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DEVELOPMENT OF AN INSTRUMENTAL MONITORING METHOD FOR MEASUREMENT OF ASBESTOS CONCENTRATIONS IN OR NEAR SOURCES

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A methodology has been developed for the determination of amount and size distribution of asbestos fibers and fibrils in air at point sources and near point sources. The technique can also be applied to ambient air samples. The method employs a scanning electron microscope with microprobe capability and an image analyzing system. Complete details for manual operation have been worked out. Feasibility study for automated operation has been completed also. Preliminary results of analysis of samples collected at point sources and near point sources are also included.

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DEVELOPMENT OF AN INSTRUMENTAL MONITORING METHOD FOR MEASUREMENT OF ASBESTOS CONCENTRATIONS IN OR NEAR SOURCES

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ABSTRACT

A methodology has been developed for the determination of the amount and size distribution of asbestos fibers and fibrils in air at point sources and near point sources. The technique can also be applied to ambient air samples.

This report describes the effort on the development of an analytical method which employs a scanning electron microscope with microprobe capability and an image analyzing system. Complete details for manual operation have been worked out. Feasibility study for automated operation has been completed also.

Preliminary results of the analysis of samples collected at point sources and near point sources are also included.

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1. INTRODUCTION

The carcinogenic properties of asbestos are now well accepted [1-7]. Langer et al [4] have recently reviewed the incidence of asbestos fibers in human lung tissue and it has been experimentally verified that "asbestos bodies" do contain asbestos fibers in their cores [8, 9]. Occupational exposure to asbestos dust is associated with serious risks of lung scarring and neoplastic disease [10, 12]. Under certain circumstances, although to a lesser degree, similar hazards may exist with indirect occupational exposure [13, 14], with family contact [15, 16] and as a result of neighborhood and environmental exposure [15, 16]. For example chrysotile asbestos has been identified in the lungs of persons in New York City [3].

However, the influence of type of asbestos, fiber size and cofactors on biologic effects is not well documented [7]. Fiber size is critically important in determining respirability, deposition, retention and clearance from the pulmonary tract and is probably an important determinant of the site and nature of biologic action. Little is known about the movement of fibers within the human body, including their potential for entry through the gastrointestinal tract. The aerodynamic properties of fibers depend largely on their diameter; fibers below 3.5μ in diameter are regarded as being in the respirable range [17]. Fiber length affects deposition, longer fibers apparently having greater fibrogenic effects [18]. Hence, ambiguities exist as to the effect of size and shape of asbestos fibers in creating lung cancer. Very recently, Stanton and Wrench [19] have found that asbestos fibers with diameters in the range of 0.5μ to 5μ and up to 80μ in length create cancer in hamsters; fibers either smaller or larger than this range are harmless. This is the only experimental study [19] which proves the importance of size and shape of asbestos fibers in causing cancer. However, chrysotile fibrils with diameters ~400Å have been observed in human lung tissue [3, 4].

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For the promulgation of any asbestos standard by EPA, asbestos fibers that can be airborne and inhaled by human beings have to be identifiable and countable. From the aforesaid, it is obvious that a method(s) need to be developed which can give the amount of asbestos and their size distribution (fibers and fibrils included) in ambient air and in or near asbestos sources.

Several experimental techniques have been studied to determine the asbestos content of air. There are, however, many uncertainties as to the best methods of sampling, identifying and quantifying airborne asbestos and interpreting the data so obtained [7]. The monitoring problem lies in identifying a very small number of asbestos fibers against a background of a very large number and variety of other particles in the same sample. Only within recent years have methods for determining concentrations of fibers for industrial hygiene purposes been standardized [20]; they use samples collected on membrane filters in which fibers are counted with phase-contrast illumination in an optical microscope. However, only fibers having diameters 0.5μ and larger can be determined by this technique. This is a critical limitation of this technique.

X-ray diffraction techniques [21] can only give the total amount of asbestos in a sample; moreover, only amounts greater than ~10μg can be determined by this technique. The amount of asbestos in ambient air is believed to lie in the range of 0 to 5,000 ng/m^3. Depending on the air being analysed the necessary volume of air to produce a useable sample may become prohibitive.

Transmission electron microscopy (TEM) has been successfully applied [22-25] in the determination of the asbestos content in ambient air. However, there are two limitations in this technique, namely, only the total amount of asbestos is determined and this technique is not easily amenable to automation. The counting is very often based on a morphology identification only with this technique. Selected area electron diffraction patterns obtained in the TEM can be used to identify asbestos fibers from all others, but diffraction cannot be used to differentiate among various

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amphibole types [26].

The electron beam microprobe has been applied [8, 9] to identify asbestos fibers in lung tissues but the resolution limits it to fibers having diameters larger than ~1μ.

Recently, Maggiore and Rubin [27] have employed a scanning electron microscope (SEM) with a field emission source to identify asbestos fibers using x-ray fluorescence analysis. Asbestos fibrils ~500Å in diameter could be identified in ~200 secs. However, no attempt was made to develop a sampling system which could be used for automated identification and counting of asbestos fibers.

Urban particulate identification and characterization by combining transmission electron microscopy and x-ray microanalysis (EMMA) has been attempted recently [28] but we feel that applying any form of transmission microscopy for the identification and counting of asbestos particles in air is unlikely to ever be "commercially" feasible.

As a step towards solution to this particulate monitoring problem, a methodology has now been developed in our laboratory. The newly developed technique employs SEM and characteristic x-ray emission analysis to identify asbestos particles even in the presence of other particles. The specimen preparation is done in such a way that automated identification and counting of asbestos particles is believed to be feasible. As it stands, samples from point sources (inside an asbestos factory) and near point sources can be analysed. Further research is needed to perfect the technique for ambient air. A method for concentrating asbestos and removing other particulates must be developed.

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2. EXPERIMENTAL PROCEDURE

2.1 STATEMENT OF THE PROBLEM

The monitoring problem can be stated as "identifying and counting a very small number of asbestos fibers against a background of a large number and variety of other particles". This implies that one is interested in determining both the amount and the size distribution of asbestos particles as they exist in ambient air. The technique used in conjunction with TEM [22-25] could satisfy the first requirement but as it destroys the original size distribution of asbestos particles in air through ashing and ultrasonification there is no way of meeting the second requirement.

The present technique aims ultimately at identifying and counting asbestos in air in an automated way. Initial sample collection is by absolute filtration using a membrane filter. The final SEM specimen prepared from the airborne particles should be on a featureless background so that the particles can be detected unequivocally by an image analyzing system [29-31]. Furthermore the x-ray emission from the asbestos particles should be without either a significant background or any extraneous x-ray emission from other particles or the substrate. Hence, the amount of air collected should be such that little superposition of particles takes place. Overcrowding of the particles not only hampers image analysis but also makes the x-ray emission from the asbestos ambiguous. All operating features of the final system should be compatible with automated image analysis and x-ray fluorescence [29].

2.2 SUMMARY OF RESEARCH LEADING TO SPECIMEN PREPARATION TECHNIQUE

Initially two types of standard membrane filters were considered, namely, Millipore and Nuclepore filters. To assist in the developmental stage standard asbestos samples were obtained. To simulate air samples

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the standard asbestos fibers were dispersed in deionized water and aspirated onto filters.

Some SEM micrographs of asbestos collected on Nuclepore filter were sent for image analysis by a Quantimet 720 system. The fibres were seen to be very bright on a dark background and were felt to be very suitable for image analysis. However, a bright crescent exists around each pore in the SEM image and although the human operator can readily ignore this it is impossible for the Quantimet system to distinguish between the pore and the bright asbestos fiber. Consequently, a method to close, or eliminate the pores of the filters after sample collection was sought.

After some experimentation a method was developed to eliminate the interfering effects of the pores in the Nuclepore filter by solvent vapour attack. The resulting SEM photographs were amenable to image analysis by a Quantimet 720 system and also the solvent treated Nuclepore filter was sufficiently stable under the electron beam for x-ray analysis. The only disadvantage was that during solvent vapour attack the Nuclepore softens and the asbestos fibers get imbedded in the polycarbonate film. This results in a suppression of the soft x-rays (Si and Mg peaks) from the asbestos fibers, particularly for fibers with diameters in the vicinity of 0.1μ.

A similar approach with Millipore filters had failed because although the solvent vapour treated Millipore is featureless, it is extremely sensitive to the electron beam and virtually disintegrates on exposure.

The next development was to completely eliminate the filter leaving the particles on a featureless substrate. An optically polished pyrolytic graphite (PG) surface parallel to the c-axis is featureless when observed by the SEM at magnifications in the range of x 1,000 to x 30,000. Moreover, carbon is not detectable by E.D. x-ray analysis and gives insignificant white radiation. Pyrolytic graphite was preferred to a possible alternative beryllium because of toxicity problems. The final approach was to mount the Nuclepore filter with collected airborne particles on an optically polished PG and then completely dissolve the filter by solvent vapour

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attack. This method was successful to a considerable extent but certain reservations remained as follows:

(1) It takes more than 40 hours of solvent vapour (chloroform) attack in order to dissolve the filter to a thickness which does not suppress soft x-ray emission from asbestos significantly. X-ray emission from fibrils (500Å - 1,000Å) was still significantly suppressed.

(2) It will take a significantly longer time to completely eliminate the Nuclepore filter. Moreover, the particle distribution could be unstable when the Nuclepore filter is completely dissolved.

(3) A Cl peak from an undissolved filter appears along with Si, Mg, and Fe peaks from the asbestos during microprobe analysis.

A solvent attack in the liquid state was not thought to be possible as the fibers or particles are not restrained as the filter dissolves. Attempts to use a similar approach with Millipore filter failed because even a very thin layer of Millipore filter left behind after the vapour attack disintegrated under the electron beam.

