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DEVELOPMENT OF SCANNING ELECTRON MICROSCOPY FOR MEASUREMENT OF AIRBORNE ASBESTOS CONCENTRATIONS

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DEVELOPMENT OF SCANNING ELECTRON MICROSCOPY FOR MEASUREMENT OF AIRBORNE ASBESTOS CONCENTRATIONS

by

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ABSTRACT

The methodology that was developed at the Franklin Institute Research Laboratories (FIRL) under the EPA Contract No. 68-02-0544, for the determination of airborne asbestos has been perfected and developed further. Moreover, the newly perfected technique has been applied to point source, near point source and ambient air samples.

This report describes the analytical method which employs a scanning electron microscope equipped with energy dispersive x-ray analysis for the identification and counting of airborne asbestos. The specimens, prepared in a unique manner, are suitable for image analysis and for a possible automated counting system.

Results of the analysis on airborne asbestos are presented, and limitations and advantages of the present technique are discussed.

1. INTRODUCTION

The problem of asbestos in the environment is a very severe one, arising from the great increase in usage of asbestos and the increasing frequency of observation of "asbestos bodies" in autopsy material. The carcinogenic properties of asbestos are well documented[1-7] and the "asbestos bodies" have been verified to 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]. Similar health hazards exist, although to a lesser extent, with indirect occupational exposure[13,14], with family contact,[15,16] and as a result of neighborhood and environmental exposure[15,16]. In New York City, chrysotile asbestos fibers have been identified in the lungs of persons with no known occupational asbestos exposure[3].

The biological effects of airborne and waterborne asbestos have been discussed recently in an international meeting[17]. Moreover, the present controversies on the safety of asbestos have been narrated by Wagner[18]. The present situation is that exposure to a high dosage of airborne asbestos is carcinogenic and that the carcinogenic effects of exposure to a constant and low dosage of airborne asbestos remains to be established.[17,18].

The influence of asbestos type, fiber size, and cofactors on biologic effects are not well documented[7]. Moreover, the health effects of the size distribution of asbestos fibers are not fully established. The investigation by Stanton and Wrench[19] indicates that respirable asbestos fibers with diameters in the range of 0.5μ to 5μ and up to 80μ in length result in the development of cancer in hamsters; fibers either smaller or larger than this range are harmless. However, single chrysotile fibrils with diameters $\sim$ 400Å have been observed in human lung tissue[3,4]. Similar experiments by Wagner[18] indicate that irrespective of the mineralogical nature, all fibers less than 0.5μ in diameter may produce tumors if innoculated into the pleural cavity of rats. In addition, evidence[18] indicates that the physical form of the fibers is an important factor in the development of experimental mesotheliomas, and that the crocidolite fiber having a particularly fine needle-like shape is more carcinogenic than other types of asbestos.

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. Timbrell[20] has carried out research in this direction and has shown that the large differences observed in the incidence of asbestos-associated cancer of the pleura in some geographical locations are likely to be related to the size distribution of asbestos fibers. Since fiber length affects deposition, longer fibers apparently have greater fibrogenic effects[21]. The investigations by Webster (reported in ref. 17) and by Cunningham and Pontefract[22] indicate that very little ingested asbestos penetrates the walls of the stomach and colon, and that almost all that does penetrate is of the smaller crysotile type. The above studies show *the importance of determining the original size distribution of airborne asbestos.*

Several experimental techniques have been investigated to determine asbestos in the environment. There are, however, many uncertainties as to the best method of sampling, identifying, and quantifying asbestos in the environment 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.

An x-ray diffraction technique has been carried out on airborne asbestos samples[22]. However, only the total amount of asbestos, without any reference to size distribution, can be determined by this technique. In addition, only amounts greater than $\sim 10 \mu g/m^3$ ($10{,}000\ ng/m^3$) can be determined by this method. The amount of asbestos in ambient air is believed to lie in the range of 0 to $5{,}000\ ng/m^3$. New refinements in specimen preparation technique are underway in some laboratories so that the detection limit by x-ray diffraction technique is expected to be lower than $\sim 10 \mu g/m^3$ [23].

Transmission electron microscopy (TEM) has been applied[3,24-29] in the determination of airborne asbestos. There are many limitations in the use of TEM techniques for the determination of asbestos in the environment. Some of the TEM techniques developed only give the total mass of asbestos[24,25]

and some give mass as well as size distribution[26-29]. A TEM technique is not easily amenable to automation. Moreover, fiber identification is very often based on morphology in this technique, which is applicable only for chrysotile. Selected area electron diffraction (SAD) can be used to identify particular type of asbestos[30-33]; however, SAD patterns can only be obtained from fibers in a particular size range[34]. Hence, asbestos fibers only in a limited size range can be identified by TEM.

Urban air particulate and airborne asbestos identification and characterization by combining transmission electron microscopy and x-ray microanalysis (EMMA) have been attempted recently[35,36]. Recently, Maggiore and Rubin[37] have employed a scanning electron microscope (SEM) with a field emission source to identify asbestos fibers using energy dispersive x-ray fluorescence analysis. The above study[37] has been carried out using only standard asbestos samples and its applicability to airborne asbestos has not been clearly delineated. Moreover, no attempt was made to develop the system for automated identification and counting of asbestos fibers.

Nearly all methods published in the literature for sizing and counting of airborne asbestos do not preserve the *original* size distribution of asbestos fibers[38]. Specimen preparation for SEM or TEM may include the following steps: filtration, centrifuging, ashing and ultrasonification. An unknown quantity of asbestos fibers are lost during centrifuging[38]. Splitting and loss of asbestos fibers may be visualized during ignition in an oven ashing. Ultrasonification is known to break down chrysolite asbestos fibers into fibrils[24,25]. The measurement and transfer of small volumes by a micropipet or syringe constitute a significant fraction of the total error in the enumeration of asbestos fibers[38].

As a step towards solution to this particulate monitoring problem, a methodology has been developed in our laboratory under contract to Environmental Protection Agency, EPA (68-02-0544). The technique is described in the EPA report[39].

The present report describes further developments that have been carried out under a continued grant from EPA. Results obtained from airborne asbestos are also presented. The current technique identifies and counts the asbestos fibers, and determines their *original* fiber size distribution using a scanning electron microscope with automated energy dispersive x-ray analysis. The specimen preparation technique aims at preserving the *original* size distribution of airborne asbestos and is such that a completely automated operation using a SEM, x-ray analyzer and image analyzer is feasible. At present, the developed technique is used in a 'manual mode' and results so obtained on airborne asbestos are presented here. The technique gives mass concentration, particle concentration and original fiber size distribution of airborne asbestos.

