

# USE OF RAMAN MICROSPECTROSCOPY TO IDENTIFY THE TYPE OF RESPIRABLE FIBER

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## Abstract

Occupational lung diseases can be caused by organic dusts during the processing of textile fibers such as cotton and cotton blends. Several studies of the health effects of these dusts have been presented at previous conferences. One major difficulty in trying to determine the cause of these diseases is the identification of the organic dust. Traditional microscopy techniques such as optical and scanning electron microscopy (SEM) can identify the dust as respirable or not. However, they do not indicate what the dust is made of. Although NMR and IR can identify the chemical species, they require relatively large samples while a single respirable particle or fiber can cause the associated lung disease. This particle or fiber may not be representative of the bulk of the material. Thus a microscopic analysis tool is needed to identify the chemical composition of individual dust particles. This article describes the development of Raman microspectroscopy for the identification of organic dusts obtained from a flocking operation. Raman microspectroscopy provides both the optical resolution of a conventional optical microscope along with the analytical chemical specificity of IR. This technique will be described along with its benefits and limitations.

## Introduction

Exposure to respirable inorganic fiber dust, such as asbestos, has been recognized as a health hazard for many years. More recently, dust from cotton fibers has also been implicated in interstitial lung disease. It had been believed that dust from synthetic organic fibers, such as nylon and polyester, posed no significant health threat. However, several cases of interstitial lung disease have recently been diagnosed at a nylon flocking plant where dust levels were quite high. (Porter, et al., 1999.) In many cases, only a single fiber type is used and most of the fiber dust can reasonably be assumed to come from that fiber type. However, a single plant may use a wide range of fiber types. In that case, the dust may arise from many different sources. In diagnosing the biological effects of a fiber dust, it is essential to determine the fiber type involved.

Optical microscopy has often been used to characterize fiber types based on the different shapes of fibers. It cannot, however, distinguish between fibers that have the same shape, but different polymer bases. The use of polarizers in an

optical microscope can determine whether the fiber is birefringent or not. However, almost all commercially significant organic fibers are birefringent, so this cannot readily be used to determine polymer type of the fiber. Scanning electron microscopy, SEM, can only determine shape. However, the shapes of the respirable fibers are highly variable for a single fiber type and the differences between the shapes of respirable fibers from different parent fiber types is smaller than the difference in shape from the same parent fiber type. These techniques cannot readily distinguish the polymer types. Coupling energy dispersive analysis of x-rays (EDAX) with SEM, it is possible to distinguish different materials, but most polymers are so similar that this is difficult. Infrared spectroscopy can easily distinguish between the various fiber types as each polymer has its own, distinctive IR spectrum. However, the small size of respirable fibers prevents the use of IR.

A relatively new technique, Raman microspectroscopy, combines the molecular specificity of IR with the resolution of optical microscopy. It gives a "finger print" of the polymer type. Because it uses visible light, it can measure fibers as small as 1  $\mu\text{m}$  in diameter, i.e. fibers in the respirable range. This article describes the procedures needed to obtain adequate determination of the fiber type for respirable fibers.

## Experiment

Flocked fibers of polyester dyed black, acrylic dyed rose, cotton dyed black, and undyed rayon, nylon 6,6, Kevlar<sup>®</sup> and cellulose were provided by Theodore Sandukas. The fibers are listed in Table 1. They were placed in small plastic bags. Aluminum foil was taped to glass microscope slides using double stick tape. The plastic bags containing the flocked fibers were then shaken. Several fibers adhered to the surface of the plastic bags. The bag was carefully opened and the aluminum foil side of the glass slide was pressed against the inside of the plastic bag. A sufficient number of fibers transferred to the aluminum foil for these studies.

The slide was then placed in a Holoprobe<sup>®</sup> 785 Research Raman Microscope manufactured by Kaiser Optical Systems. Respirable fibers (diameter < 3 $\mu\text{m}$ , length to diameter ratio > 5) were located by scanning the slide with a 50x objective to give a total magnification of 1520x. Once a respirable fiber was located, the excitation laser was focused onto it, and the Raman spectrum was collected for 10 minutes with the cosmic ray filter turned on and with noise subtraction activated. This gave an adequate signal to noise ratio for determining the fiber type. A background spectrum of the aluminum foil was also obtained and used to remove the background from the respirable fiber spectra. A few spectra were smoothed using the "Smooth" routine in Grams 5.0 to improve visualization of the spectral features. The resultant spectra were compared to undyed fibers of the same polymer.