Following considerable experimentation a satisfactory technique to study airborne particles by SEM along with energy dispersive x-ray analysis and image analysis was finally developed. The technique is based on the system described above but with one or two critical variations. The details of the technique are described in the following Section 2.3. We believe that this technique is reliable and could be repeated in any laboratory without undue expense or difficulty.

2.3 DESCRIPTION OF METHODOLOGY FOR THE ANALYSIS OF ASBESTOS IN AIR

2.3.1 Sampling

Airborne particulates are first collected on a Millipore filter of either 0.45μ or 0.8μ pore size. The pore size of the Millipore filter is not a critical variable but does influence the superposition of particles.

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Using a 0.45μ Millipore filter a large number of ~0.1μ size spherical particles are collected on the filter. These airborne particles are not asbestos and are not collected with a 0.8μ Millipore filter. For the determination of asbestos in the air the 0.8μ Millipore is therefore preferable. One can sample a larger volume of air with a 0.8μ size filters than with a 0.45μ size filters without overcrowding the background with the small spherical particles. Minor differences in image analysis that arise with different size Millipore filters will be discussed further in Section 3.1 on SEM Observations. Virtually all fibers are collected with the 0.8μ size Millipore filter [25] even though the 0.8μ pore size is larger than the largest dimension of some asbestos fibrils. It has been found [25] that the surface charge properties of the filter and the asbestos, as well as the circuitous path through the filter result in virtually complete collection of all asbestos material.

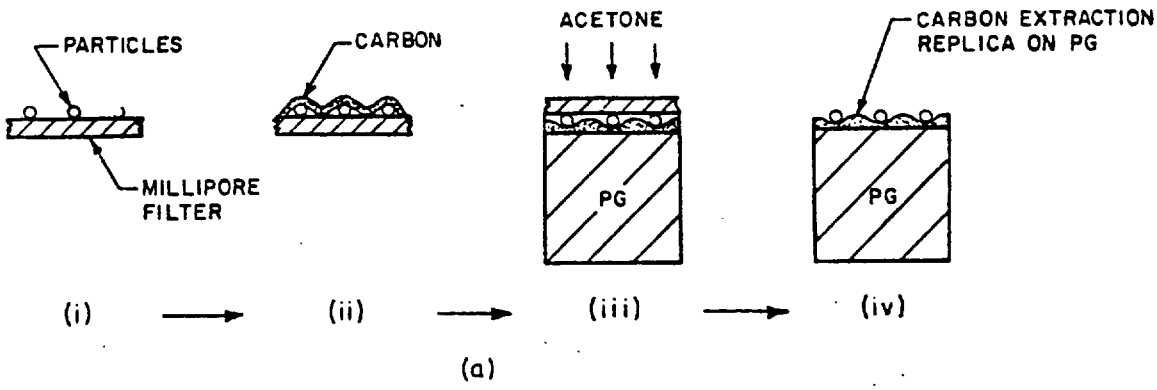
The volume of air filtered lies in the range of $0.1m^3$ to $0.15m^3$. If the sample volume exceeds $0.15m^3$, overcrowding of particles occurs and if the volume is much less than $0.1m^3$, the number of asbestos fibers is too few to permit reasonable counting statistics. The rate of air collection is not thought to be an important variable.

The above discussion is for point source (inside an asbestos factory) or near point source (adjacent to an asbestos source) sampling. As will be discussed in Section 5.1, further research is needed to perfect a system for ambient air samples. A process of concentrating asbestos fibers and eliminating extraneous particles is needed for ambient air samples.

2.3.2 Specimen Preparation for Scanning Electron Microscopy and Microprobe Analysis

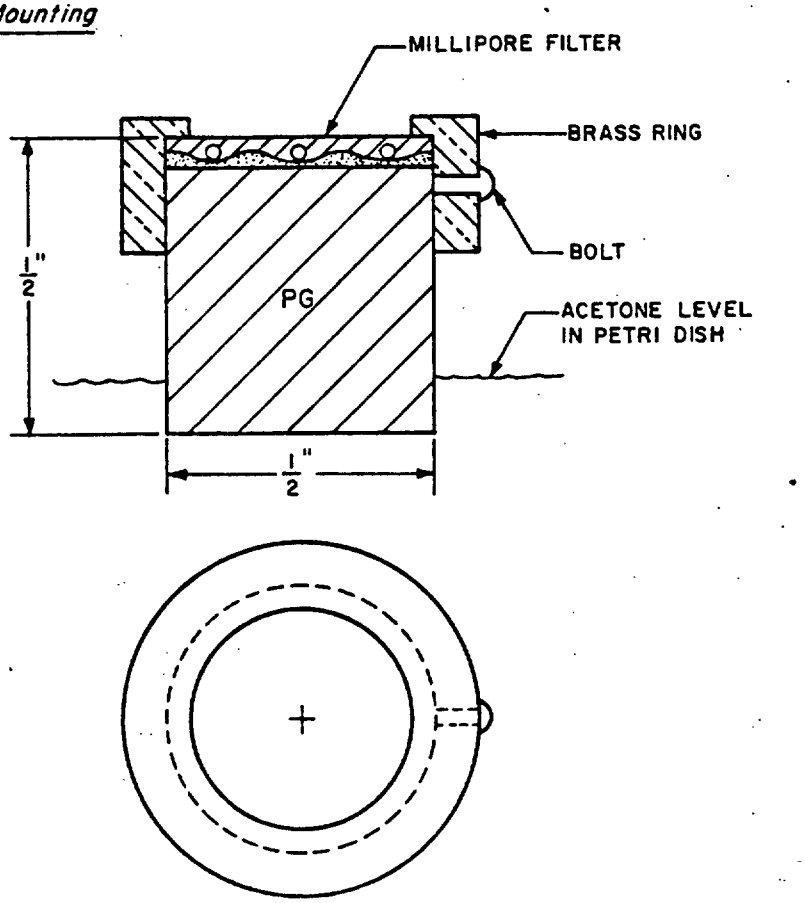
The steps involved in specimen preparation are shown schematically in Figure 1. The Millipore filter is mounted on a clean metal disc; mounting is done with rubber cement which is put only at the periphery of the filter. A very thin carbon layer (~100Å) is evaporated onto the filter in a vacuum evaporator. (The thickness of the carbon layer is monitored by observing the surface of a drop of oil resting on glazed

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(a)

Mechanical Mounting



(b)

Figure 1. Schematic Diagram of the Steps Involved in Specimen Preparation

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ceramic. As soon as the oil drop is distinctly visible with respect to the darkened glazed surface, evaporation is stopped.) A thicker carbon layer embeds the asbestos fibrils and suppresses x-ray emission from them.

A 1/2" diameter circular piece of the "composite" film is now cut out with a sharpened hollow tool (hardened tool steel). Four such specimens can be made from a standard 47mm Millipore filter. The "composite" film is put on optically polished pyrolytic graphite* stud and mounted mechanically with carbon side down as shown in Figure 1(b). As stated before the surface parallel to the c-axis can be polished to a featureless finish at magnifications in the range of x1,000 to x30,000.

The PG stud (Figure 1(b)) is next put in a covered petri dish containing acetone. Care should be taken to see that the level of acetone in the petri dish is such that the liquid does not attack the filter paper directly. The specimen undergoes acetone vapour attack for about half an hour. Initially, the composite film swells due to the vapour attack but then settles down on to the PG.

The brass ring serves to keep the film in position while swelling occurs. During vapour attack the Millipore filter becomes transparent. Occasionally, a few bubbles form when the film is settling on the PG causing breaks in the continuous film. This does not affect the general procedure and on average, 90% of the film remains continuous.

After the film has completely settled on the PG (as observed visually), the stud is totally immersed in acetone for a minimum of 2 hours. Accelerating the dissolution by slow stirring is not recommended because of the fragile nature of the carbon replica.

After the brass ring is removed, the specimen is ready for SEM observation. A thin layer of Millipore filter is left behind on the PG around the periphery of the carbon extraction replica, (Figure 1(b)). A line of silver paint is put over this to avoid charging under the electron beam.

* Obtained from Union Carbide

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PG studs can be used repeatedly if the carbon extraction replica is removed by ultrasonic cleaning in acetone.

To summarize the technique produces a carbon extraction replica of all airborne particles lying on polished PG. All airborne particles are retained unless there is excessive overcrowding of particles leading superposition. The carbon layer preserves the original distribution of the particles as collected on the Millipore filter. The carbon extraction replica adheres well to the PG, so that the stud can be handled with ease.

2.3.3 Specimen Preparation TEM

Although transmission electron microscopy was not specifically explored in this project, a modification of the above specimen preparation technique was shown to be a convenient method of sample preparation for transmission microscopy.

The specimen is prepared in the same way as described in Section 2.3.2 up to the acetone vapour attack. At this stage, the brass ring is removed and the composite film peeled from the PG with a pair of tweezers. The film is put on a clean glass slide and sections to fit a copper TEM grid are cut out. The composite film with carbon side down is placed on a copper grid and dipped into acetone for half an hour. The Millipore filter completely dissolves in the acetone and the copper grid (200 mesh) supports a carbon extraction replica containing the airborne particles. This technique is complementary to other similar techniques [22, 32].

2.3.4 Measurement Techniques

The following summarizes the counting proceedure in a totally manual mode. Operational modes for automatic operation will be described and discussed in Section 4.2 on Feasibility Study - Automated. Operational modes are described for a scanning electron microscope JSM-50A with a guaranteed resolution of 100Å. The E. D. x-ray analyzer is based on a detector having a 0.0007mm Be window with a resolution of 160 ev.

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The specimen is first observed in the picture-mode at a condenser lens setting which gives an electron beam current of ~2×10^{-11} amps. At this setting, the resolution is ~100Å. The carbon replica does possess a surface structure which is a replica of Millipore filer, but at a beam current of 2×10^{-11} amps (normal picture mode operation) the replica is featureless. Asbestos fibers appear as bright images against a dull background with an intensity that depends on their size. Fibers with larger diameters appear brighter than those with smaller diameters. To observe asbestos fibrils (~500Å in diameter), the contrast has to be increased by increasing the electron beam current thus enhancing the secondary electron yield. This also results in the appearance of the background structure from the carbon replica but this can be suppressed by the image analyzer for particle counting.