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 fibers as they exist in air. Any steps to isolate and concentrate asbestos fibers with respect to other particles should aim to preserve the original size distribution of the asbestos fibers. There is a greater chance for fibrillation during the specimen preparation steps of oven ashing and ultrasonification. Low temperature oxygen plasma ashing is preferable to oven ashing. Unknown quantities of fibrils are lost during centrifuging, and, as stated previously, measurement and transfer of small volumes of liquid containing dispersed particles by a micropipet or syringe constitute a significant fraction of the total error in the enumeration of fibers using electron microscopy.[38]

The present technique consists of specimen preparation steps that reduce fibrillation to a minimum and aims at determining original asbestos fiber size distribution. Moreover, the technique aims ultimately at identifying and counting asbestos in air in an automated manner. Initial sample collection is by absolute filtration using a membrane filter. The final specimen for scanning electron microscopy (SEM) or for transmission electron microscopy (TEM) prepared from the airborne particles should be on a featureless background so that the particles can be analyzed unequivocally by an image analyzing system[39-41]. Furthermore, the x-ray emission from the asbestos fibers should be without either significant background or any extraneous x-ray emission peaks from other particles or the substrate. Similarly, selected area electron diffraction (SAD) patterns from a fiber obtained in the TEM should not be superimposed by SAD patterns from neighboring particles. Hence, the amount of air filtered should be such

that little or no superposition of particles takes place. All operating features of the final system should be compatible with automated image analysis[39].

2.2 Description of Methodology for the Analysis of Airborne Asbestos

Following considerable experimentation a satisfactory technique to analyze airborne particles by SEM along with energy dispersive x-ray fluorescence analysis and image analysis was developed under an EPA grant[42]. Further developments have been achieved in the specimen preparation techniques which are presented here. We believe that this technique is reliable and could be repeated in any laboratory without undue expense or difficulty.

2.2.1 Sampling

Airborne particulates are first collected on a Millipore membrane (MF type: mixed esters of cellulose) filter having a diameter of 47mm and an average pore size of 0.45μ. Though the Millipore filter of the above specification is preferred, the present technique is applicable to MF-type Millipore filters of different pore sizes and diameters. The pore size of the filter is not a critical variable but does influence the superposition of particles. Using a 0.45μ Millipore filter, a large number of ∿ 0.1μ size particles are collected on the filter. These airborne particles are not collected on a 0.8μ pore size Millipore filter[42]. Even though the 0.8μ pore size is larger than the largest dimension of some asbestos fibrils, it has been observed[27] that the surface properties of the membrane filter and the asbestos fibers, as well as the circuitous path through the filter, result in virtually complete collection of all asbestos material. However, no systematic study was undertaken to verify such a proposition in the present investigation.

The volume of air filtered lies in the range of $2m^3$ to $15m^3$ for a 47mm diameter Millipore filter with an average pore size of 0.45μ. If the sample volume exceeds $\sim 15m^3$, overcrowding of particles occurs. The rate of filtration is not deemed to be an important variable; however, longer time of filtration with a slow rate is recommended.

2.2.2 Specimen Preparation for Scanning Electron Microscopy and Transmission Electron Microscopy

The steps involved in the specimen preparation are shown schematically in Figure 1. The Millipore filter with collected airborne particles is mounted on a clean metal disc; mounting is done with rubber cement which is put only at the periphery of the filter. A thin carbon layer ($\sim$ 100Å) is evaporated onto the filter in a vacuum evaporator. A thicker carbon layer is not recommended since the time to eliminate the carbon extraction replica during low temperature (LT) ashing increases considerably.

A $\sim$ 25mm diameter circular piece of the "composite" film is now cut out by a razor blade. The composite film is held on an electroplished single crystal berryllium (Be) stud which is featureless and mounted with carbon side down, as shown in Figure 1(b), in a brass specimen holder. Single crystal beryllium studs exhibit better featureless surface than polycrystalline studs which usually contain oxide inclusions.

If TEM study along with SEM observation is being contemplated, then two or three BeO substrates on copper grids are inserted between the Be-stud and the composite film, Figures 1(a)(iii) and 1(b). The BeO substrate side of the copper grid faces the carbon side of the composite film. Details of the preparation of BeO substrates are given in Appendix A.

The specimen holder, Figure 1(b), is next put in a covered petri dish containing acetone which is a solvent for mixed esters of cellulose. The level of acetone in the petri dish is such that the solvent does not attack the membrane filter directly, Figure 1(b). The specimen undergoes acetone vapour attack for about half an hour. Initially, the composite film swells under the solvent attack but settles down on

