

Attachment A
RJ Lee Group's Explanation of Analytical Methods for Asbestos

Explanation of Analytical Methods for Asbestos Analyses Associated with Sampling from Specialty Granules LLC's Charmian Quarry

Prepared for Specialty Granules LLC

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RJ Lee Group Project No. LLH808740

At the request of Specialty Granules LLC (SGI), RJ Lee Group has reviewed the technical deficiency letter of the Pennsylvania Department of Environmental Protection (PA DEP) dated September 30, 2019 in relation to issues concerning testing and analyses performed at or in relation to SGI's Charmian Quarry (see, particularly, PA DEP September 30 letter, items 1, 6, 25, 26, and 27).

This memorandum describes the analytical methods that were used for the SGI samples as well as alternative procedures that could have been used. The procedures that were used are appropriate for the different types of samples.

1. Analytical Procedures

The analytical procedures used on samples from SGI are appropriate for the determination of any possible asbestos content. RJ Lee Group has received samples representing three different matrices: water, airborne particulate, and bulk (rock) samples. The water samples have been analyzed using transmission electron microscopy (TEM); the airborne particulate samples have been analyzed using phase contrast microscopy (PCM) and electron microscopy (both scanning electron microscopy and TEM); and the bulk samples have been analyzed using polarized light microscopy (PLM). A brief description of the various analytical procedures is included in Appendix A.

1.1 Water Samples: Water samples were analyzed using two US Environmental Protection Agency (EPA) approved analytical procedures: EPA 100.1 (*Analytical Method for Determination of Asbestos Fibers in Water*) and 100.2 (*Determination of Asbestos Structures Over 10 μ m in Length in Drinking Water*). Both methods use TEM as the analytical instrument but differ in the dimensions of asbestos fibers reported. Both the EPA 100.1 and 100.2 methods are designed to analyze water that is drinking water or drinking water supplies. It is noted that there is no EPA approved analytical procedure for analyzing non-potable water from lakes or streams. Because of there is no approved EPA method for water from streams, the drinking water methods are adapted for application to water with (comparatively) high suspended solids by changing the target analytical sensitivity (0.2 MFL).

RJ Lee Group has analyzed nine (9) samples of water from the SGI site and has found only one (1) asbestos fiber (a sample from the Pitts pond) at a concentration 35 times lower than the maximum contaminant level (7 MFL) allowed by the EPA in safe drinking water. Where appropriate, to provide additional clarification to the morphology of an observed particle, the observed samples were also evaluated using a field emission scanning electron microscope (FESEM).

1.2 Air Samples: Samples of airborne particulate have been collected at 10 locations around the perimeter of the SGI operation. Two different types of sampling have been conducted: 1) passive monitors were placed at the site and particulate was collected for a week between August 28 and September 6, 2018; and 2) active samples were collected September 18 and 25, 2019, with each sample collected for a period of about 8-hours. Passive monitors provide information on long-term average concentrations at a sampling site while active monitors provide an indication of conditions over a shorter sample period. The samples collected via passive monitors were examined using scanning electron microscopy (SEM) while samples obtained via the active samples were examined using both PCM (NIOSH 7400, *Asbestos and Other Fibers by PCM*) and TEM (ISO 10312, *Ambient air - Determination of asbestos fibres - Direct-transfer transmission electron microscopy method, Annex E*). No asbestos fibers were observed in the samples from the active samples, while one asbestos fiber on each of two samples was observed in the samples from the passive monitors. Where appropriate, to provide additional clarification to the morphology of an observed particle, the observed samples were also evaluated using a FESEM. These analyses have focused on particles that meet the dimensions used for EPA and OSHA risk evaluations: minimum length of 5 μm and a minimum aspect ratio (length:width) of 3:1.