A magnification of x1,000 or x3,000 is suitable for observing and counting asbestos fibers in air samples. Fibrils can be detected at about x3,000. The optimum magnification depends on the concentration of fibers or particles and is such that about 5 to 10 fibers are within a field of view. Twenty five random areas are selected and the fibers in them counted for statistical analysis.

The x-ray microprobe analysis for positive identification of asbestos is done in the following way. First, the number of fibers and fibrils are counted on the viewing screen and the size (diameter and length) of the fibers recorded. Each fiber is then brought to the center of the screen and the beam current increased to 1.5×10^{-9} amp. by adjusting the condenser lens. At this current, the resolution is adequate and fibers and fibrils are still observed distinctly. The microscope is now brought to the spot-mode and the spot centered on the fiber. X-ray counts are accumulated for 5 secs. to 60 secs. depending on the fiber size; smaller fibers take a longer time to yield significant Si, Mg, and Fe peaks. The same procedure is repeated for other fibers in the field of view. Fibers which do not show Si, Mg, and Fe peaks are rejected as being non-asbestos material. The field of view is then changed to another area.

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The reason for getting an image first at a current of 1.5×10^{-9} amp and then changing to spot-mode is that there is a shift in the picture when the beam current is changed. One could operate at a current of 1.5×10^{-9} amp during the whole operation but two difficulties arise. Firstly, as the resolution is degraded the accuracy of determining the diameter of the fiber is decreased considereably. Secondly, the background structure due to the carbon replica becomes less desirable at a current of 1.5×10^{-9} amp.

2.3.5 Analysis of Microscopic Data

The technique developed aims at identifying and quantitating the asbestos in air samples. The identification of the asbestos is by means of the characteristic x-ray emission spectra, Si, Mg, and Fe are the vital elements. Langer et al [8, 9] have used the intensity ratios of Si, Mg, and Fe peaks to classify asbestos into chrysotile and amosite, etc. However, such a classification was not stressed in the manual approach as it is quite time consuming. The present technique aims at identifying and quantifying asbestos in air rapidly. With our present capabilities, asbestos fibers down to 0.2μ diameter can be identified in 5 secs; fibers with diameters less than 0.2μ need counting time up to 60 secs.

The total amount of asbestos and its size distribution are determined in the present technique. Twenty-five random areas are counted at a convenient magnification, preferably x3000, for a statistical measurement using the following two formulae:

$$\frac{\text{Average number of fibers} \times K}{\text{Volume of air collected } (m^3)} = \text{Number of fibers}/m^3 \qquad (1)$$

$$\frac{\text{Average weight of fibers} \times K}{\text{Volume of air collected } (m^3)} = \text{Weight of fibers}/m^3 \qquad (2)$$

where, $K = \dfrac{\text{Filter area } (mm^2)}{\text{Field area } (mm^2)}$

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As noted earlier, the length and diameter of each fiber are recorded at a given magnification; the weight of each fiber is calculated knowing its density [33, 34].

The size distribution of asbestos fibers is represented by a cumulative frequency distribution of length of fibers. The diameter of the fibers is also another important variable; however, the length distribution is the criterion that will be used in the present work. Most of the fibers in air samples have diameters less than 5μ whereas their length variation is considerable. Moreover, longer fibers apparently have greater fibrogenic effects [18]. One could use an equivalent (spherical) radius for asbestos fibers. Recognizing that no conclusive results exist to determine which physical parameters for asbestos controls the health hazard we have chosen to present a cumulative frequency distribution asbestos fibers lengths.

The total number of particles that need to be counted for presenting a statistically reliable cumulative frequency distribution is debatable and depends on the technique used to count them [35]. We believe that the total number should be about 100 for a good distribution plot. This is achievable without making the counting very time consuming. Counting is continued in the present technique until about 100 asbestos fibers are counted, generally involving surveying rather more than 25 random areas.

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3. EXPERIMENTAL RESULTS

3.1 SEM OBSERVATIONS

The surface structure of 0.45μ pore size Millipore filter is shown in Figure 2(a). Unlike Nuclepore filter, both sides of a Millipore filter show identical structure. Figure 2(b) illustrates standard crocidolite fibers aspirated onto the Millipore filter.

Figure 3(a) shows standard amosite fibers aspirated onto a Millipore filter; the specimen has been prepared according to Section 2.3.2. The brightness of the fibers with respect to the background depends on the diameter of the fiber. The picture, Figure 3(a), was taken under high contrast condition and a surface structure of the carbon extraction replica (0.45u Millipore filter) is observed. Airborne particles with chrysotile fibers from a point source are shown in Figure 3(b).

An air sample was collected on a 0.8μ pore size Millipore filter inside an asbestos factory dealing with chrysotile fibers only; the volume of air collected was $0.135m^3$. As was mentioned in Section 2.3.4, the background structure of the carbon extraction replica from a 0.8μ pore size Millipore filter is worse than that from a 0.45μ pore size Millipore filter (compare Figures 3(a) and 3(b)) particularly at high magnifications. However, this background structure is easily suppressed by the Quantimet 720 image analyzer, and does not hinder counting of fibers either manually or by the contemplated automated operation.

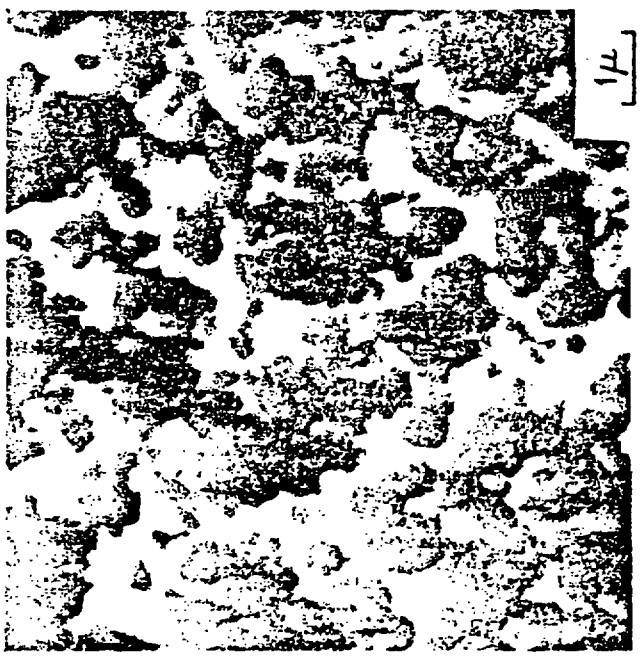
SEM photographs of near-point-source and ambient air samples are shown in Figure 4 and Figure 10(a) respectively. Comparison of Figures 3(b), 4(a) and 10(a) indicates that the ratio of asbestos particles to extraneous particles decreases progressively from the point source to ambient air samples. The air sample in Figure 10(a) was obtained with a 0.45μ pore size Millipore filter, and the point-source and near-point-source

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(b)

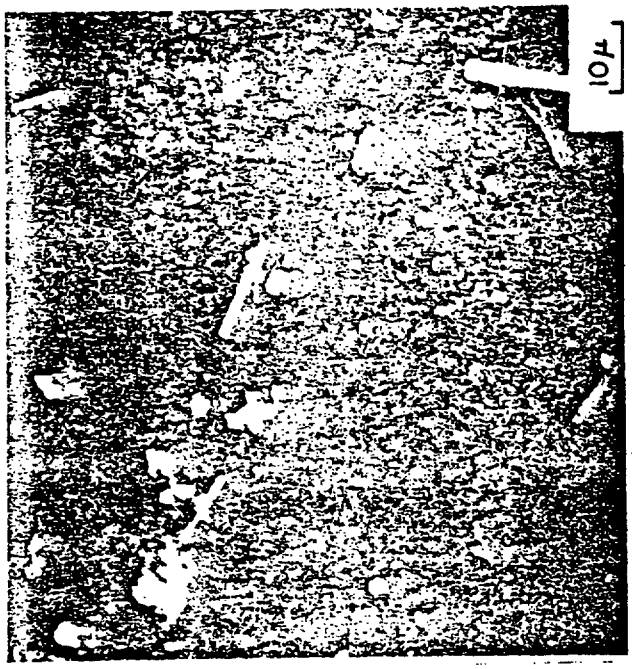
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(a)

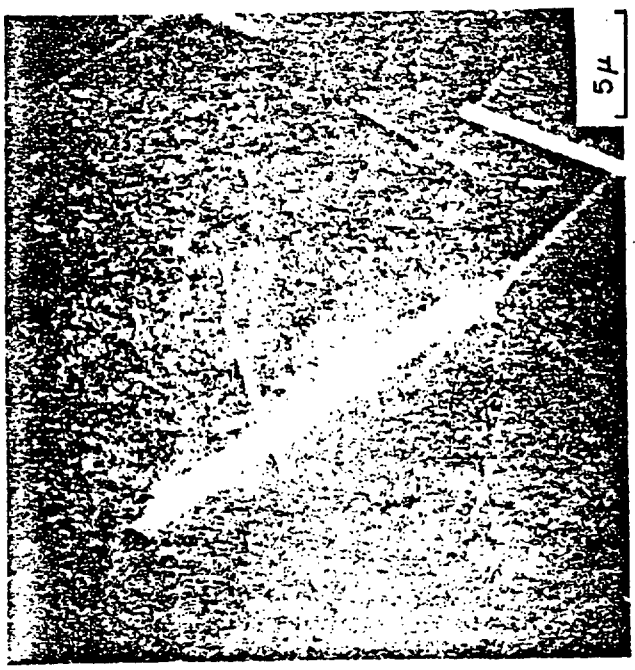
Figure 2. SEM Photographs of Millipore Filter with Standard Crocidolite
(a) Blank (b) With Crocidolite; X 10,000

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(b)

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(a)

Figure 3. SEM Photographs of Standard and Point-Source Samples
(a) Standard Amosite; 0.45 μ filter; X 3,000
(b) Point-Source; 0.8 μ filter; X 1,000

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samples in Figures 3(b) and 4(a) respectively, were obtained with a 0.8μ size filter. A large number of ~0.1μ size extraneous particles are visible in the air sample, Figure 10(a), but not in Figures 3(b) and 4(a). For present purposes a 0.8μ Millipore filter is preferable. *Occasionally*, asbestos fibers are seen in conglomeration with other particles as shown in Figure 4(b); although an operator can cope with such a situation, automated counting in such an area would present difficulties.