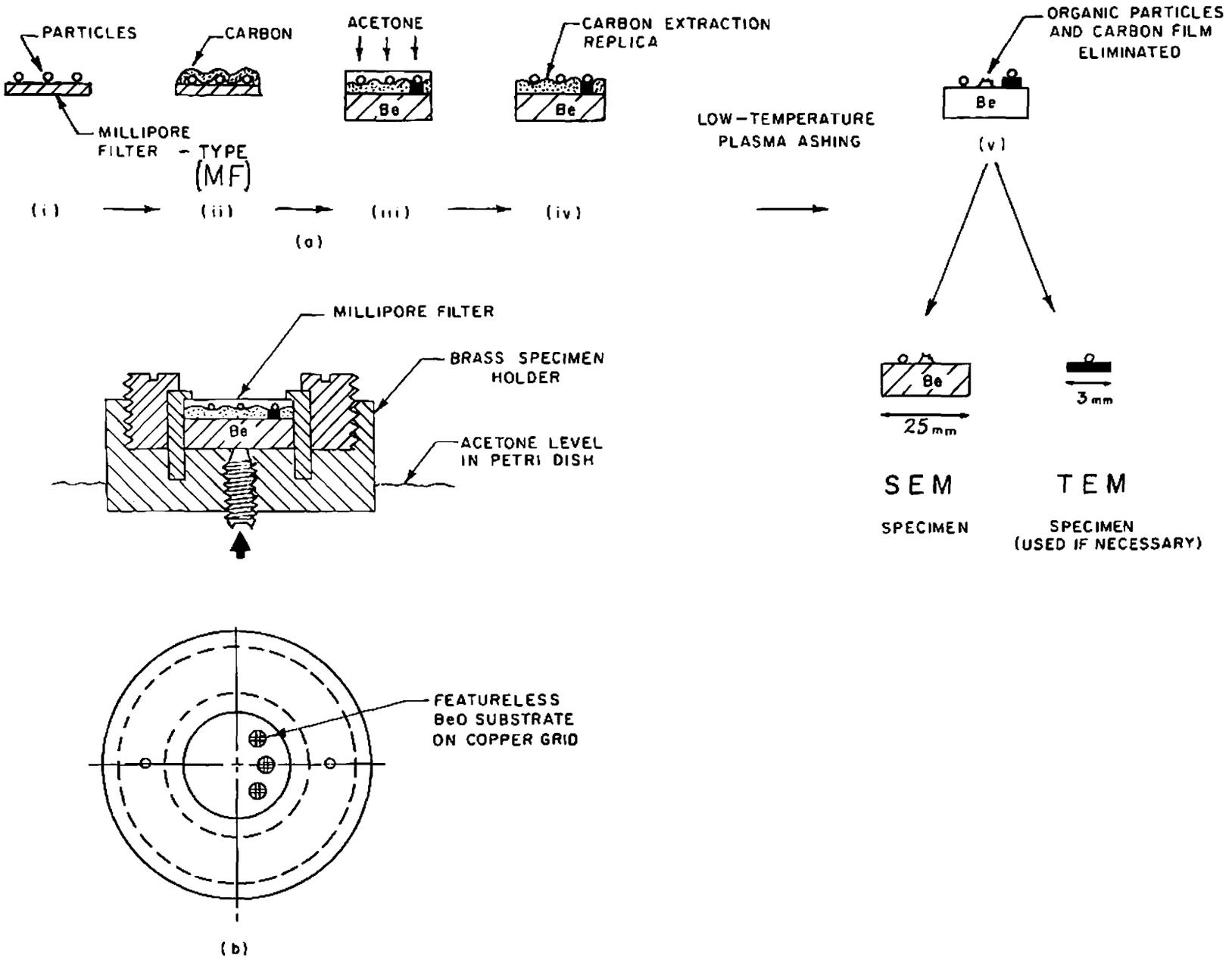


Figure 1. Schematic Diagram of the Steps Involved in Specimen Preparation

the Be-stud, which can be observed visually. The settled composite film adheres to the Be-stud in such a way that the following steps can be undertaken.

The brass specimen holder, Figure 1(b), serves to keep the film in position while swelling occurs. During solvent vapor attack, the Millipore filter is rendered transparent. Occassionally one or two bubbles form when the film is settling down on the Be-stud causing breaks in the continuous film. This does not affect the general procedure and on an average, 90% of the film remains continuous.

After the film has completely settled down on the Be-stud, the brass specimen holder is placed in a beaker in an inclined position (∿30°) and acetone is poured slowly in order to immerse the film completely. The solvent dissolution of the filter is carried out for one to two hours; accelerated dissolution of the filter by stirring the solvent is not recommended because the fragile carbon extraction replica is often disturbed or broken up by mechanical forces. Later the acetone is sucked out of the beaker slowly using a large capacity pipet. After the specimen is dry the Be-stud is put in a low temperature oxygen plasma asher for nearly 12 hours (overnight). The plasma stream flows directly over the stud ashing all the organic particles and the carbon extraction replica. This results in the collection of all inorganic particulates on the featureless Be-stud without disturbing the original particulate distribution. No evidence has been found as to the loss of small particulates along the plasma stream in order to warrant indirect plasma flow over the particulates. The rate of flow of oxygen through the system is ∿ 0.3 liters/min. The oxygen plasma is excited by a high frequency induction coil. Specimens prepared from standard U.I.C.C. asbestos fibers exhibit no degradation of the fibers due to plasma ashing when observed either in the SEM or in the TEM. When the specimen cools down to the room temperature, it is ready for EM observation.

If TEM copper grids with BeO substrates had been used, they are removed from the Be-stud carefully with a pair of tweezers. The Be-studs can be used repeatedly if the particles are removed by repeated ultrasonic cleaning in acetone.

In summary, the above technique results in two types of specimens, namely, one ∿25mm size Be-stud and one or two EM grid specimens (BeO substrate), on which all the airborne particulates lie on a featureless background. The Be-stud specimen is used in the SEM primarily. The BeO substrate specimen is either used in the SEM or in the TEM depending on the type of investigation being contemplated, i.e., either x-ray fluorescence analysis or SAD analysis of asbestos fibers respectively. The Be-stud or the BeO substrate gives rise to no extra x-ray fluorescence peaks during an energy dispersive (E.d.) analysis either in the SEM or in the TEM.

2.2.3 Measurement Techniques

Even though a feasibility study of a completely automated counting system for airborne asbestos has been carried out[42], the following summarizes counting procedure for 'semi-automated' mode of operation. Most of the steps are carried out manually except the identification of asbestos fiber, which is performed by a computer.

Operational modes are described for a scanning electron microscope, JSM-50A, with a guaranteed resolution of ∿100Å. The E.D. x-ray analyzer, Northern Scientific NS-880, has a resulution of 160ev and is highly computerized with respect to handling x-ray fluorescence data.

The Be-stud specimen is first observed in the 'picture-mode' at a condenser lens setting, which gives an absorbed electron current of ∿2 x 10^{-11} amps. At this setting, the resolution of the microscope is ∿100Å. However, an electron current of $\geq$ 2 x 10^{-10} is necessary for x-ray fluorescence analysis giving reasonable count rates. An electron current of ∿ 2 x 10^{-10} is an optimum value for which the resolution is adequate and count rates are reasonable. The accuracy of determining the size

of fibers decreases to a certain extent at a current of $\sim 2 \times 10^{-10}$ amps. due to a loss of resolution. Generally, the fibers appear larger than their actual sizes. The asbestos fibers appear brighter at this current of 2×10^{-10} amp. due to increased secondary electron yield. Iterating between the two current levels of 2×10^{-11} amps. and 2×10^{-10} amps. is time consuming since an image shift is observed when the electron current is changed.

A magnification of X1,000 or X3,000 is suitable for observing and counting airborne asbestos, particularly for near point-source samples which usually contain large fibers as well as fibrils. Fibrils can be detected at a magnification of X3,000 which was the usual magnification used in the present investigation.

The E.D. x-ray fluorescence analysis for the identification of asbestos fibers is carried out in the following manner. First, the number of fibers and fibrils are counted on the viewing screen and the size (diameter and length) of the fibers is recorded at a magnification of X3,000. The magnification is usually increased to a suitable higher magnification for accurate determination of the size of relatively small fibers. Each fiber is then brought to the center of the screen approximately and the magnification increased to as high a value as necessary to carry out x-ray fluorescence analysis. The 'picture mode' is changed to a 'small-square-scan' mode (5mm x 5mm on the screen) and the small square is centered on the fiber accurately. Iteration between the 'picture mode' and the 'small-square-scan' mode is done to verify that the small square lies indeed on the fiber. X-ray counts are accumulated from 5 secs. to 200 secs. depending on the fiber size; small fibers take a longer time to yield significant Mg, Si, Ca and Fe peaks. The type of asbestos fibers (e.g., chrysotile, amosite etc.) is identified by their characteristic x-ray fluorescence peaks by a computer program on the NS-880, Appendix B. The same procedure is repeated for other fibers in the field of view. After all the fibers in a field of view have been analyzed, the field of view is changed to another location.

The number of fields of view usually observed for the analysis of asbestos fibers in a statistical manner ranges from 25 to 100 depending on the sample. Counting is continued until 60 to 100 asbestos fibers have been identified and their sizes recorded. The fields of view observed usually form a square-grid pattern that covers as much area as possible on the ∿ 25mm diameter Be-stud. Hence, a better statistical average is obtained than when scanning a small area out of a 47mm diameter filter paper.