## Discussion

A typical Kevlar® respirable fiber formed in the flocking process is shown in Figure 1. The Raman spectrum is collected in the region indicated by the circle in the middle of the image. The Raman spectrum of this fiber is shown in Figure 2 along with a spectrum of a Kevlar® fiber taken from a yarn sample. Even though the signal-to-noise ratio of the Raman spectrum of the respirable fiber is low, all of the major Kevlar® Raman bands are easily seen. Thus this respirable fiber is clearly identified as a Kevlar® respirable fiber.

Figure 3 shows a typical nylon 6,6 respirable fiber formed by the flocking process. Its Raman spectrum is shown in Figure 4 along with that of a nylon 6,6 industrial fiber. Although the signal-to-noise ratio is poor for the respirable fiber, it is clearly a nylon fiber. The Raman scattering from nylon 6,6 is weaker than from Kevlar®, so longer collection times should be used. Nevertheless, an adequate determination can be made with a collection time of 10 minutes.

The Raman spectra for a PET fiber and for a respirable fiber from the flocking of PET fibers that have been dyed black are shown in Figure 5. PET is a strong Raman scatterer so that a 10-minute collection time is adequate. There is no doubt that the fiber is made from PET. However, Raman microscopy uses very high power densities to excite the scattering. Although only 3 mW of laser light is incident on the sample, this corresponds to roughly  $5 \times 10^5 \text{ W/cm}^2$ . If any absorption of the light occurs, significant temperature rises can occur. While attempting to collect the Raman spectrum of the black respirable fiber, the fiber melted. After melting, the Raman spectrum could still be obtained in this case, but the spectrum differs from that of the original PET.

Similar spectra are given for rayon (Figure 6) and for cellulose (Figure 7). Both are weak Raman scatterers, but can easily be identified by comparison with the reference spectra. Notice that, although rayon and cellulose are quite similar, their Raman spectra are uniquely different, and no confusion exists between them.

A common problem with the use of Raman spectroscopy on organic fibers is interference of the Raman spectrum by intense fluorescence from the fibers. This is especially true when the fibers are dyed. This problem was observed in these experiments, but a sufficient Raman signal was obtained for all fibers except the cotton. Figure 8 shows the Raman spectrum of a respirable acrylic fiber that was made from acrylic fibers which had previously been dyed rose. A substantial fluorescence background is observed in the region of  $600\text{-}1900 \text{ cm}^{-1}$ . The Raman signal is barely observable above the background fluorescence. However, in this case there is the characteristic CN-triple bond band at  $2250 \text{ cm}^{-1}$ .

The existence of this band in the Raman spectrum indicates that the fiber is an acrylic fiber. Although an intense fluorescence signal is present, it is still possible to identify this respirable fiber as originating from an acrylic polymer.

Although all of the respirable organic fibers described above could be readily identified via their Raman spectra, the black dyed cotton fiber could not be identified through its Raman spectrum. Figure 9 compares the Raman spectrum of a natural cotton fiber and a respirable cotton fiber made by the flocking process after the fiber was dyed black. It is quite clear that the spectrum of the respirable cotton fiber does not look at all like the natural cotton fiber. When fibers are dyed, the Raman spectrum can be due to the dye and not the fiber, itself. To test this, the Raman spectrum of a non-respirable black cotton fiber from the same flocking sample was measured, as shown in Figure 10. Comparing this spectrum with that of the respirable fiber from Figure 9 (repeated in Figure 10 for clarity) shows that the Raman spectra of these two fibers are identical. Thus, by measuring the Raman spectrum of the (dyed) fibers being processed at the time that the respirable fiber sample is obtained and comparing the Raman spectra of this fiber with that of the respirable fiber, one should be able to uniquely determine whether or not the respirable fiber is the same as the fiber being processed.

## Summary

Respirable dust created during flocking of organic fibers has recently been implicated in several cases of interstitial lung disease. Since respirable dust can be generated by a number of textile processes it becomes imperative to be able to identify the type of fiber from which the respirable dust originates. In this article, it has been shown that in most cases Raman microspectroscopy is capable of identifying the type of fiber from which the respirable dust originates. However, when a fiber has been dyed, fluorescence from the dye or the Raman spectrum of the dye may make it difficult to identify the type of fiber from its Raman spectrum alone. The respirable fibers in the current study could all be readily identified by their Raman spectra whether they were dyed or not, with the sole exception of a respirable fiber from black dyed cotton fibers. In this case, the cotton Raman spectrum could not be seen. However, the Raman spectrum of the respirable fiber in this sample matched the Raman spectrum of a much larger, non-respirable fiber contained in this sample. Raman microspectroscopy can uniquely identify respirable organic fibers and should prove valuable in identifying the sources of respirable fibers.

## References

Porter, D. W., V. Castranova, V. A. Robinson, A. F. Hubbs, R. R. Mercer, J. Scabilloni, T. Goldsmith, D. Schwegler-Berry, L. Battelli, R. Washko, J. Burkhart, C. Piacitelli, M.