3.2 MICROPROBE ANALYSIS

For x-ray fluorescence analysis the JSM-50A is operated at a beam current of ~1.5×10^{-9} amp. Voltage and current can be optimized for the best count rate from asbestos fibers [27] but all data presented in the following were obtained at 25 KV and at ~1.5×10^{-9} amp. X-ray emission data is obtained in the spot-mode rather than picture-mode as the background radiation is high in picture-mode. The energy dispersive spectrometer is equipped with a detector having a 0.0007mm Be window thus allowing a high counting rate at the soft X-ray end of the spectrum (Mg and Si).

Most of the counting was done on chrysotile which is the most common type of asbestos used in the U.S.A. [33]. Moreover, chrysotile asbestos fibers easily break down to fibrils of ~500Å diameter when subjected to ultrasonic vibration. Mg is leached out of chrysotile asbestos in many environments [25]; hence, our x-ray studies were mostly done on chrysotile collected from air at a point source. However, the standard crysotile was used after ultrasonification in order to get asbestos fibrils whose diameters are less than 0.1μ. This was necessary in determining the limit of detection of the smallest fibrils with the present capabilities.

A distinct x-ray spectrum of chrysotile asbestos is obtained in 5 secs from fibers having diameters greater than 0.2μ; an example for a 0.5μ diameter fiber is shown in Figure 5. To know the limit of detection, x-ray spectra from 0.1μ and 500Å diameter fibers were also obtained and are presented in Figures 6 and 7 respectively; corresponding SEM photographs are

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(b)

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(a)

Figure 4. SEM Photographs of Near-Point-Source Samples (a) X300; (b) X1,000

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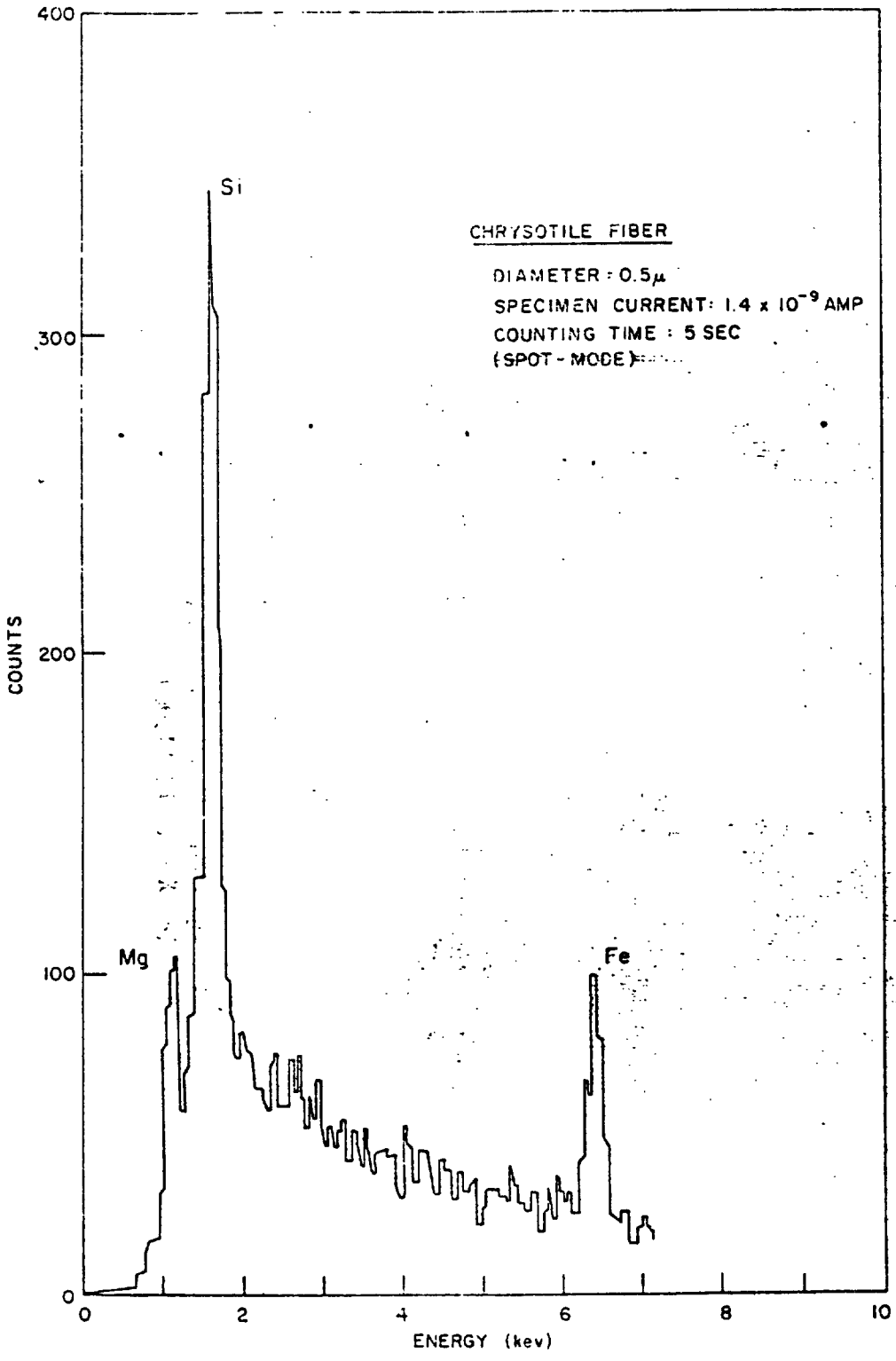


Figure 5. X-ray Spectrum from a 0.5μ Diameter Chrysotile Fiber

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shown in Figures 8(a) and 8(b). Photographs were taken after the x-ray counts were recorded and the white spots represent the points at which the electron beam was directed. As can be seen in Figures 6 and 7, the count rate is not good and the peak to background ratio is rather low. The count rate could be improved considerably by avoiding charging effects on the fibers, which is manifested as bright spots after irradiation (Figures 8(a) and 8(b)). Charging of the fibers leads to an effective reduction of the applied voltage and hence a low count rate. This aspect needs further investigation and we believe, a 500Å fibril could be detected in less than 30 secs with our present system if the charging effect is removed. A thin layer of carbon coating after final specimen preparation (Section 2.3.2) should remove the charging effect.

3.3 IMAGE ANALYSIS

For an automated determination of the amount and size distribution of asbestos in air samples, it was planned to use an Image Analysing System (e.g. Quantimet 720 [30, 31]). For the feasibility study, SEM photographs of standard asbestos and air samples were sent to IMANCO*. The following questions were raised to assess the plausibility of a fully automated operation, Section 4.2.

1. The total count of distinguishable particles of all aspect ratios.
2. What are the total number of fibers with an aspect ratio of greater than 3 to 1?
3. Are you able to generate automatically a histogram of the size distribution?
4. What x, y coordinates would be available from the IMANCO system to locate an individual fiber?
5. Are there problems with variations in brightness that make it impossible to count all the fibers without generating extra counts?

*Manufacturer: IMANCO, Image Analysing Computers, 40 Robert Pitt Drive, Monsey, New York 10952.

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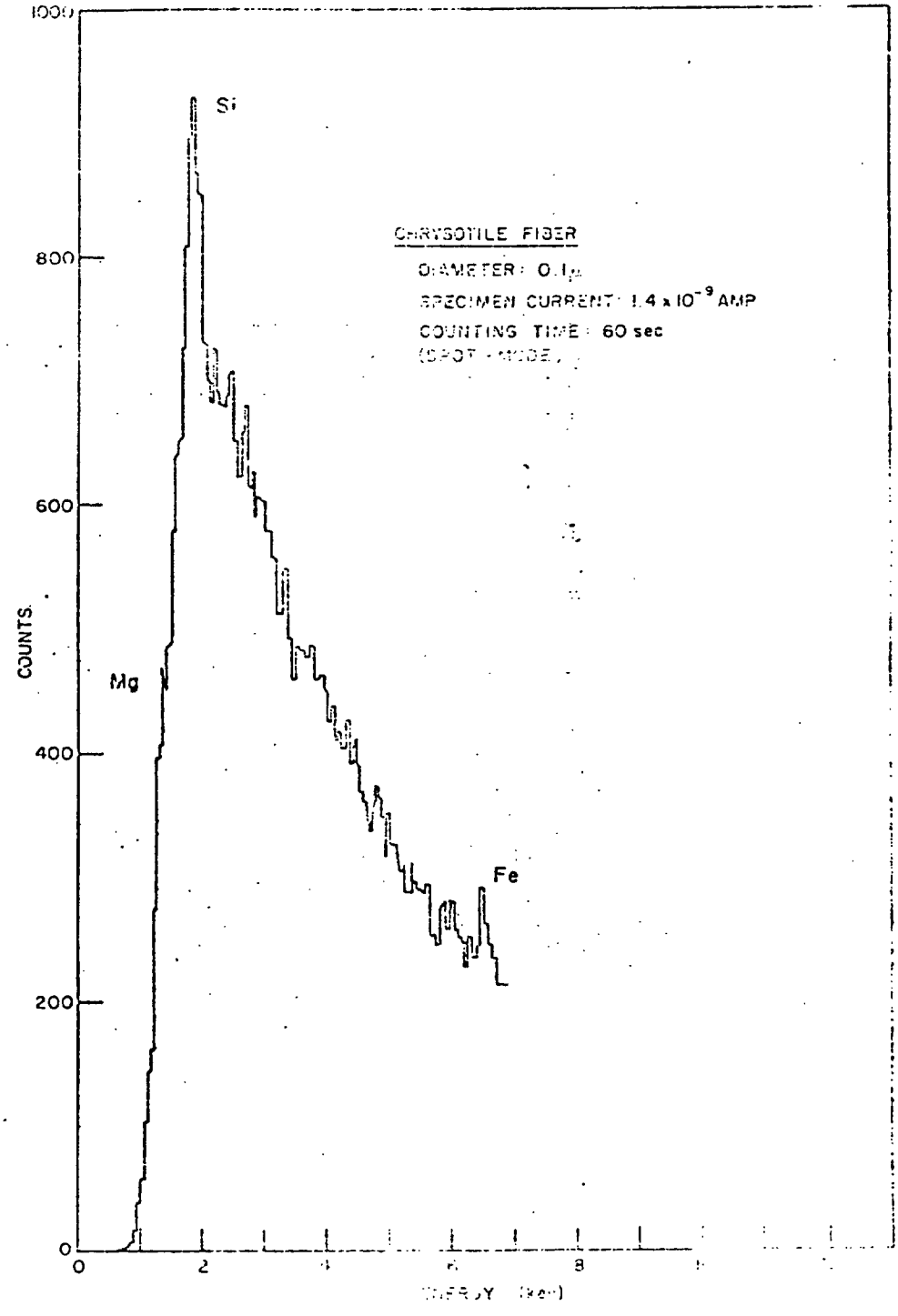


