q$</th>
<th>$D_q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.678</td>
</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>6</td>
<td>9.206\cdot10^{-3}</td>
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</tr>
<tr>
<td>13</td>
<td>1.225\cdot10^{-3}</td>
</tr>
</tbody>
</table>

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SCORES

Calculate the standard deviation vector $s_i = \sqrt{C_{i,i}}$

Calculate the score matrix, it is $m \times n$

$Z := \frac{B}{s_k}$

Project the z-scores onto the new basis $Y := W^T Z$

These are the scores plotted against each other to find correlations

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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See if it works on a few spectra, still have to scale them
Output the average file and the principal components

\[
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\]

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APPENDIX C

Reference of group paper to be published

Infrared absorption spectra of individual, respirable, 1-5 μm, dust particles using plasmonic metal mesh

Katherine E. Gilwa, Lloyd D. Corwin, Marvin A. Malone, Michelle M. Lew, and James V. Coe
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100 West 18th Avenue, Columbus OH 43210-1173
(Dated: May 17, 2010)

The extinction of a single, isolated, wavelength-scale particle is dominated by scattering (as compared to absorption) as is well described for homogeneous spherical particles by Mie theory. Furthermore, vibrational/phonon spectral lineshapes of such particles are distorted (the Christiansen effect) from their pure absorption profiles when scattering is strong. These scattering effects have been diminished or eliminated by placing a single, isolated dust particle in the hole of a plasmonic metal mesh (a metal film with an array of subwavelength holes). A new method is described for recording ‘scatter-free’ infrared absorption spectra of single 1-5 μm-sized particles using a standard, benchtop Fourier transform infrared (IR) imaging microscope. Dust particles are important in a range of fields including astronomy, geology, atmospheric science, environmental science, and human health. Airborne particles in the 1-5 μm size regime are among the largest that make it into the human lungs, getting past the filtering of the nose and throat, i.e. they are respirable. The ability to record large numbers of ‘scatter-free’ single particle IR absorption spectra will be key to characterizing the chemical composition of respirable particulate matter in this important size regime for human health.

ACS numbers: 73.20.Mf, 82.80.Ck,42.48.Mj

INTRODUCTION

Indoors or outdoors, dust is unavoidable. And a marvellous fraction of that dust holds the secret to our past.[1] On cosmological timescales, much matter spends time as dust. In fact, we collect dust from outer space to learn about earlier times in our solar system.[2-4]. Dust in our atmosphere arises from a variety of sources including minerals from the soil, volcanic eruptions, pollution, biological material, and meteorites.[5] Dust in our homes and workplaces includes skin cells, pollen, fabric fibers, hair, road dust, local soil, minerals from deserts half way around the world, and just about anything else found in the local environment. Interest in the characterization of dust, often referred to as particulate matter, spans a wide range of fields including environmental science[6, 7], atmospheric science[8, 9] and geological studies[10-13], health related industries[14, 15], and astronomy.[16-18]. While the majority of atmospheric particulate matter is natural in origin, the remaining fraction is anthropogenic (estimates range from 6-23% [19]) providing evidence of human environmental impact. In short, dust is diagnostic for us and our world.

Infrared (IR) studies of wavelength-scale particles[20, 21] can provide vital, nondestructive chemical information, but are limited by two issues: 1) spectra of wavelength-scaled particles are dominated by scattering effects and vibrational lineshape distortions (Christiansen effect[22, 21]), and 2) insufficient intensity of light is transmitted with conventional techniques as aperture size is reduced to the range of the particles of interest. Infrared microscopy using free electron lasers of synchrotrons can have 1000 times more IR power (although at significantly more expense) than the blackbody sources of benchtop Fourier Transform IR (FTIR) instruments and has been used to study dust grains collected from space[24, 25]. However, this method still falls prey to scattering problems that might, for instance, require mechanical crushing of some samples.[25] Our solution places the particle within a comparably-sized hole of an IR plasmonic metal film with an array of such holes - to provide a metallic, but transmitting confinement for the particle.