1.3 Bulk Samples: Numerous samples of SGI bulk materials (granules, sections of drill cores, etc.) have been analyzed by RJ Lee Group using PLM in general accordance with EPA 600/R-93/116 (*Method for the Determination of Asbestos in Bulk Building Materials*). If the received sample comprised particulate that was too large to be analyzed by the PLM, then the sample is ground using a disc grinder as described in CARB 435 (*Determination of Asbestos Content of Serpentine Aggregate*). These PLM analyses are not restricted to the regulated asbestos minerals, but also include the examination looking for any mineral particle that exhibits an asbestiform growth habit. PLM is appropriate for these types of samples since asbestos occurs in nature as veins or plugs in the rock; it does not occur as finely disseminated fibers randomly dispersed in the rock matrix. When that rock is pulverized prior to analysis (using any analytical procedure), the asbestos will remain (due to its high tensile strength) in sizes that are visible using the PLM.

2. Comparison of Analytical Methods

PA DEP has requested a comparison of analytical procedures for the examination of natural occurrences of asbestos (NOA). One such comparison is CARB 435 and EPA 600/R-93/116 (see PA DEP September 30, 2019 letter, item 1.e). Both utilize PLM to evaluate appropriately prepared materials; and both require an extensive detailing of the optical properties of the observed minerals in order to classify a particle as a regulated asbestos fiber. The EPA method provides a detailed description of the asbestiform morphology while the CARB method provides no guidance on this subject. Neither method discusses the identification of non-regulated asbestiform minerals (such as winchite, richterite, or glaucophane), but these minerals are not present at the SGI site. CARB 435 does provide a detailed description of the sample preparation (pulverization) required before PLM analysis while the EPA method provides details on matrix reduction (ashing and/or acid-washing) that could eliminate particles that could obscure an asbestos fiber. Both methods quantitate the asbestos content using a point-counting procedure, though the EPA method also permits visual estimation as an alternate technique. For both methods, a well-trained microscopist is needed in order to properly examine a sample. Following sample preparation, in the hands of a well-trained microscopist, there are no significant differences between the methods, and they are essentially equivalent.

As noted above with respect to analyses of bulk samples, RJ Lee Group utilized PLM in general accordance with EPA 600/R-93/116, because that method provides a detailed description of the asbestiform morphology while the CARB 435 does not; RJ Lee Group also utilized CARB 435 to grind samples that were

too large to be analyzed by the PLM, because the CARB method provides a protocol for grinding while the EPA method does not. For counting, RJ Lee Group utilized the EPA point counting method; both methods quantitate the asbestos content using a point-counting procedure and it is unlikely that the selection of the CARB 435 counting method would have materially changed the result.

One other comparison requested by PA DEP is between TEM methods used to analyze bulk samples, such as EPA 600/R-93/116 (Section 2.5 of the method) and an unspecified CARB-modified analytical protocol (but presumably a modified AHERA-type analysis). We also considered the analytical portion of ASTM D5756 (*Microvacuum Sampling and Indirect Analysis of Dust by Transmission Electron Microscopy for Asbestos Mass Surface Loading*). All three methods, when properly used, require the analyst to observe an asbestiform morphology, and also to document that the elemental composition (energy dispersive x-ray spectrum, EDXA) and the selected area electron diffraction (SAED) pattern are consistent with one of the regulated asbestos minerals. Neither the EPA method nor the CARB-modified method provides detailed descriptions of the preparation and analysis of the particles, but rather each refers to other methods. ASTM D5756 provides detailed analytical instructions. All three techniques essentially analyze the same particle sizes. And all three methods require that the microscopist be well-trained.

When analyzing bulk samples by TEM, RJ Lee Group first grinds the sample (if needed) using the CARB 435 procedure. The ground material is then suspended in water and an aliquot deposited onto a filter in accordance with the ASTM D5756 method. The samples are then analyzed in the TEM in accordance with the EPA and ASTM methods (which use the same counting rules).

PA DEP requested (items 26 and 27b in September 30, 2019 letter) that SGI consider using the TEM method ISO 10312 (*Ambient air - Determination of asbestos fibres - Direct-transfer transmission electron microscopy method*) for the analysis of perimeter air samples as suggested by EPA OSWER Directive #9200.0-68. According to that directive, the ISO procedure is recommended such that “the analytical procedure used to analyze samples from a site should capture information concerning the specific mineralogy of asbestos fibers that are present.” The intent of the directive is to develop a “a risk management-based response strategy that is protective of human health and the environment.” EPA Risk procedures for inhaled asbestos are found at the EPA IRIS website¹ where it is noted that the fibers used in the risk estimation are called “phase contrast microscopy equivalent” (PCME). These fibers may be counted using Annex E of ISO 10312 (*Determination of the concentration of asbestos fibres and bundles longer than 5 µm, and PCM equivalent asbestos fibres*). This method (ISO 10312 Annex E) is the same as NIOSH 7402 in both sensitivity and mineral identification. RJ Lee Group requires that amphibole minerals (the possible asbestos minerals at SGI) be identified using both EDXA and SAED procedures, with the SAED patterns measured and compared to published databases of minerals (such as are found in the ICDD database² or in CrystalMaker[®].³ There is no substantive difference between ISO 10312 Annex E and NIOSH 7402.