Figure 6. X-ray Spectrum [illegible] a 0.1μ Diameter Chrysotile Fiber

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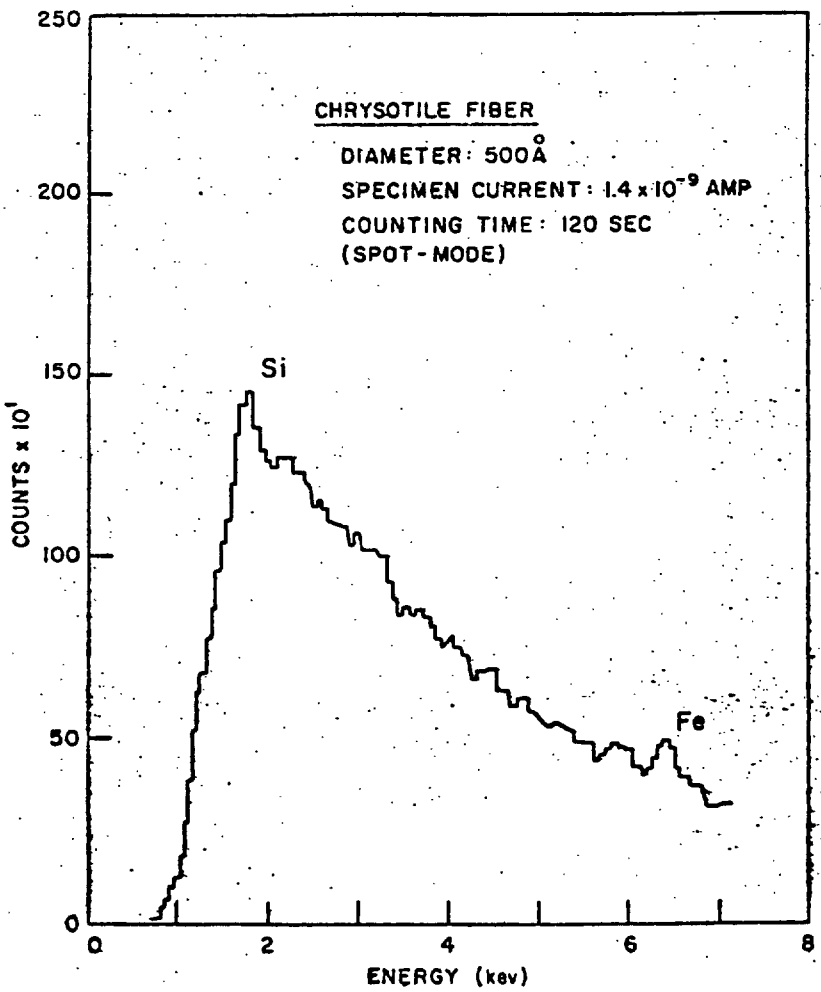


Figure 7. X-ray Spectrum from a 500 Å Diameter Chrysotile Fiber

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(b)

(a)

Figure 8. SEM Photographs of Chrysotile Fibers from which X-Ray Spectra were Obtained (a) 0.1 μ diameter fiber; X10,000 (b) 500 Å diameter fiber; X10,000

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(a)

(b)

Figure 9. SEM Photographs of Standard Crocidolite and Its Corresponding IMANCO Images (a) SEM Image X1,000; (b) IMANCO Image Counting All Particles

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F-C3415

(e)

(d)

(c)

Figure 9. SEM Photographs of Standard Crocidolite and Its Corresponding IMANCO Images (c) IMANCO Image Counting Fibers Only; (d) IMANCO Image with Perimeter Display; (e) IMANCO Image with "Count Flags"

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The results are very encouraging with regard to automated counting. The results, presented in the following, are based on certain image analyzing concepts which are dealt with in detail by Jesse [31] and will not be repeated here.

Figure 9(a) shows a SEM image of an aspirated standard crocidolite. The IMANCO image showing the total number of all particles is shown in Figure 9(b). The system was run "wide open" and there are 193 particles of all aspect ratios within the measuring frame. Figure 9(c) shows the total number of fibers with a greater than 3 to 1 aspect ratio. The fibers were identified from other particles using the Form Separator [31] having an $Area/Perimeter^2$ ratio of 0.050 or less. This resulted in a count of 58 fibers. After isolation of "fibers" on the basis of their form factor, artifacts were sized out using an area discrimination factor of 50 picture points. This resulted in a count of 51 acceptable fibers. Figure 9(d) shows the perimeter display of all acceptable fibers; a perimeter distribution is easily obtained from Figure 9(d). A length distribution of the fibers is in turn easily found from the perimeter distribution as the perimeter of a fiber is twice the length approximately. A small error is introduced by the fact that some are wider than others but this is not enough to skew the curve. Later, the IMANCO analyzing computer can be asked to find the shortest dimension of each fiber; this will give the approximate diameter of each fiber assuming that the fibers do not have varying diameters. Figures 9(a), 10(a) and 3(b) show that in fact asbestos fibers have nearly constant diameters. From the diameter and length of each fiber, the volume of each fiber can be determined; this is required to determine the average weight of asbestos fibers. Moreover, a histogram of length distribution can be plotted automatically.

In order to carry out microanalysis on each fiber on an automated basis, the coordinates of each fiber need to be known. This is also accomplished by the Quantimet 720 system. Each fiber is assigned a "count flag" as evidenced as a tiny white spot at the bottom of each feature accepted by the pattern recognition logic. The X-Y coordinates are available via the Feature Data Interface which is compatible with most mini-

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computer systems. The X is available as the digital value (1-880) of the picture-point at the leading edge of the flag (there are 880 picture-points on each scan line). The Y is available as the line (1-688) number on which the flag is located (there are 688 lines per frame). The "count flags" are not visible in Figures 9(c) and 9(d); but are made visible in Figures 9(e) and 9(b). Knowing the X-Y coordinates of each fiber the computer can guide the electron beam to the fiber for x-ray microprobe analysis.

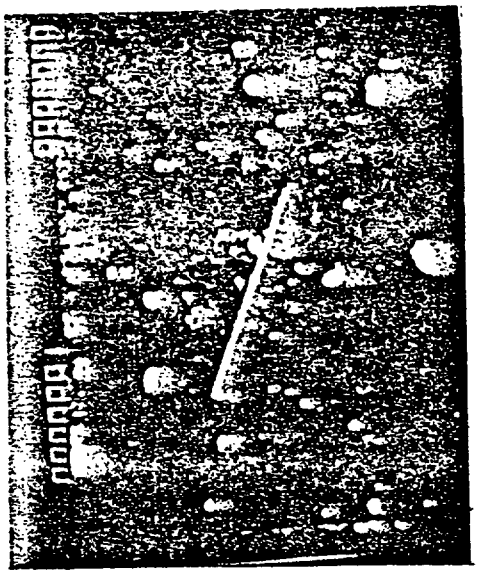
There is some problem with the brightness of different fibers (see Figure 9(a)). However the operator has a number of variables with which to deal with this problem when actual interfacing is done between a Quantimet 720 and a JSM-50A.

Figure 10 shows a SEM photograph of an air sample and its IMANCO image. There is a single asbestos fiber in the presence of innumberable extraneous particles. After going through the procedures described earlier with respect to Figure 9, the Quantimet 720 counts 1 fiber as seen in Figure 10(b). This result is very encouraging as actual air samples are similar to Figure 10(a). It is obvious that point-source and near-point-source photographs (Figures 3(b) and 4(a) respectively) will be analyzed by the Quantimet 720 system with ease.