2.2.4 Analysis of Microscopic Data

The total amount (number or mass) of asbestos and its size distribution are determined in the present technique. Twenty-five to a hundred areas are scanned at a convenient magnification, preferably X3,000, for a statistical count using the following two formulae:

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

$$\frac{\text{Average mass of fibers X K}}{\text{Volume of air filtered } (m^3)} = \text{Mass of fibers/m}^3 \qquad (2)$$

where

$$K = \frac{\text{Filter area } (mm^2)}{\text{Field area } (mm^2)}$$

The mass of an asbestos fiber is calculated from its length and diameter knowing its density[31,43].

Recognizing that no conclusive results are available as to determine which physical parameters of asbestos fibers control health hazards, the

size distribution of asbestos fibers is represented by cumulative frequency distributions of lengths and diameters separately. Moreover, respirable and non-respirable fibers are analyzed together in the present investigation.

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[44]. The total number of asbestos fibers identified and counted in the present investigation lies in the range of 60 to 100 in order to get a good distribution plot. The total time necessary to carry out such an analysis in the SEM lies between 2 and 4 hours.

2.2.5 Transmission Electron Microscopic Observation

Usually the Be-stud specimen was used for identification and counting of airborne asbestos in the present investigation. However, transmission electron microscopic (TEM) observation using the BeO substrate specimen was occasionally warranted in some cases. It has been well documented[3,8,9,45,46] that partial leaching of Mg from chrysotile asbestos fibers occurs in aqueous and some other environments. Under such circumstances, the chemical composition of the asbestos fiber changes, which hinders unique identification of the type asbestos by x-ray fluorescence analysis. Fortunately, the amount of Mg-leaching is such that even though the chemical composition changes partially, the chrystalline structure still remains intact. Under such situations, asbestos fibers can be identified by selected area electron diffraction (SAD) patterns obtained in a TEM[30-33].

However, TEM study of asbestos fibers is very cumbersome and time consuming, and SAD pattern can only be obtained from asbestos fibers in a particular size range.[34] Nevertheless, the use of TEM for identification of asbestos was occasionally warranted in the present investigation. Airborne asbestos does not usually exhibit any change in chemical composition in contrast to waterborne asbestos.

The BeO-substrate specimen can also be used in new generation transmission electron microscopes in which E.D. x-ray fluorescence analysis can be carried out with great advantage[47] in addition to usual SAD analysis.

Additionally, the BeO-substrate specimen can also be used in a scanning electron microscope either in a 'transmission mode'[37] or in a 'semi-transmission mode' (to be described in Section 3.1). Under these two modes of operation, the x-ray fluorescence spectrum from an asbestos fiber has a negligible background spectrum, which aids identification considerably (Section 3.2.2) and smaller fibers and fibrils can be identified with more confidence than that is achievable in the standard SEM mode.

3. EXPERIMENTAL RESULTS

3.1 Scanning Electron Microscopic (SEM) Observation of Standard Asbestos

A specimen was prepared by aspirating Johns Manville chrysotile on a 0.45μ Millipore filter and then following the sequence of steps shown in Figure 1. The specimen was observed in the JSM-50A SEM before and after low temperature (LT) oxygen plasma ashing. A representative area at a relatively low magnification is shown in Figure 2. Two organic fibers (upper left and right) and the carbon extraction replica of the Millipore filter have been eliminated. Some of the small fibers which were not visible in Figure 2(a) appear distinctly in Figure 2(b).

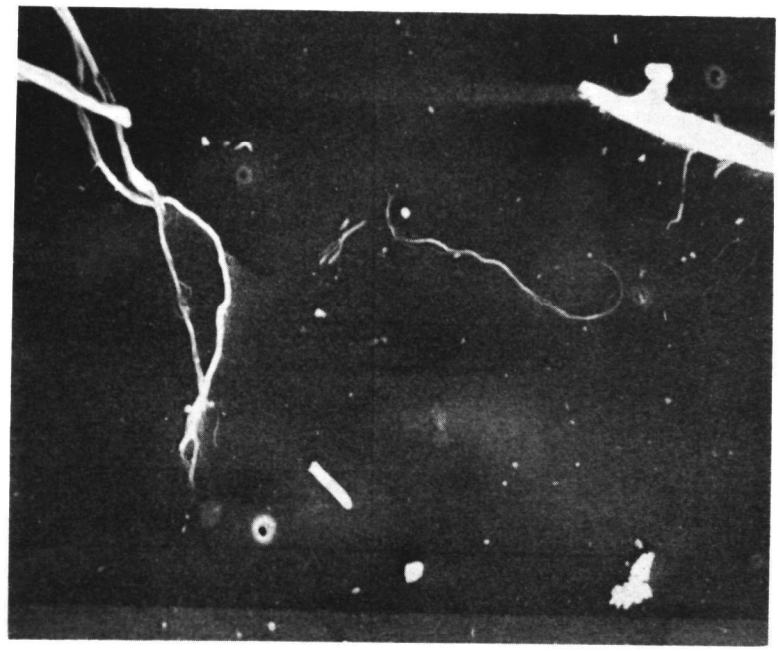
The advantages of LT ashing are better shown in Figure 3. The structure of the carbon extraction replica with an embedded fiber is clearly visible in Figure 3(a); the same area is shown in Figure 3(b) after partial LT ashing. As the carbon extraction replica is eliminated due to oxidation of carbon, the embedded fibers are freed and lie on the featureless Be-stud. After complete ashing of the carbon replica, fibers and fibrils appear distinctly on a featureless background, Figure 3(c).

This LT ashing step has been developed during the present program and constitutes an additional step to the technique that was originally developed under an earlier EPA contract[42]. Beryllium studs stand LT ashing without any degradation unlike pyrolytic graphite studs used earlier[42]. The LT ashing step has the following advantages:

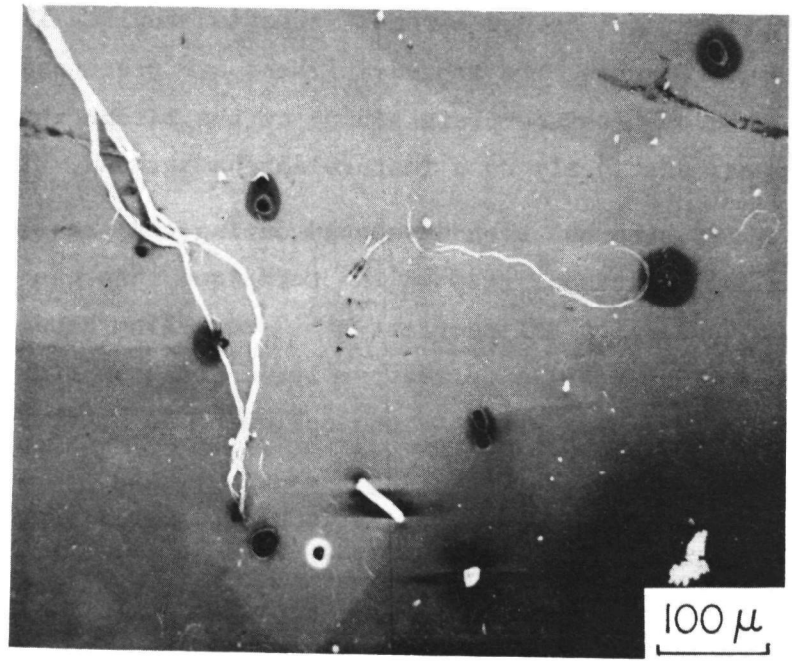
(i) It is a concentration process. Since all organic particulates are eliminated, the ratio of the asbestos fibers to all other particles increases.