FIG. 1: (a) Scanning electron microscope (SEM) image of plasmonic Ni mesh. (b) Optical image of an isolated dust particle in 5 μm mesh hole in reflectance (left) and transmission (right) mode. (c) SEM of airborne micron sized dust particles sucked into 5 μm mesh holes.
Plasmonic metal films perforated with arrays of sub-wavelength holes (mesh) have been the topic of a number of our own reviews[26, 27], much previous work[28–54], and several enhanced spectroscopic techniques[27, 46, 48, 51, 53, 55–58]. A scanning electron microscope (SEM) of our mesh and its dimensions are given in Figure 1(a). By placing 5 μm diameter latex (polystyrene) spheres within the 5.5 μm wide holes of this mesh, we recently demonstrated[54] greatly reduced scattering effects and undistorted absorption lineshapes using a benchtop FTIR microscope, i.e. an instrument which is considerably less expensive and more convenient to use than a synchrotron. Other recent work[54] involved detecting absorbance as a function of distance from an absorbing line of microspheres within the optical system of the previously mentioned IR microscope (range of angles or nonzero wavevector values parallel to the surface, i.e. k≠0, which is very different than schemes for surface plasmon polaritons on a smooth metal surface). In a preliminary round of these measurements, we discovered a dust particle that was adversely affecting the signal averaging strategy. An optical image of this particle is given in Figure 1(b). It became apparent that it was relatively easy to record a scatter-free, IR absorption spectrum of a 3 μm dust particle and we will show this discovery shortly. In the main body of this work, we purposely place dust particles in the holes of IR plasmonic metal mesh by the evaporation of a dusty aqueous solution and record high quality IR spectra of 1.5 μm dust particles using a conventional FTIR imaging microscope. Dust particles may also be collected by sucking air through the mesh with a small pump and SEM images of dust particles collected in this manner are shown in Figure 1(c). This subject method might be described as the wedding of metallic confinement at the scale of the particle size with a plasmonically transmitting cavity. It constitutes a new method for the study of individual micron-scale dust particles which might be useful in a variety of dust related sciences. It should be complimentary to other methods of studying single dust particles, including (to name only a few) mass spectrometry[59–61], electron microscopy and x-ray methods[62–64], and Raman spectroscopy[2, 65, 66]. This new method will make possible the study of a greater number and variety of particles facilitating a catalog library approach to particles within this size range. These particles also turn out to have great significance in human health.

Airborne particles of about 1.5 μm width are among the largest spherical particles that get past the filtering of the nose and throat, making it into the lungs, i.e. they are respirable. A typical urban concentration of airborne particulate matter is about 30 μg/m^3. A rise of only 10 μg/m^3 from such typical values has been correlated with a rise of 0.25% in the all-cause human mortality rate[60] and a rise of 0.75% in respiratory-related mortality rate. It has also been correlated with stroke which leaves one wondering how the breathing of particulate matter could affect the cardiovascular system[14]. To make this point more dramatically, it is thought that particulate matter rose to as much as 14,000 μg/m^3 during the great London Smog Disaster[19] (p. 2 therein) in 1952 in which at least 4000 people were killed as a result. In fact, the EPA regulates particulate matter http://www.epa.gov/pm/standards.html with a national ambient air quality standard of an annual mean of 15 μg/m^3 and a 24 hour mean of 35 μg/m^3 for particulate matter smaller than 2.5 μm (PM2.5). The standard for particulate matter smaller than 10 μm is a 24 hour average of 150 μg/m^3. Respirable dust particles in the 1.5 μm range fall right between the 'fine' and 'course' designations and are under increased scrutiny by the EPA. There are many known diseases associated with occupations involving the specific dusts breathed by workers[19, 66, 67] like silicosis (from cutting sandstone), asbestosis or mesotheliomas (from asbestos mining, milling, or fireproofing), and black lung disease (coal dust). Therefore the chemical characterisation of respirable dust particles is an important problem.

EXPERIMENTAL

An SEM image (JEOL JSM-5500 instrument) of empty mesh is given in Figure 1(a). The mesh is commercially available in nickel from Precision Eforming. While Ni is not a good plasmonic metal in the visible, it has good smooth-metal plasmonic properties (|ε' | > |ε''|) below 4400 cm⁻¹. The mesh has a square lattice with a lattice parameter of 12.6 μm, square holes of 5.5 μm in

![FIG. 2: IR absorbance spectrum of an isolated 3 μm dust particle. Black dots are the raw data and the solid line is smoothed. Insets show an optical image of the isolated dust particle and adjacent empty hole below the contour IR absorbance plot of the particle at 1424 cm⁻¹. White boxes in insets indicate location of coadded spectra of particle (left) and empty mesh as background location (right).](image-url)
width, and a thickness of 2 \( \mu \text{m} \). Our first results concern a lone, 3 \( \mu \text{m} \) dust particle that landed of its own accord in one mesh hole of a microsphere-on-microsphere experiment. We do not know its origin and it is used only to document the discovery of this new technique. An optical image of the 3 \( \mu \text{m} \) dust particle is shown in Figure 1(b) in both reflectance (left) and transmittance (right) modes using the microscope of the Perkin Elmer Spectrum Spotlight 300 instrument. The microscope is not of the highest optical quality because it is optimized for recording IR spectral images. It has a Cassegrain optical system (NA=0.6) and was used in imaging mode. FTIR transmission spectra were recorded from 670-4000 cm\(^{-1}\), at 4 cm\(^{-1}\) resolution, with 32 scans per spectrum, spectra at each point on a square grid with steps of 8.25 \( \mu \text{m} \) within an imaging region of 250 \( \mu \text{m} \) by 100 \( \mu \text{m} \) (i.e. 640 spectra in a 40x16 array), using a 16 detector array of liquid nitrogen-cooled MCT elements. The insets in Figure 2 show an optical image of the holes with the dust particle and an adjacent empty hole which is just below a corresponding chemimaps (image of absorption) at 1424 cm\(^{-1}\). The IR absorption spectrum of the lone dust particle is shown in Figure 2. It was obtained by co-adding spectra within the white box containing the dust particle (see chemimaps inset) and using the co-added spectra within a same size box with an empty hole as the background. The spectrum shows a number of vibrational features which occur with undistorted absorption line-shapes, as well as a broad generic absorption background.