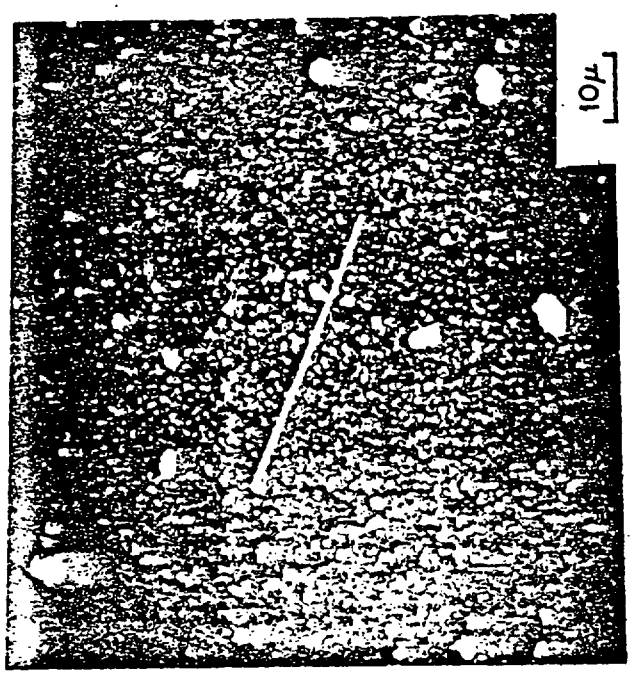
3.4 ANALYSIS OF ACTUAL AIR SAMPLES

Point-source, near-point-source, and air samples were collected on Millipore filters and specimens from these were prepared for SEM observation. Manual counting was done on the point-source and near-point-source samples; all the fibers counted in these samples were not confirmed as asbestos for the following *preliminary* results. Total number of fibers per m^3 and total weight of asbestos per m^3 were determined according to Eqs. 1 and 2; the data is presented in Table I. In order to gain confidence in the technique, one specimen was prepared with a known amount of asbestos, i.e, 10×10^{-5} gms. A statistical count gave a value of 8.1×10^{-5} gms., which is in excellent agreement. Also included in Table I is a

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(b)



(a)

Figure 10. SEM Photograph of Air Sample and Its Corresponding IMANCO Image
(a) X1,000

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Table I. Analysis of Point-Source and Near-Point-Source Samples (Preliminary)

Sample*	Type**	Air Volume (m^3)	Magnification	Number of Fibers Counted	Asbestos (fibers/$m^3 \times 10^3$)	Asbestos (gm$\times 10^{-9}/m^3$)
A-228	PS	0.135	X1,000	40	1012	200,000
A-224	PS	0.090	X1,000	63	1060	76,000
A-225	PS	0.135	X1,000	44	1077	78,000
A-227	PS	0.135	X1,000	41	1040	130,000
A-226	NPS	0.135	X1,000	45	1140	50,000
A-223	NPS	0.135	X500	22	140	11,000
1	Standard	10×10^{-5} gms of Asbestos Filtered	X20,000			8.1×10^{-5} gms
Battelle[22] Report	NPS 3/4 mile from factory	1.4 m^3				8,200

*Different designation like A-228, etc., refer to different places inside the factory.
**PS: Point Source (inside factory)
NPS: Near Point-Source (20 feet from factory)

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data point from the Battelle Report [22] for comparison with our values of mass concentration.

To illustrate the possible importance of size distribution specimens A-226 and A-227 were chosen for comparison. Specimen A-226 has 1140×10^3 fibers/m^3 and $50{,}000 \times 10^{-9}$ gm/m^3 whereas A-227 has 1040×10^3 fibers/m^3 and $130{,}000 \times 10^{-9}$ gm/m^3. Although the number concentrations of fibers are approximately equal a weight difference arises because of their respective size distributions as is shown in Figure 11. According to Stanton [19], the critical length of the hazardous asbestos fibers is put at 80μ (tentative only). From a plot similar to Figure 11, one can draw many conclusions. For example, 90% of the asbestos fibers in A-227 is in the "harzardous" region whereas all of A-226 is in this hazardous region. Considering only the total weight of asbestos in the two samples, A-227 would seem worse than A-226 from a health hazards point of view. The above analysis is speculative but is used to illustrate the potential significance of size distribution.

Air samples collected at FIRL had very few asbestos fibers and hence a statistical analysis could not be carried out. However, asbestos fibers have been identified positively in air samples and an example is shown in Figure 10(a). A process of concentrating asbestos fibers in air samples has to be devised to permit meaningful statistical counts.

3.5 TEM OBSERVATIONS

Carbon extraction replicas of standard asbestos and air samples were successfully made as described in Section 2.3.3. An example of a standard chrysotile specimen is represented in Figure 12. The replicas were observed at 100KV in a JEM-7 Electron Microscope. It is interesting to note that the carbon extraction replica has a surface structure (replica of Millipore filter) which is distinctly visible in the TEM, Figure 12(a); but does not appear nearly as distinctly in the SEM. Selected area electron diffraction patterns were difficult to obtain because the fiber has to be thin enough to be electron transparent. We believe that this represents a serious

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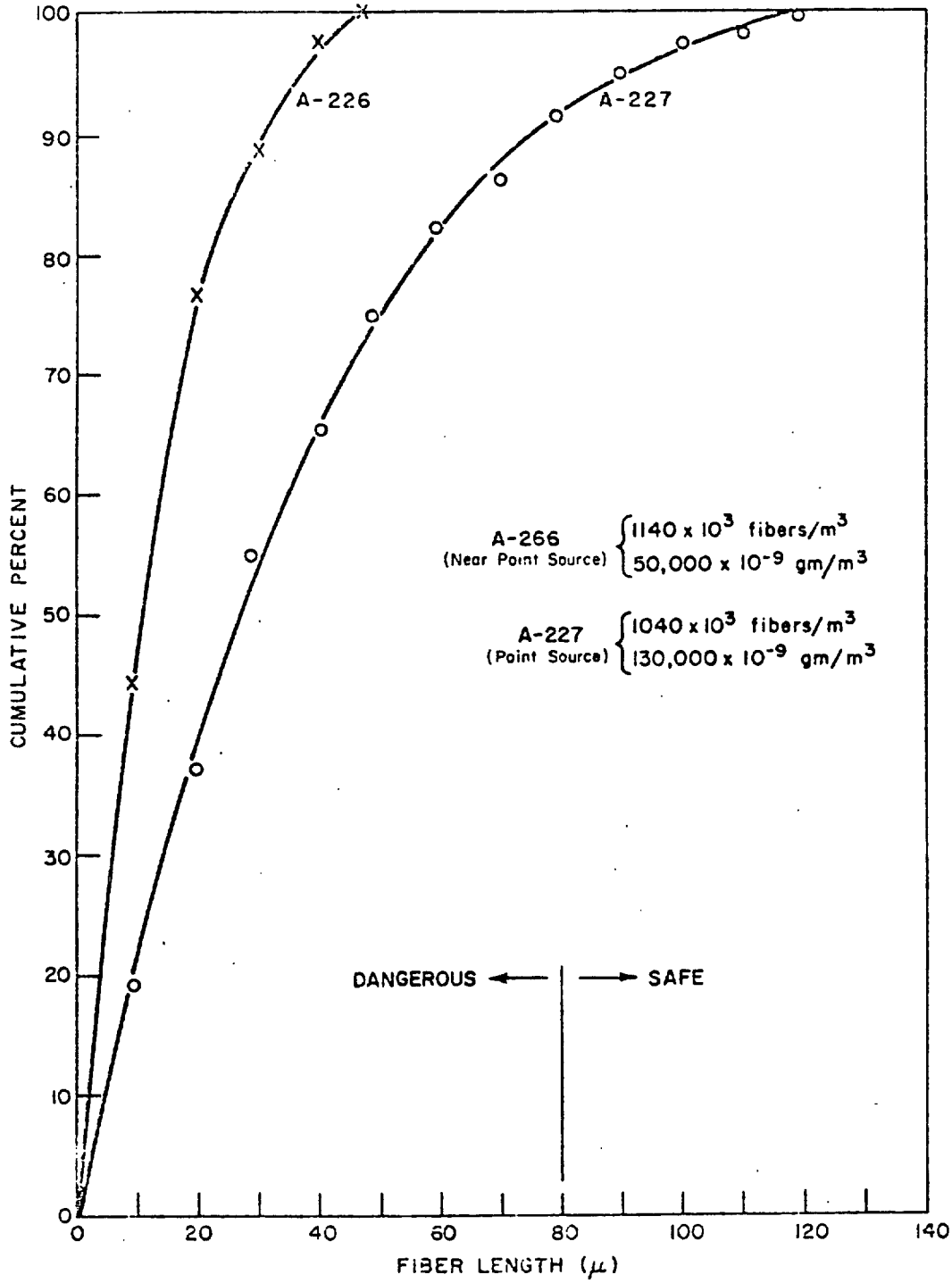
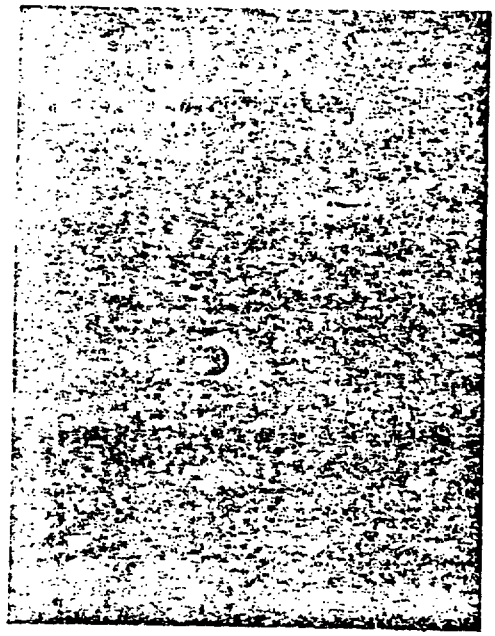


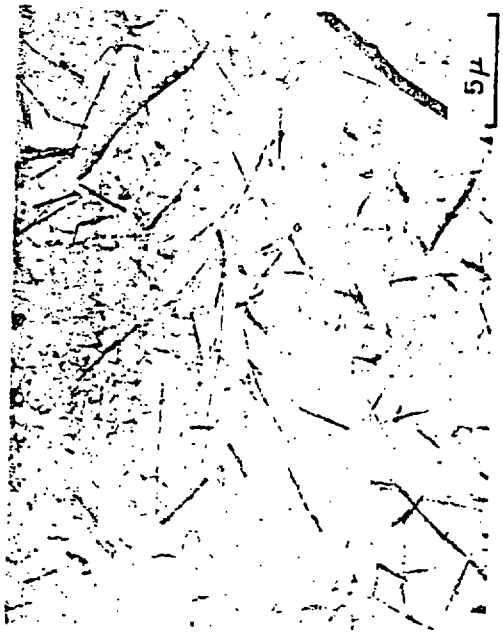
Figure 11. Cumulative Distribution of Fiber Lengths in Point-Source and Near-Point Source Samples

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(b)

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(a)

Figure 12. TEM Photographs: Carbon Extraction Replica of Aspirated Standard Chrysotile and Selected Area Electron Diffraction Pattern from Chrysotile (a) X3,200

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limitation to identifying asbestos fibers by TEM which could perhaps be offset by using high voltage transmission microscopy. Another limitation is the difficulty of differentiating between amphibole asbestos fibers by their electron diffraction patterns [26].