(ii) The visibility of small fibers and fibrils in the SEM improves considerably.

(iii) The x-ray fluorescence spectra from small fibers and fibrils are improved considerably since background spectrum from a physically rough surface, Figure 3(a), is eliminated. This will be discussed further in Section 3.2.1

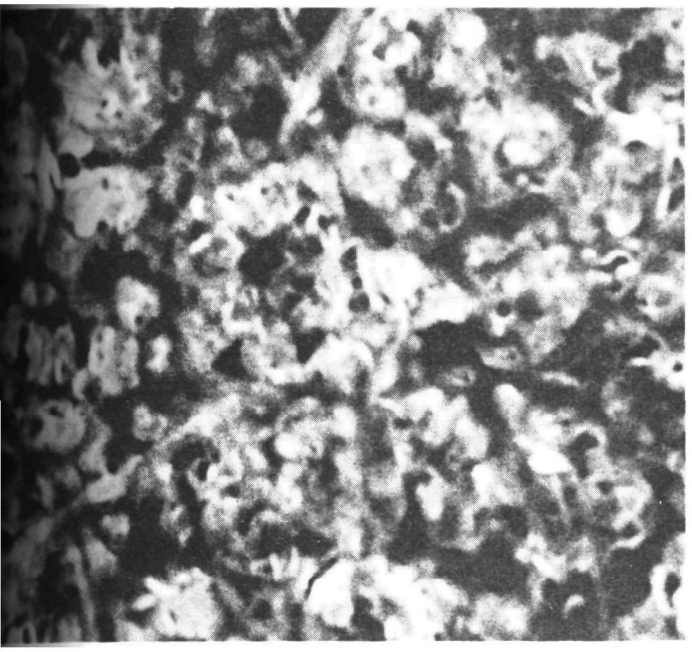


(a)

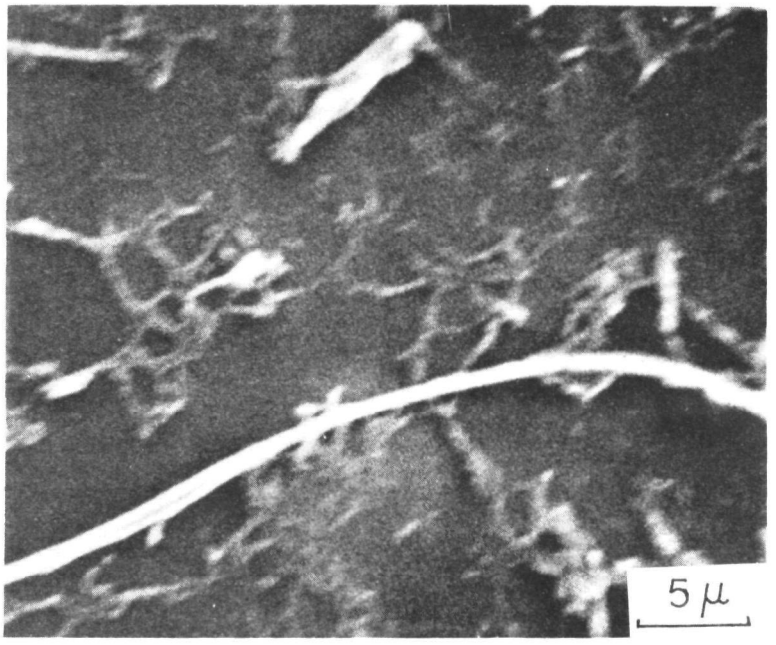


(b)

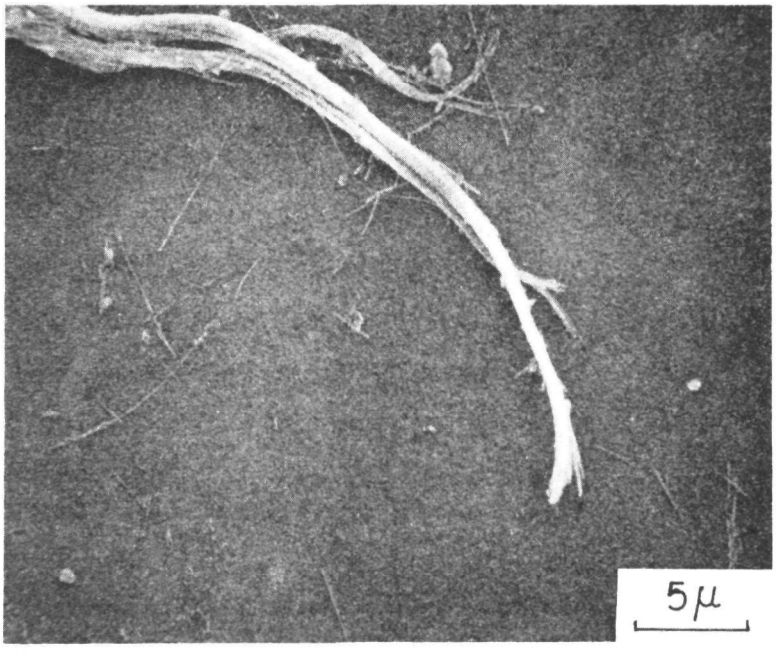
Figure 2. SEM Micrographs of Johns Manville Chrysotile Asbestos, X150. (a) Before LT Ashing, (b) After LT Ashing



(a)



(b)



(c)