Whitmer, W. Jones. 1999. Acute inflammatory reaction in rats after intratracheal instillation of material collected from a nylon flocking plant. *Journal of Toxicology and Environmental Health, Part A*, 57: 25-45.

Table 1. Flocked fiber types and their colors.

Polymer Type	Color
Kevlar®	natural
nylon 6,6	full dull
PET	black
rayon	natural
cellulose	natural
acrylic	rose
cotton	black

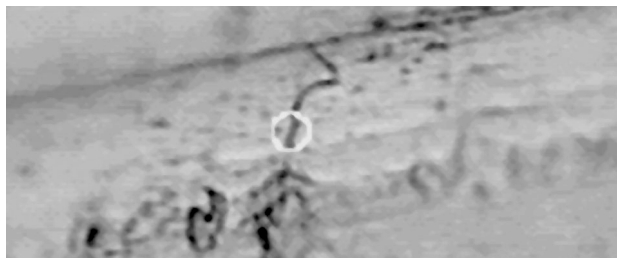


Figure 1. A Kevlar® respirable fiber is shown in the center of the figure. The circle indicates the region from which the Raman spectrum is collected. The diameter of the circle is approximately 3  $\mu\text{m}$ .

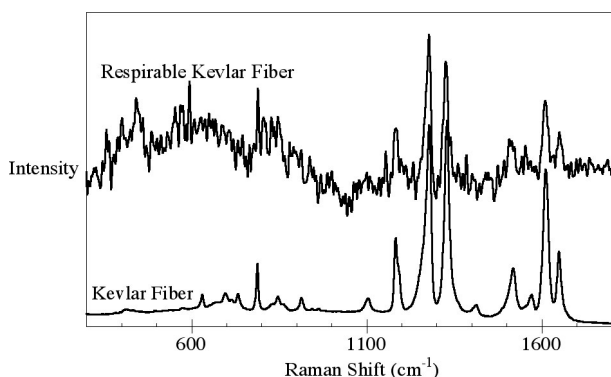


Figure 2. Raman spectra of a Kevlar® fiber and of the respirable Kevlar® fiber shown in Figure 1.

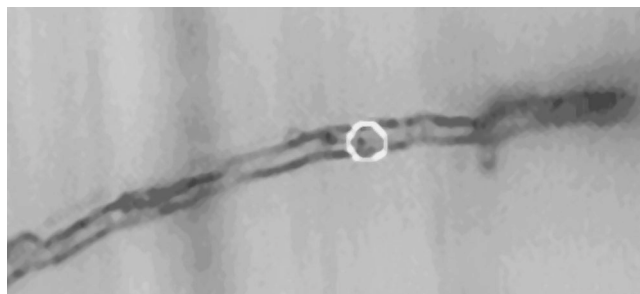


Figure 3. Image of nylon 6,6 respirable fiber. The circle indicates the region from which the Raman spectrum is collected. The diameter of the circle is approximately 3  $\mu\text{m}$ .

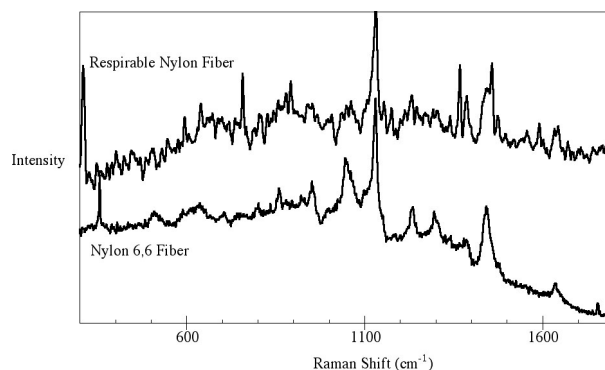


Figure 4. Raman spectra of a nylon 6,6 industrial fiber and of the respirable nylon 6,6 fiber shown in Figure 3.

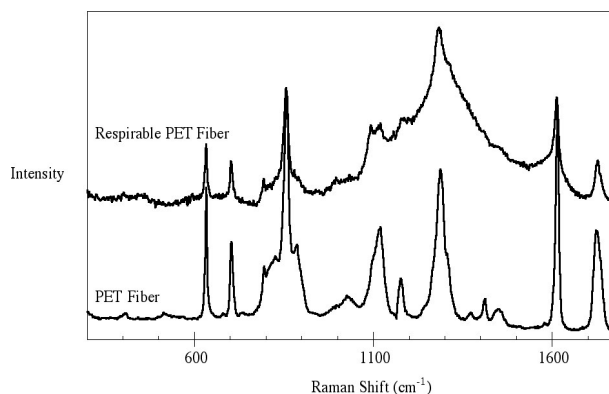


Figure 5. Raman spectra of a PET fiber and of a respirable PET fiber that has been dyed black.