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4. DISCUSSION

4.1 FEASIBILITY STUDY-MANUAL METHOD

A technique has been developed to determine the total amount of asbestos and its size distribution in air at point sources and near point sources. The size distribution of the asbestos fibers which is obtained by the present technique corresponds to the distribution of the fibers as they actually existed in the air. No steps are involved which might disturb the original fiber distribution. In contrast the techniques which employ current TEM techniques destroy the original distribution of fibers; the fibers are broken into fibrils by ultrasonification [22-25]. Also violent procedures like ashing, ultrasonification and aliquoting are not involved in the present technique.

All the problems relating to a manual operation have been solved. A systematic counting of asbestos fibers can be done for point-source and near-point-source samples. For ambient air samples, a process of concentrating asbestos fibers has to be investigated. Even if suitable technique for concentrating asbestos fibers could not be developed the amount of asbestos in ambient air samples could probably be determined by scanning all the areas in a prepared specimen instead of a limited number such as 25.

Unlike optical microscopic techniques [18], the present technique permits positive identification and counting of asbestos fibers and fibrils in the same sample (fibrils cannot be observed in optical microscopes). TEM techniques [22-25] can be used to count fibers and fibrils; however, unambiguous identification of asbestos, particularly the amphibole types, is not possible. The salient advantage of the present technique is that it is amenable to automated identification and counting. Maggiore and Rubin [27] have developed a technique very similar to the present one but, their technique appears much less amenable to automated counting.

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To date, the present technique is the only method available for determining the total amount of asbestos and its size distribution either manually or automatically. At the present stage of development the technique is only applicable to point-source and near-point-source samples; however, ambient air samples could be handled with the following two modifications: (1) a pre-concentration of asbestos in air samples or, (2) scanning all areas in a specimen instead of a limited number of random areas.

4.2 FEASIBILITY STUDY-AUTOMATED METHOD

A feasibility study for an automatic determination of the amount and size distribution of asbestos fibers in or near sources has been completed. In the original proposal we contemplated to use a SEM with microprobe facility in conjunction with an image analyzing system. The image analyzing system would have been interfaced directly with SEM viewing screen and a minicomputer with certain software would have controller the whole operation. The details of the steps involved in the development of such a system have been worked out and will be described in the following. Given suitable financial resources such a system will be developed at FIRL.

1. Specimen Preparation:

Air is collected on 0.8μ pore size Millipore filter; the required volume of sampled air lies in the range of $0.10m^3$ to $0.15m^3$ for point sources and near point sources. The volume of air collected is determined to by the need to avoid overlapping at the high end and to have sufficient fibers to count at the low end.

The details of the specimen preparation for SEM observation are described in Section 2.3.2. Basically, a carbon extraction replica of airborne particles is carefully mounted on an optically polished pyrolytic graphite stud. Asbestos fibers appear as bright features in either a clear background or a background of extraneous particles. It has been

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shown, in the present investigation, that image analysis by the Quantimet 720 system can be performed on specimens prepared according to Section 2.3.2.

2. Automated Operation:

The following are the steps contemplated for an automated analysis. The proposed analytical system would typically consist of a Scanning Electron Microscope (JSM-50A) with E. D. X-ray analyzing capability (NS-880), an Image Analyzing System (Quantimet 720) directly interfaced with the SEM, software to manipulate the SEM for automatic shifting of the sample and the electron beam (from picture-mode to spot-mode etc.), and a minicomputer with input and output terminals to control the whole operation.

A suitable magnification is chosen for counting; our experience shows a magnification of x3,000 is most suitable. Depending on the specimen size and shape, the computer can guide the system to choose 25 random areas for counting, alternatively the computer could guide the system to scan all the areas instead of a few random areas. For a particular field of view, the Quanitmet 720 detects and counts "fibers", records the length and diameter of each fiber, and gives X, Y coordinates of each fiber to the computer. The "picture-mode" is now changed to "spot-mode" on the SEM and the electron beam is guided on to a fiber knowing its X, Y co-ordinates. At this stage an x-ray spectrum of the fiber is taken for, say, 30 secs. and compared with standard asbestos spectra; if the spectrum matches with one of the four possible spectra the computer counts that "fiber" as an "asbestos fiber". This is repeated for all the "fibers" in the field of view. Then the field of view is changed to another by shifting the specimen automatically.

The computer can now calculate the total number of asbestos fibers and total weight of asbestos from which fibers/m^3 and weight/m^3 of asbestos can be determined. Moreover, a histogram of size distribution (either length or diameter) can be automatically plotted.

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It is our conclusion that the feasibility of a fully automated system for determining the amount and size distribution of asbestos fibers in air has now been established.

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5. FUTURE WORK

5.1 PRE-CONCENTRATION OF ASBESTOS IN SAMPLES OF AMBIENT AIR

As pointed out in Section 2.3.5, a statistical determination of the amount and size distribution of asbestos fibers in point-source and near-point-source samples is readily done by the present technique. However, the amount of asbestos fibers in ambient air samples (in a volume of 0.100 m^3 to 0.150m^3) is such that an unsatisfactory statistical determination is gained by scanning a few random areas. Two variations are possible. Firstly, all the filter area can be scanned instead of a few random areas. Secondly, the asbestos fibers can be concentrated so that the ratio of asbestos fibers to extraneous particles is increased.

No experimental work has been done in this laboratory towards such a goal but some possibilities are immediately evident. Ambient air particulate samples can contain up to 30% of organic matter. A suitable solvent can be chosen which will remove these organics from airborne particulates. Some research has been done [36] in this direction. Ideally, the organics should be removed without disturbing inorganic particulates on the Millipore. If the Millipore filter dissolves in the solvent then a solvent exchange could be effected and the inorganic residue filtered through another Millipore filter. This might well be enough to concentrate the asbestos particles to such an extent that a statistical count can be made by the present technique. Failing this some further approaches could be investigated based on preliminary research that was carried out to concentrate asbestos fibers in airborne particulates at Battelle Laboratories [22]. Dielectric separation, electrophoretc batch separation, continuous particle electrophoresis and density separation were tried out. All these techniques met partial success and need further research to make them workable. We firmly believe that a workable technique can be developed to concentrate asbestos fibers. For the present analytical technique to

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be workable, only partial concentration is sufficient.

5.2 FIELD SURVEY

Due to limited time, the present technique could not be applied systematically to field samples. However a field survey on the following samples would be a most desirable and logical follow-on subsequent to the present work.

1. Point Source:

Air samples would be collected at different sites inside an asbestos plant. There may well be a wide variation in the amount of asbestos at the different sites. A complete size distribution of the fibers will be obtained as well as total fiber concentration.

This survey will be done at different asbestos plants if funds allow.

2. Near Point Source:

Air samples will be collected outside an asbestos plant; the main variable will be the distance from the source, for example, 20 ft, 1/2 mile, 2 miles, etc.. Construction or demolition sites may also be included in this experimental study.

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Submitted by

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Manager, Physics of Materials Laboratory