¹ https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?&substance_nmbr=371.

² <http://www.icdd.com/pdf-4-minerals/>.

³ <http://crystallmaker.com/crystallmaker/index.html>.

Appendix A

Description of Analytical Procedures

Depending on the type of material that is to be analyzed for asbestos content, there are a variety of analytical procedures that can be used. For samples of bulk materials (such as products, ore/rock and settled dust), the analytical procedures typically used include x-ray powder diffraction, optical microscopy (generally polarized light microscopy), and/or electron microscopy (either scanning electron microscopy or transmission electron microscopy). For samples of airborne particulate, optical microscopy (usually phase contrast microscopy) and/or electron microscopy (typically either scanning electron microscopy or transmission electron microscopy) are employed. Water samples require the use of transmission electron microscopy. The following paragraphs will briefly discuss the accepted techniques.

X-Ray Powder Diffraction (XRD): In this technique, a coherent beam of x-rays is directed at the sample (usually a powder packed into a holder). The x-rays are diffracted by the crystals in the sample. In modern usage, an x-ray diffractometer measures the intensity of the x-rays from the sample and also records the angle (from x-ray source to sample to diffractometer) of the x-rays. This results in a pattern such as shown in Figure 1, below. The height and location of the peaks are compared to known reference materials and are used to identify the various minerals.

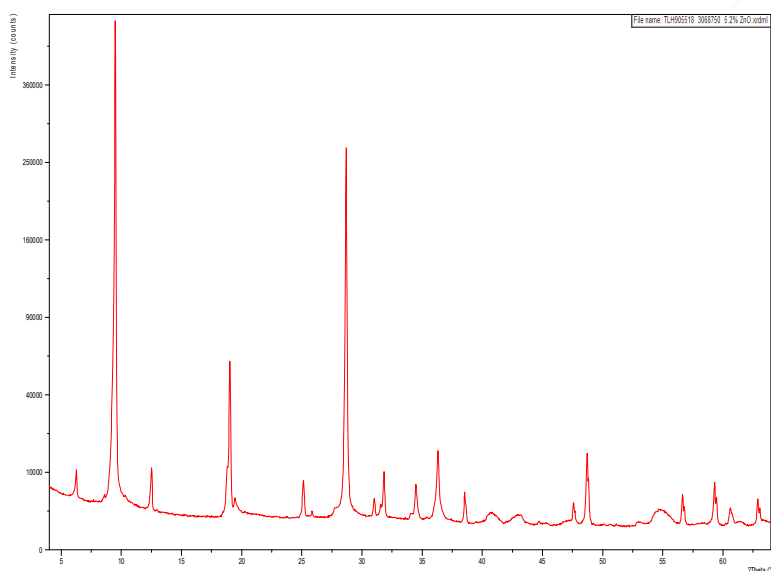


Figure 1. A typical x-ray powder diffraction pattern of a bulk sample. The intensity of the detected x-rays are shown as vertical peaks (the higher the peak, the greater the intensity). The angle at which the x-rays are detected is shown in the horizontal axis of the graph and may be shown as “ 2θ ”.

The XRD procedure is used for bulk samples to determine the components that are crystalline in nature. Non-crystalline materials (such as polymers) are not readily observed using the powder technique. The XRD powder procedure typically uses up to a gram of material for each analysis. The XRD procedure is prone to errors if the powder is not packed correctly (can cause the locations of the peaks to shift up to $0.4^\circ 2\theta$) or if the particles in the powder are packed in a preferred order so that some peak intensities are exaggerated while others are reduced. In addition, for minerals that can form in multiple habits (such as amphibole minerals), the XRD cannot differentiate between asbestos fibers and non-asbestos particles of the same mineral (that is, XRD cannot determine the morphology of the minerals).