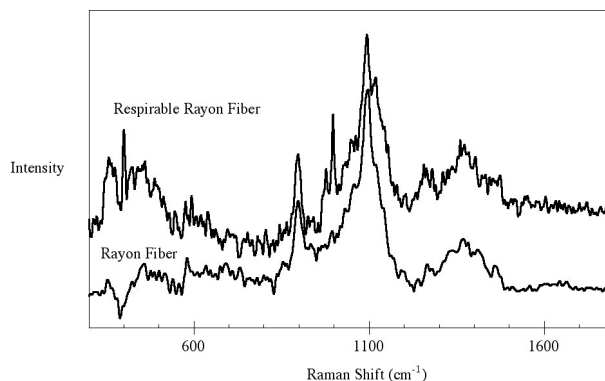


Figure 6. Raman spectra of a rayon fiber and of a respirable rayon fiber.

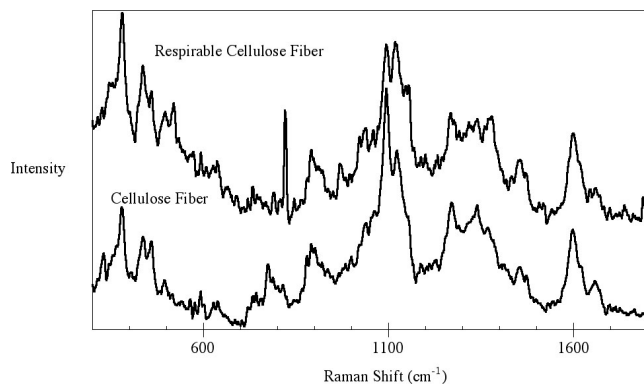


Figure 7. Raman spectra of a cellulose fiber and of a respirable cellulose fiber.

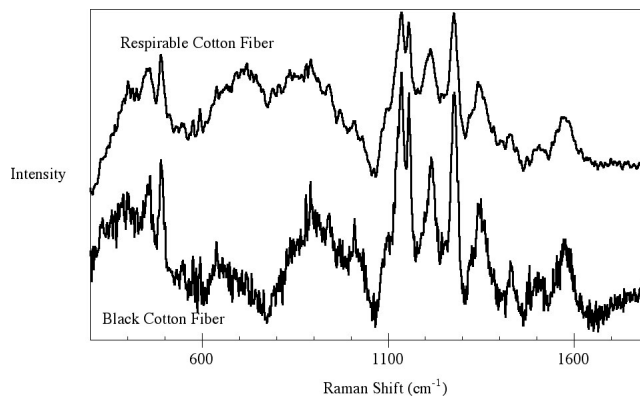


Figure 10. Raman spectra of a cotton fiber dyed black and a respirable fiber made from flocking the black dyed cotton.

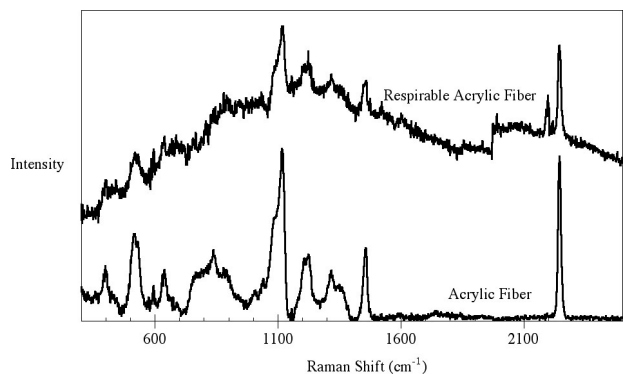


Figure 8. Raman spectra of an acrylic fiber and of a respirable acrylic fiber dyed rose.

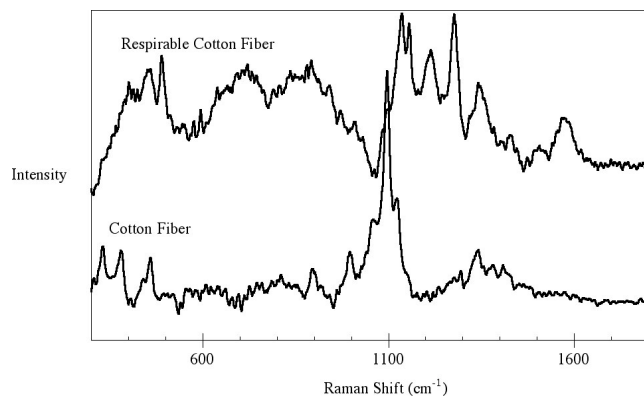


Figure 9. Raman spectra of a cotton fiber and of a respirable cotton fiber dyed black.