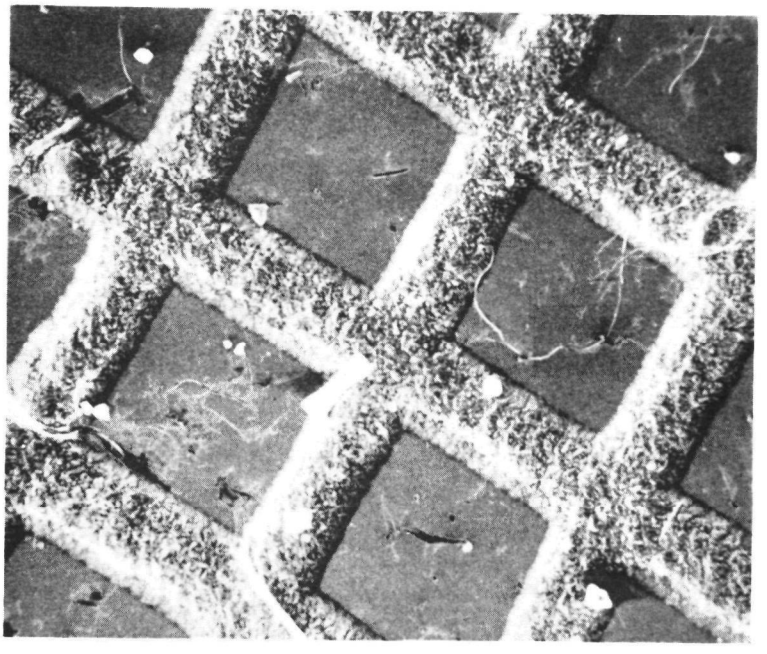
Figure 3. High Resolution SEM Micrographs of Johns Manville Chrysotile Asbestos. (a) Before LT Ashing, Structure of the Carbon Extraction Replica of Millipore Filter, X3,000. (b) After Partial LT Ashing, Note the same fiber in (a) and (b), X3,000 (c) After Complete LT Ashing, X3,000

It is of interest to note here that the SEM micrographs, shown in Figure 3, were taken at a resolution of ∿100Å. However, a specimen containing relatively large asbestos fibers can be observed and analyzed without the LT ashing step, Figures 2(a) and 3(a) particularly when the SEM is operated at a higher electron current. With higher electron current and correspondingly lower resolution, inorganic fibers and particulates appear brighter with respect to a tolerable background appearing from the carbon extraction replica. This was the method used earlier in this laboratory[42] to analyze airborne asbestos. However, fibril observation and identification, even though possible, was not easily carried out (see Figures 7 and 8 in ref. 42).

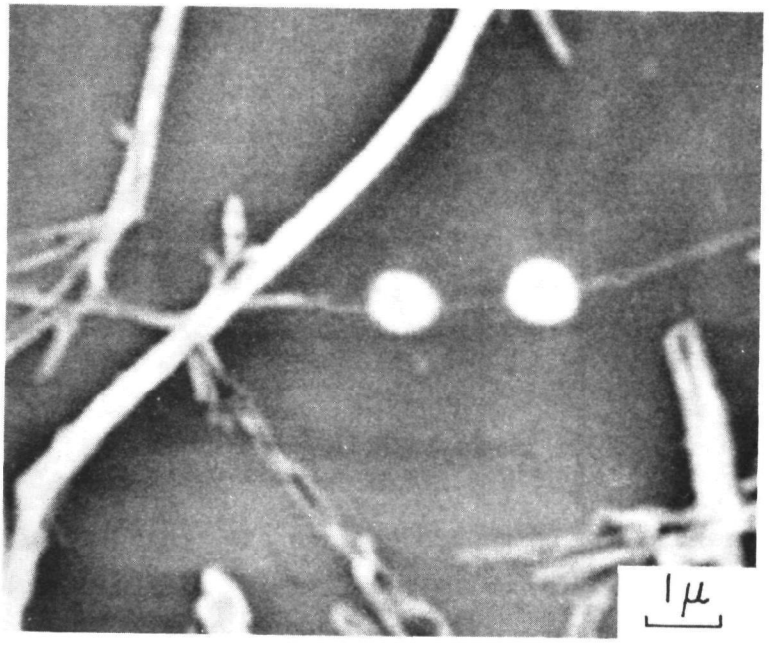
SEM micrographs of Johns Manville chrysotile aspirated on a BeO substrate, held on a EM copper grid, are shown in Figure 4. The copper grid is placed on a graphite block with a cavity, and conductive graphite paint is used to reduce charging effect. Moreover, unlike silver paint, graphite paint is not detected by E.D. x-ray detector. The specimen is observed in the secondary electron mode, Figure 4, and E.D. x-ray fluorescence analysis is carried out simultaneously. The advantage of using the BeO substrate instead of the Be-stud under similar conditions is that the background spectrum produced by bremsstrahlung is reduced to a minimum during x-ray analysis, Section 3.2.2., since the electron beam penetrates through the BeO substrate. This mode of operation is referred to here as 'semi-transmission' mode in contrast to true transmission mode[37], in which a transmission electron detector is used under the specimen.

3.2. Energy Dispersive (E.D.) X-Ray Fluorescence Analysis of Standard Asbestos

Asbestos fibers are identified by their characteristic x-ray fluorescence spectra, Figure 5, in the present investigation. E.D. x-ray analysis is carried out using a highly computerized Northern Scientific NS-880 system interfaced with the JSM-50A SEM. Unknown asbestos spectrum is identified by matching it with the spectra from standard U.I.C.C. asbestos;



(a)



(b)

Figure 4. SEM Micrographs of Johns Manville Chrysotile Fibers Aspirated on a BeO Substrate, Secondary Electron Mode. (a) X300; (b) X10,000, White spots correspond to the points where x-ray analysis was carried out.