Using the XRD procedures, asbestos can be routinely detected at the 0.5% level, absent interferences and other analytical issues. Published XRD analytical procedures can be found in NIOSH⁴ and EPA^{5,6}.

Optical Microscopy: For bulk samples (powders or dust, rock and ore), while a stereo binocular microscope can be used to evaluate the general characteristics of the sample (color, size, and homogeneity), the minerals are identified using a polarized light microscope (PLM). The minerals are suspended on a glass slide in oil that has a known refractive index. When observed in the PLM, light will bend (refract) as it passes through the mineral particles. Based on how much the light bends relative to that of the oil, the refractive index of the mineral can be determined. The use of the refractive indices, as well as the color of the particle (pleochroism), the sign of elongation, and the birefringence of the mineral help to identify the mineral. Figure 2 shows the image of chrysotile asbestos as observed in a stereo binocular microscope (left) and as seen in the PLM (right).

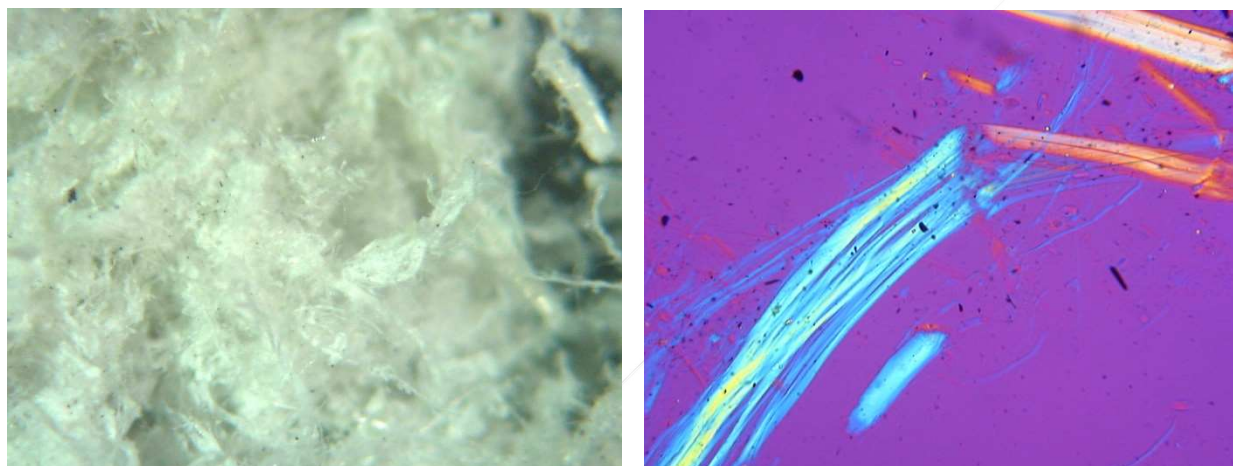


Figure 2. Stereo binocular microscope photograph (left) of NIST SRM 1866 chrysotile showing it to be a fine, white, fibrous material. The polarized light microscope photograph (right) of the chrysotile demonstrates the mineral's different optical properties depending on the orientation of the fibers.

The PLM technique is used to identify minerals in a sample. Compared to the XRD, the PLM technique uses less material (typically on the order of a milligram of material) to make a slide. The particles have to be small enough that light can pass through them (though not all minerals are translucent or transparent), generally less than 100 μm in size, but large enough to be visible in the microscope (approximately 0.5 – 1 μm in width and greater). Serpentine and amphibole minerals (the minerals of interest in asbestos analyses) are transparent in a PLM. In addition, the PLM technique can observe the morphology of the particle and can determine if a particle is an asbestos fiber or a non-asbestos particle. Typical magnifications used for the analyses range from 10X to 400X. The PLM technique can detect asbestos in trace quantities in samples, though quantitative results for visual estimation procedures are not considered accurate until the concentration exceeds 1%.