Since IR light (in the form of surface plasmon polaritons) can run laterally along the mesh[54], it was important to find out the propagation distance in order to judge whether a particle is sufficiently isolated from any neighboring contributions. Figure 3(a) shows an optical image of the dust particle with an overlay of the positions at which full FTIR spectra were obtained during the imaging experiment. The IR microscopes software allows one to extract absorbances of specific vibrational features at these positions. Absorbances at 1424 cm\(^{-1}\) of about 37 grided positions about the dust particle were fit to a two dimensional Gaussian function of position in order to find the position of maximum absorption even though it was between grid points. Then a plot of absorbance vs the distance of each grid point relative to the dust particle position was plotted in Figure 3(b). For most of the IR range, a particle is well isolated if there are no particles in adjacent holes.

Once it was apparent that spectra of individual, isolated dust particles could be recorded, an experiment was devised that involved the intentional filling of the holes with dust particles. Household dust particles were collected from a window sill in an apartment in Idaho Falls, Idaho, using a spatula and deposited within a glass vial. Some of the dust sample was suspended in deionized water and a drop was placed on the Ni plasmonic mesh. The dust particles were sucked into the mesh holes as the drop evaporated. The process was expedited by withdrawing some of the excess water with the edge of a Kimwipe\textsuperscript{TM} while allowing the remaining water to evaporate. An optical image of a 118 x 296 \( \mu \text{m}^2 \) region with 4 particles in the mesh holes (labeled A-D) is shown to the right side of Fig. 4. FTIR spectra were recorded in imaging mode, over a range of 720-4000 cm\(^{-1}\), at 4 cm\(^{-1}\) resolution, 512 scans/spectrum, 6.25 \( \mu \text{m} \)/pixel, 627 total spectra, requiring 4 hr of acquisition time, using a region of empty mesh.

![FIG. 3: (a) Grid point locations of absorbances sampled in IR imaging experiment of 3 \( \mu \text{m} \) isolated dust particle that were used to find the fitted position of maximum absorption, (b) exponential fit of absorbance at 1424 cm\(^{-1}\) vs distance away from the position of maximum absorption of the isolated particle yielding a 1/e propagation length of \( \tau=6.42 \pm 0.2 \mu \text{m} \).](image1)

![FIG. 4: (a) Optical image (far right) of an 118 x 296 \( \mu \text{m}^2 \) region with four dust particles in mesh holes for IR transmission imaging and corresponding contour absorbance plots at 1493, 2965, and 1021 cm\(^{-1}\) (from left to right). The dust particles are labelled A-D.](image2)
as background. Images based on absorption at 1493, 2925, and 1021 cm\(^{-1}\) are shown to the left of the corresponding optical image. The location and absorbance of each dust particle is clearly observed although at different wavelengths. Co-added spectra in the region of an empty hole were used as the background for the co-added spectra in the region of an adjacent hole containing a dust particle. The resulting IR absorption spectrum of each particle is shown in Figure 5. Labels correspond to the optical image in Figure 4 and the spectra are offset for better viewing. Each particle has a different IR spectrum demonstrating variation in composition of the dust microparticles.

RESULTS

The IR absorption spectrum of the 'accidental', 3 μm-wide dust particle is shown in Figure 2 under fairly modest FTIR conditions (only 32 scans). All of the vibration/phonon peaks look normal, i.e. they are not distorted with the Christiansen effect just as was observed for latex microspheres in the mesh holes[50]. The IR spectrum is dominated by the carbonate symmetric stretch (1424 cm\(^{-1}\), ν\(_4\)). The carbonate combination bands at 1798 cm\(^{-1}\) (ν\(_{1}+ν\(_4\)) and 2996 cm\(^{-1}\) (ν\(_{1}+ν\(_{3}\)+ν\(_{4}\)) are suggestive of CaCO\(_3\)). There could be some organic material with aliphatic CH stretches at 2848 and 2916 cm\(^{-1}\), however carbonate also has overtone combination bands in this region. There are other bands at 1087, 1124, 1178, and 1580 cm\(^{-1}\) which indicate other materials in lesser amounts. So the particle is largely a mixture of carbonate and other minerals with perhaps some organic material. To address the plasmonic issue of lateral propagation of surface plasmon polaritons along the mesh, the absorption data at 1424 cm\(^{-1}\) vs distance from the particle was fit (see Figure 3) with an exponential tail yielding a 1/e propagation radial distance of 6.0±0.3 μm. With a mesh lattice parameter of 12.6 μm, this propagation length indicates that each hole is reasonably isolated at most wavelengths of the spectrum with the possible exception of peaks around 700 cm\(^{-1}\) (where the plasmonic resonances are strongest). This result compares well with our previous propagation length experiments[54]. Finally, the spectrum seems to have a generic background that rises with increasing wavenumber. This appears to be a very general feature of the absorption spectra of such particles.