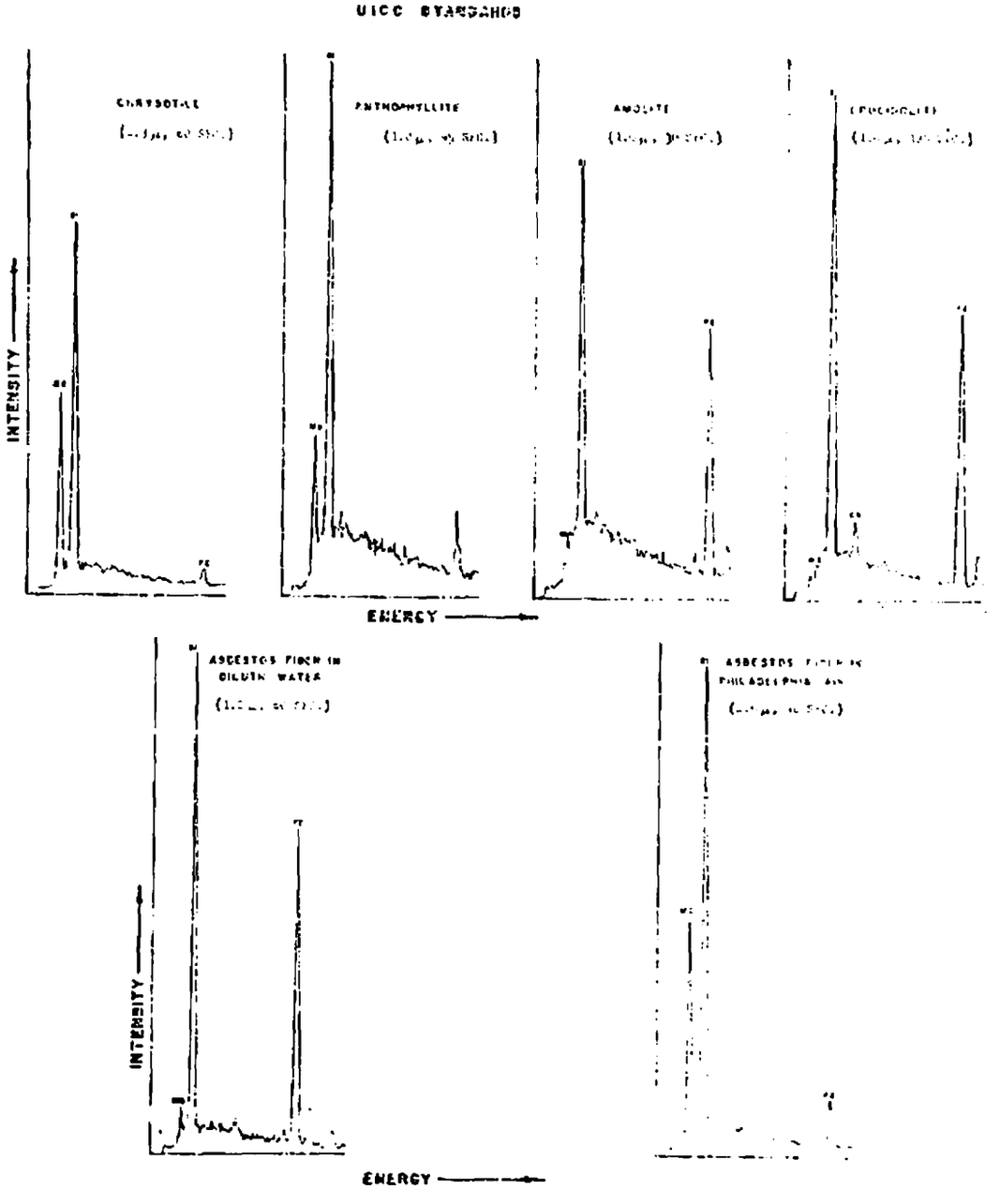


Figure 5. X-ray Fluorescence Spectra from U.I.C.C. Standard Asbestos Fibe and from Asbestos Fibers in Duluth Water and Philadelphia Air.

this is carried out automatically be a computer program, Appendix B.

E.D. x-ray analysis was carried out either on Johns Manville chrysotile or on U.I.C.C. Canadian chrysotile in order to determine the minimum time required to identify asbestos fibers of all sizes. However, not all the variables were optimized in the SEM-E.D. x-ray analysis system in the present study. Chrysotile was preferred to other asbestos since 90% of asbestos used in this country is chrysotile[43] and the smallest fibril (300Å - 400Å) that can be observed among different asbestos belongs to the chrysotile type.[32]

3.2.1 Beryllium (Be)-Stud Specimen

E.D. x-ray fluorescence analysis of Johns Manville chrysotile on a Be-stud specimen was carried out with the NS-880 system interfaced with the JSM-50A SEM. The minimum times required to identify chrysotile fibers at 18kV and at 6×10^{-10} amp. were determined and the data is presented in Figure 6. It was observed that an unwanted background spectrum produced by bremsstrahlung is reduced with decreasing applied voltage. Using the Be-stud specimen, the smallest chrysotile fiber that can be confidently identified is 0.15μ in diameter. Chrysotile fibers with 0.1μ diameter could be identified sometimes but not always. Counting longer than 150 secs. on 0.1μ diameter fibers, Figure 6, does not improve the spectrum significantly.

3.2.2 Beryllium Oxide (BeO) - Substrate Specimen

Similar studies were carried out using BeO-substrate specimen; the SEM was operated in a 'semi-transmission' mode. X-ray fluorescence spectra from chrysotile fibers of similar diameters, Section 3.2.1, are presented in Figure 7. Even though the minimum times required to identify asbestos fibers of similar diameters studied in Section 3.2.1 are not reduced, the spectra are much more distinct due to a reduced background spectrum produced by bremsstrahlung (compare similar spectra on 0.2μ and 0.1μ diameter fibers). The smallest fiber analyzed in this mode was