⁴ NIOSH Manual of Analytical Procedures. NIOSH 9000. <http://www.cdc.gov/niosh/docs/2003-154/pdfs/9000.pdf>

⁵ EPA, Code of Federal Regulations, 40 CFR §763, Appendix E to Subpart E, Section 2.
http://edocket.access.gpo.gov/cfr_2009/julqtr/pdf/40cfr763EAppE.pdf

⁶ EPA 600/R-93/116, Method for the Determination of Asbestos in Bulk Building Materials

NIOSH⁷, OSHA⁸, and the EPA^{5,6} have published procedures for PLM analyses of building materials. Other organizations have published methods or guidelines for asbestos analyses in bulk materials.

For airborne samples, an optical microscopy technique called phase contrast microscopy (PCM) is used to count fibers that are collected on filters. PCM counts all fibers; it cannot identify a fiber as asbestos. A portion of the filter containing the particles is excised and placed on a glass slide. The filter is made transparent to allow the viewing of the collected particles. Using a magnification of 400X, the PCM counts all particles that appear to be fibers and that are at least 5 µm long and have an aspect ratio (length:width) of 3:1 or greater. The PCM cannot differentiate between various minerals and cannot differentiate between minerals and non-minerals (such as cotton fibers). PCM analyses are typically used to document the amount of airborne fibers in accordance with various Federal regulations, in particular OSHA (29 CFR §1910.1001) and MSHA (30 CFR §71.702). Figure 3 shows the view seen by a microscopist when viewing a sample in the PCM. Finally, the PCM cannot reliably observe very thin particles (such as those thinner than 0.25 µm). PCM procedures have been published by NIOSH⁹, OSHA¹⁰, ASTM¹¹, and others.

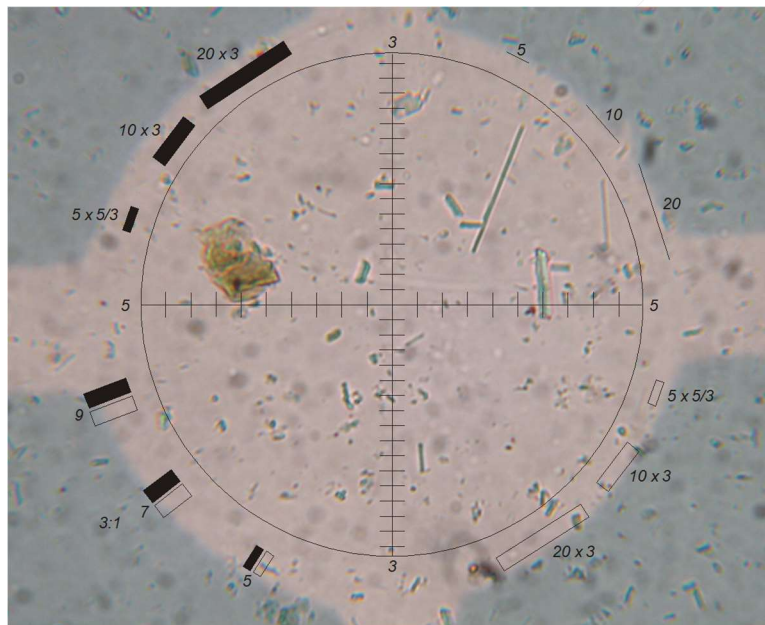


Figure 3. Fibers observed in a phase contrast microscope. A graticule (black overlay) is used to delineate fields of view. Fibers falling within or on the graticule that are at least 5 µm long are counted.

Electron Microscopy: Regardless of whether the sample comprises water or airborne particulate, there are two primary techniques used to observe particles in an electron microscope – 1) an electron beam passes through a particle and the particle is observed (essentially) as a shadow on a phosphor screen (transmission electron microscopy, TEM); and 2) the electron beam is reflected off the particle, captured

⁷ NIOSH Manual of Analytical Methods, NIOSH 9002, <http://www.cdc.gov/niosh/docs/2003-154/pdfs/9002.pdf>

⁸ OSHA, Code of Federal Regulations, 29 CFR §1910.1001, Appendix J, http://edocket.access.gpo.gov/cfr_2009/julqtr/pdf/29cfr1910.1001.pdf

⁹ NIOSH Manual of Analytical Methods, NIOSH 7400, <http://www.cdc.gov/niosh/docs/2003-154/pdfs/7400.pdf>

¹⁰ Code of Federal Regulations, 29 CFR §1910.1001, Appendix A, http://edocket.access.gpo.gov/cfr_2009/julqtr/pdf/29cfr1910.1001.pdf

¹¹ ASTM, D7201, <http://www.astm.org/Standards/D7201.htm>

by a detector, and the image viewed on a TV screen (scanning electron microscopy, SEM). Figure 4 shows a comparison of the images of the same particle as seen in both electron microscopes.