The IR absorption spectra of the 4 isolated particles in Figure 5 have much better signal-to-noise ratios than the first particle, which is reasonable because the first correspond to 512 scans. Again, each of these spectra is 'scatter-free', that is none of the vibrational/phonon peaks are distorted by the Christiansen effect. The baselines have not been flattened and show a broad, generic feature rising at higher wavenumbers. We believe that these baselines could reveal the imaginary component of the complex index of refraction of these particles, although a bit more calibrating work would be required to extract the values. Most importantly, these spectra show variation in composition. Each spectrum reveals varying amounts of carbonate by virtue of symmetric stretch in the range of 1423-1450 cm\(^{-1}\) and combination bands near 1580, 1750-1881, 2925, and 2873-2923 cm\(^{-1}\).

Detailed analysis would indicate that the carbonates are from minerals such as calcite, dolomite, and magnesite[68-70]. Peaks seen from 1000-1100 cm\(^{-1}\) indicate the presence of silicate and/or sulfate containing minerals (quartz, clay, feldspar, and sulfate[71]) and are found at some concentration in each particle. The presence of peaks at 798 and 1098 cm\(^{-1}\) (shoulder) in the spectrum of particle B (Figure 5) indicates the presence of quartz, and 1030 cm\(^{-1}\) absorbance indicates the presence of clay (perhaps illite). The weak vibration at 1610 cm\(^{-1}\) and the broad feature centered at 3400 and 3588 cm\(^{-1}\) may point to the presence of gypsum[71] in particle A. Broad asymmetry of the main carbonate and silicate/sulfate features suggests mixtures of crystalline orientations and/or amorphous structures. Clearly, the mineral composition of each dust particle is quite different. Absorptions within the aliphatic C-H stretch region are observed in all spectra which may be due in part to combination bands of minerals (like carbonate) or organic compounds. The presence of organic constituents in at least some particles is further supported by vibrations at 3050 cm\(^{-1}\) (unsaturated C-H bend) in both the spectra of particle A and D along with aromatic C=C out-of-plane bends as seen for particle A at 1506, 1540, and 1556 cm\(^{-1}\). Features at 1540 cm\(^{-1}\) will be investigated as possible organic partners (i.e. amide bands) for the CH stretches. There seems to be a reasonable prospect of quantifying the organic material in these particles. Particles B and C exhibit broad features around 1600 cm\(^{-1}\) which could be water bends (especially paired

![Graph](https://via.placeholder.com/150)

**FIG. 5:** Extracted absorbance spectra of dust particles in imaging region. Labels correspond to dust particles in Figure 4.
with the absence of C=O out of plane bends), while broad features from 3100-3600 cm⁻¹ likely represent the O-H stretch of hydrated minerals or acid.[1] The dust particles appear to share common classes of mineral spectral features, but with different amounts of the specific compounds. As more spectra of individual particles are accumulated, more quantitative analyses can be accomplished.

CONCLUSION

IR absorption spectra of single, isolated, wavelength-size particles have been recorded in transmission mode by placing 1–5 μm size dust particles into the 5.5 μm holes of IR plasmonic metal film. The arrangement provides a metallic confinement of the particle which turns off Mie scattering effects, but the plasmonic nature of the hole still allows IR transmission. The "scatter-free" spectra are recorded with a conventional benchtop IR imaging microscope, in contrast to the competing technique which requires a synchrotron free electron laser IR source. A 1/e propagation distance of 6.0 μm along the air path was determined at 1424 cm⁻¹ which shows, by comparison to the 12.6 μm lattice parameter, that the spectra are largely isolated by and confined to the hole in which they sit as probed with the IR microscope optical system, although this may not be the case with the primary plasmonic resonances at low k values and around 700 cm⁻¹. With this new nondestructive method, a greater number of particles can be sampled and a library of single particle spectra may be created. Principal component analysis can be employed to reveal variation in particle composition with size and geographical location for application on respirable dust in a number of scientific fields.

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