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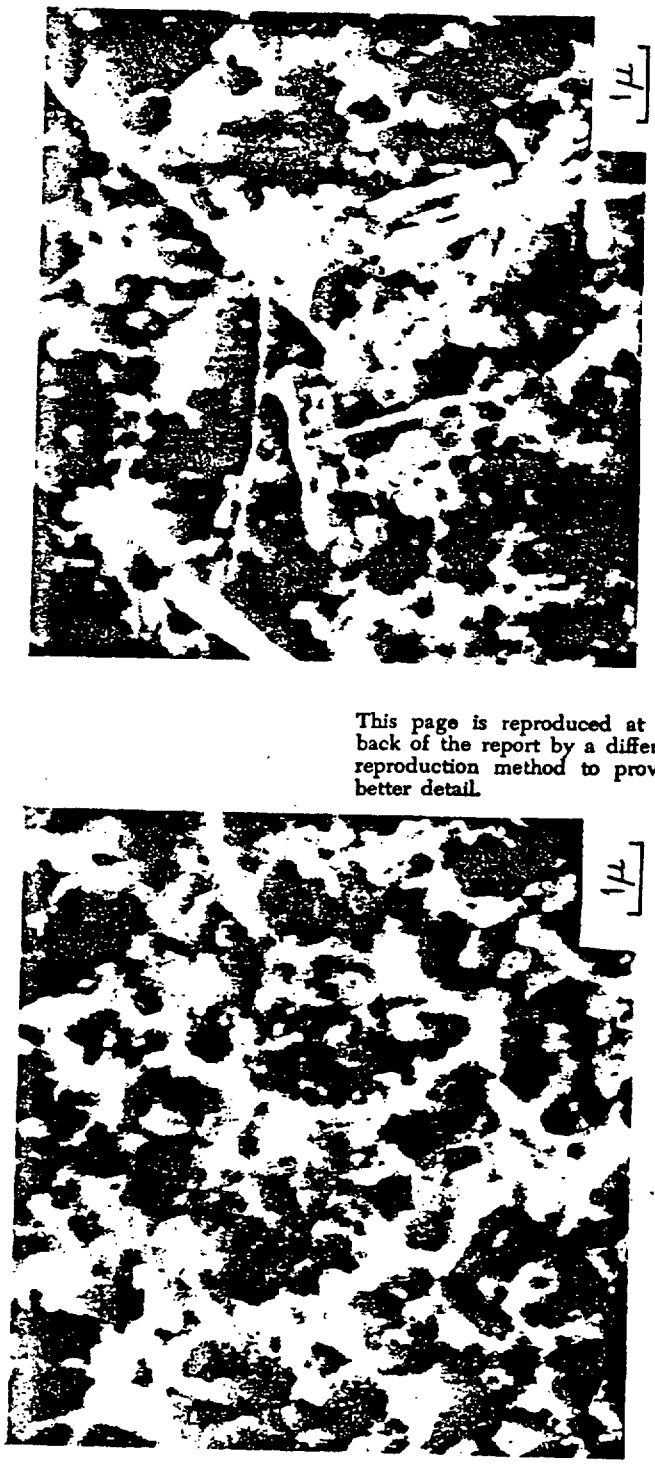
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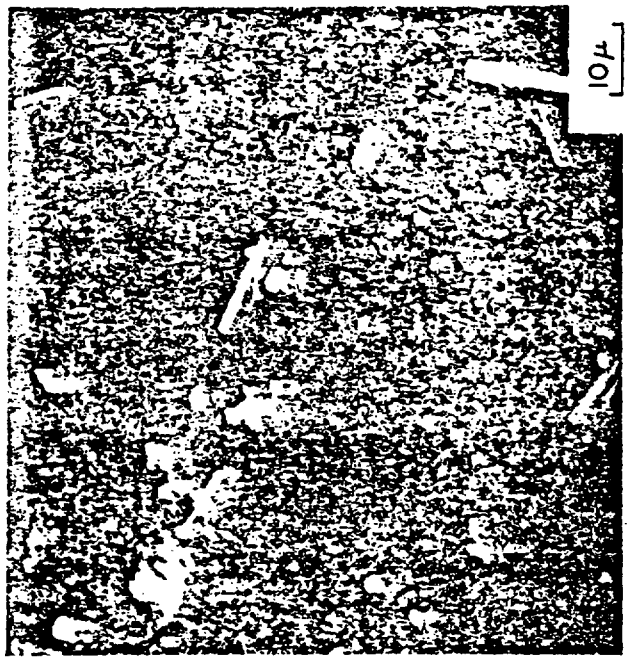
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(a)

Figure 2. SEM Photographs of Millipore Filter with Standard Crocidolite
(a) Blank (b) With Crocidolite; X 10,000

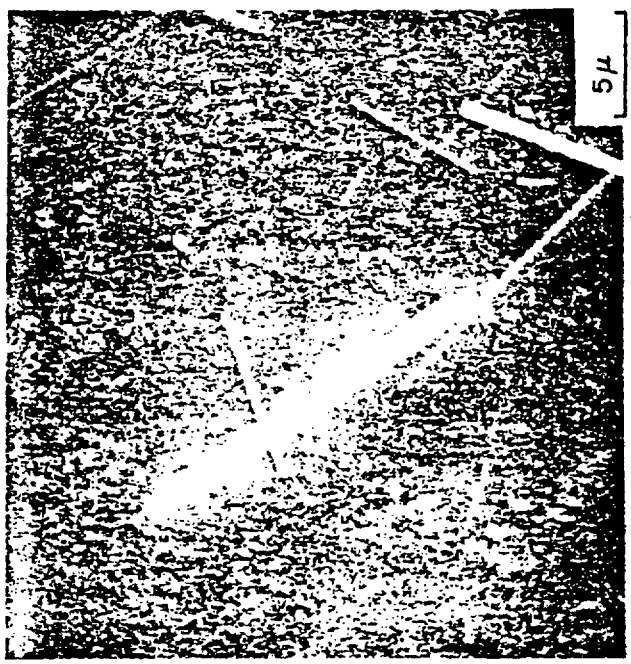
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(b)

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(a)

Figure 3. SEM Photographs of Standard and Point-Source Samples
(a) Standard Amosite; 0.45 μ filter; X 3,000
(b) Point-Source; 0.8 μ filter; X 1,000

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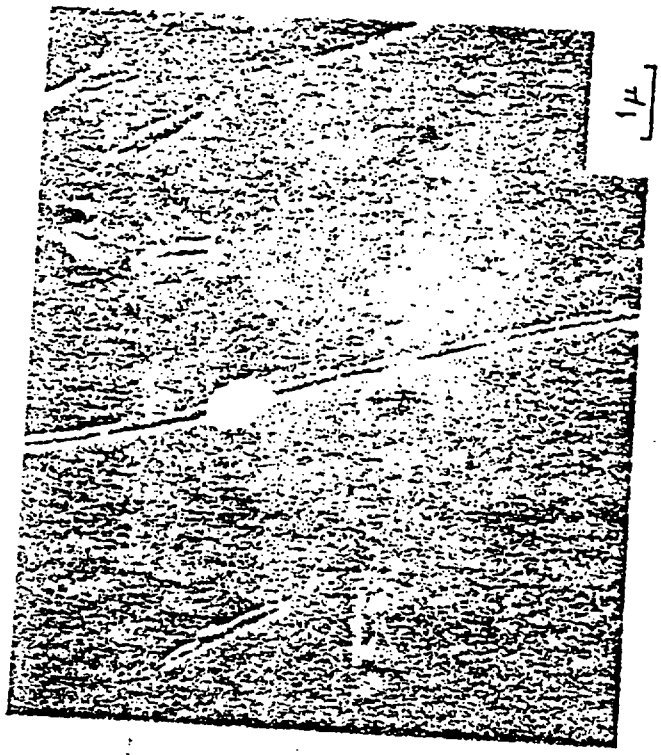
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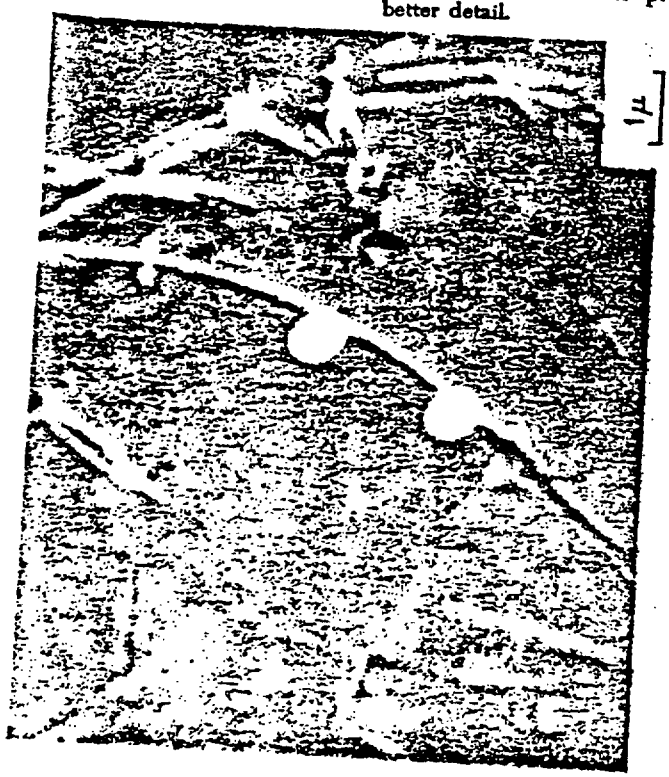
Figure 4. SEM Photographs of Near-Point-Source Samples (a) X300; (b) X1,000

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(a)

Figure 8. SEM Photographs of Chrysotile Fibers from which X-Ray Spectra were Obtained (a) 0.1 μ diameter fiber; X10,000 (b) 500 Å diameter fiber; X10,000

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(a)

(b)

Figure 9. -SEM Photographs of Standard Crocidolite and Its Corresponding IMANCO Images (a) SEM Image X1,000; (b) IMANCO Image Counting All Particles

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(c) (d) (e)

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Figure 9. SEM Photographs of Standard Crocidolite and Its Corresponding IMANCO Images (c) IMANCO Image Counting Fibers Only; (d) IMANCO Image with Perimeter Display; (e) IMANCO Image with "Count Flags"

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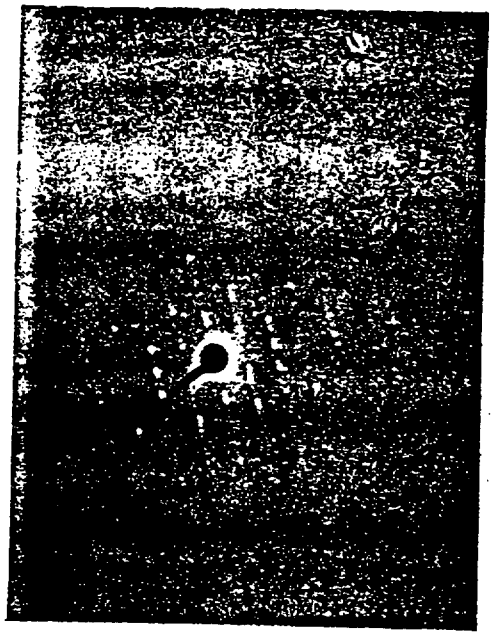
(a)

(b)

Figure 10. SEM Photograph of Air Sample and Its Corresponding IIANCO Image
(a) X1,000

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(a)

Figure 12. TEM Photographs: Carbon Extraction Replica of Aspirated Standard Chrysotile and Selected Area Electron Diffraction Pattern from Chrysotile (a) X3,200

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