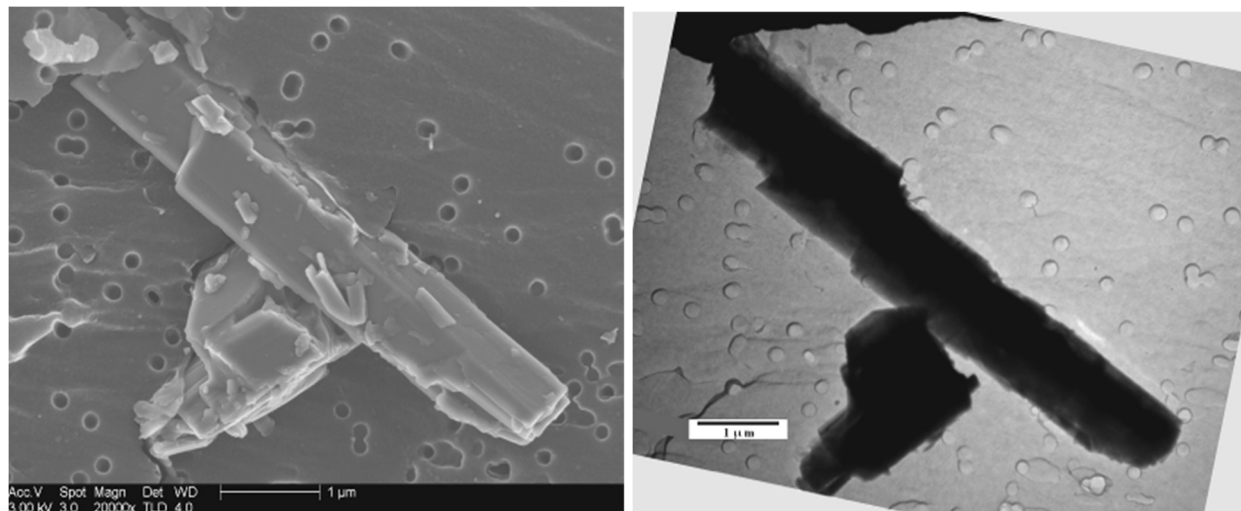


Figure 4. Photographs of the same particle as viewed in a scanning electron microscope (field emission-type) and a transmission electron microscope. The particle is approximately 6.5 µm long and about 1 µm wide. The small circles visible in the pictures are the pores in the filter media.

In addition to viewing images of the particles, both electron microscopes generate additional information that can be used to identify the mineral. With the addition of an energy dispersive x-ray detector and analyzer (EDXA) to either microscope, the chemistry of a particle can be determined. X-rays generated from the interaction of the electron beam and the particle are captured and counted. A typical spectrum is shown in Figure 5. The presence of various elements, along with their relative proportions, is used to identify minerals.

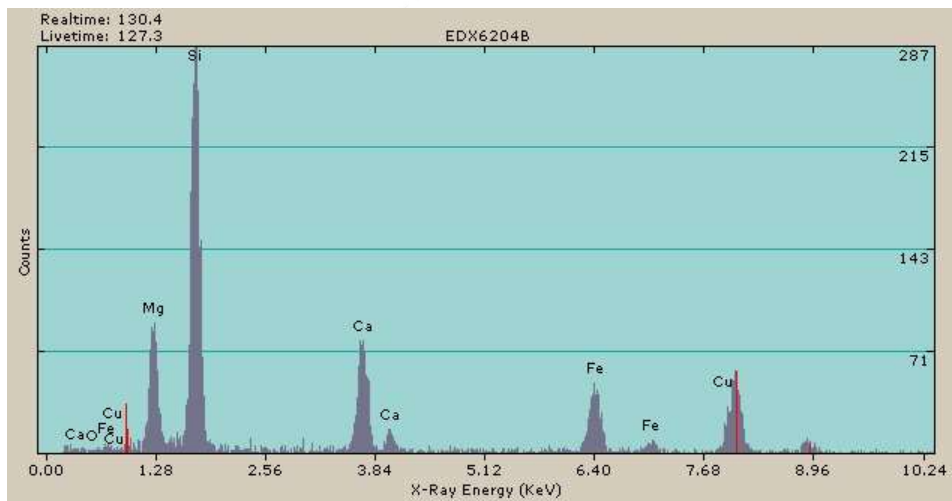


Figure 5. An energy dispersive x-ray spectrum of a particle showing the elements observed in the particle (Mg, Si, Ca, and Fe) along with copper (Cu) from the grid. The presence of the various elements and their relative proportion to each other are used to help identify the mineral.

The TEM can be used to obtain selected area electron diffraction (SAED) patterns of crystalline materials. These patterns provide information on the crystal structure of a particle and, combined with the EDXA, are used to obtain a definitive identification of the mineral. A typical SAED pattern is shown in Figure 6.

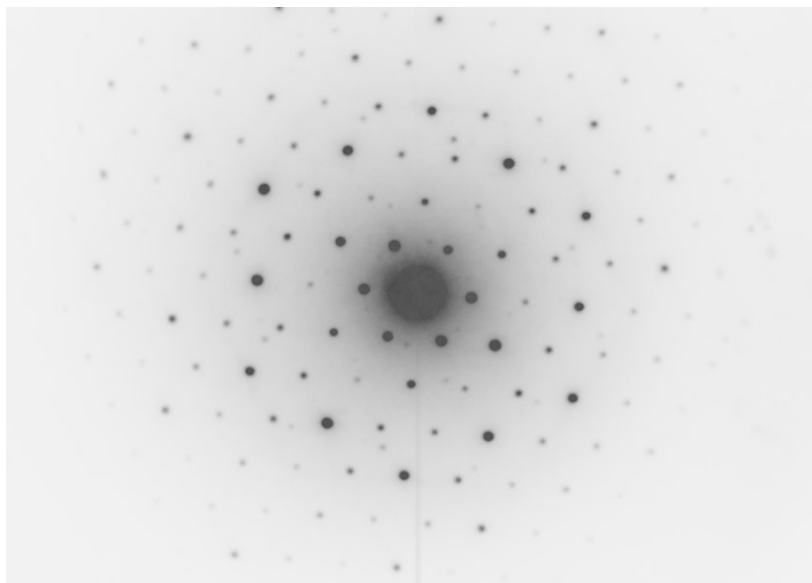


Figure 6. A typical selected area electron diffraction pattern (SAED) of a mineral particle will contain “spots” at regularly spaced intervals. The dark region in the center is the electron beam of the TEM.

While some models of electron microscopes are capable of very high magnification, most SEM analyses are performed at magnifications between 500X and 5,000X. At the lower magnifications, the very fine particles are somewhat difficult to observe. In addition, the SEM relies on a difference in contrast between the background (usually some form of carbon) and the particle. If the particle is very small or very thin, the contrast may be too low and the particle may not be observed. While SEM mineral identification is based on the EDXA, the observed patterns of some minerals appear very similar (such as between pyroxene and amphibole minerals), so the mineral identification is not definitive without additional information.

In the TEM, most analyses are performed at magnifications between 1,000X and 20,000X, with the latter most frequently used. At these magnifications, even the finest particles are readily observed. However, for practical reasons, particles that are smaller than approximately 10 μm (aerodynamic diameter) are those that are examined in the TEM. The amount of material examined in a TEM is also very small, usually in the microgram range (compared to a gram in the XRD). While much of the SEM analyses for particle characterization can be automated (at least since the 1970's) and run by computer, the TEM analyses are manual and require a well-trained microscopist for accurate analyses. Finally, in order to improve the reproducibility of the analyses between microscopists, most TEM procedures restrict the particles that are counted to those that are at least 0.5 μm long.