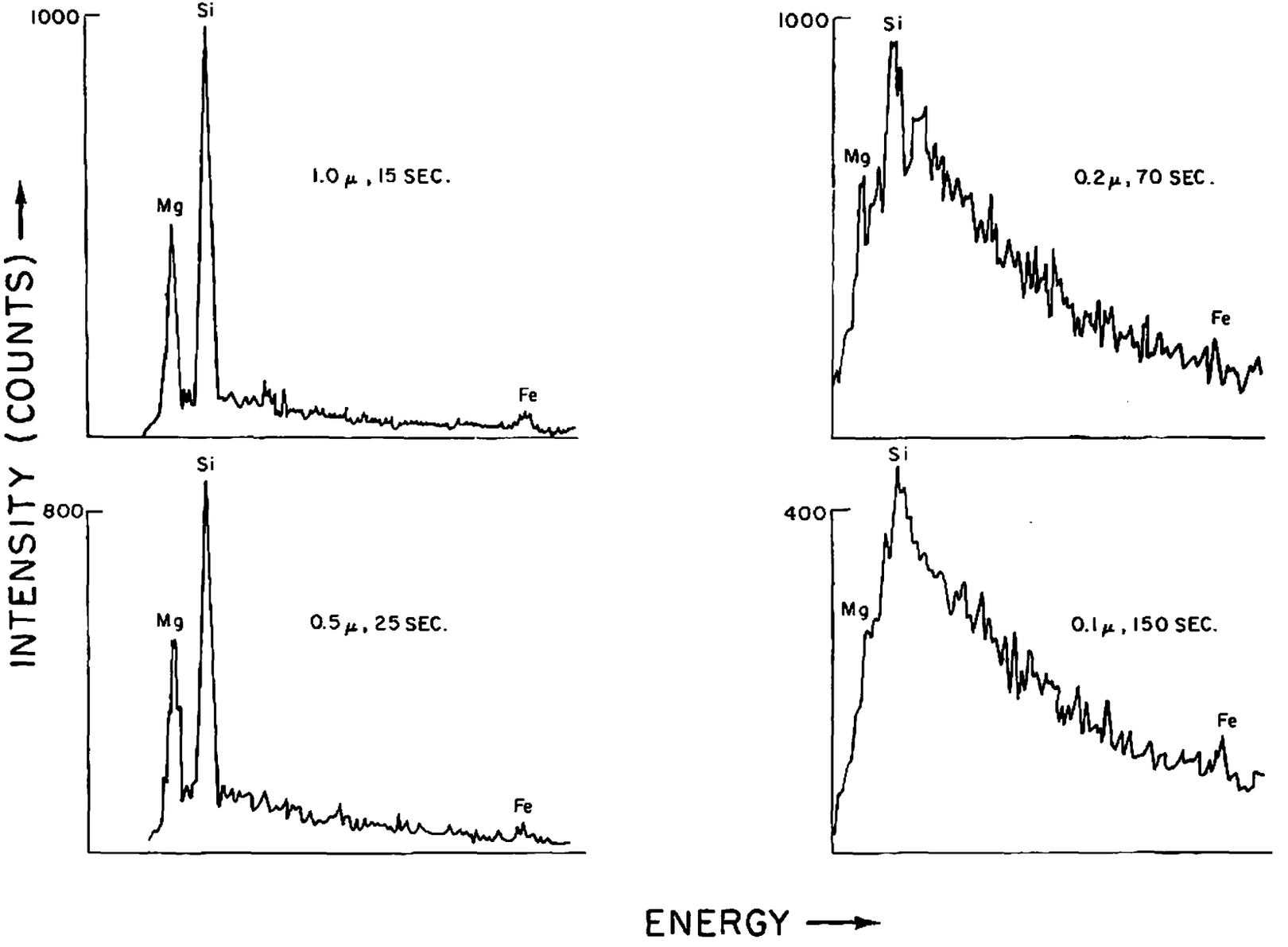


Figure 6. X-ray Fluorescence Spectra from Johns Manville Chrysotile on Be-Stud Specimen at 18 KV and 6×10^{-10} amp, Minimum Times used for Identification.

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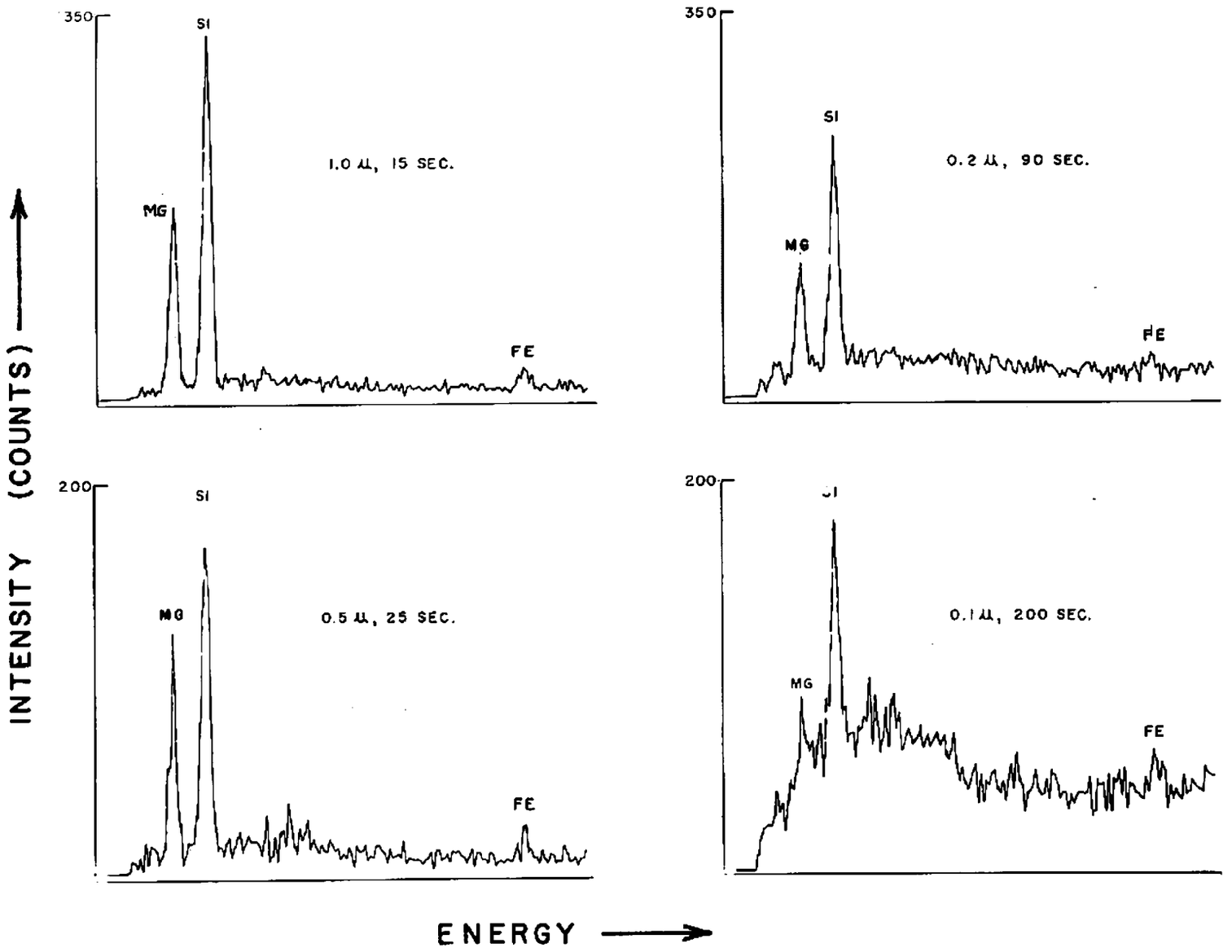


Figure 7. X-ray Fluorescence Spectra from Johns Manville Chrysotile on BeO Substrate Specimen at 25 KV and 2 x 10^{-9} amp, Minimum Times used for Identification

0.1μ fiber; however, it may be concluded from Figure 7 that even smaller than 0.1μ fibers can be identified, probably 0.05μ diameter fiber.

Study of Figures 6 and 7 leads one to conclude that BeO substrate specimens are superior to Be-stud specimens as far as positive identification of small asbestos fibers are concerned. However, other considerations make the Be-stud preferable to the BeO substrate as delineated below.

(i) A 25mm diameter Be-stud specimen is easier to handle.

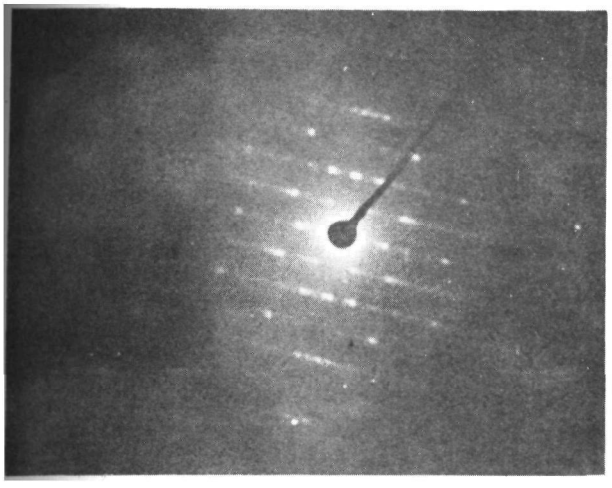
(ii) The overall area on the Be-stud is about X50 that on the BeO sample giving much better counting statistics.

(iii) The continuous featureless background of the Be-stud specimen is more amenable to automated image analysis than the BeO substrate specimen (compare Figure 2 with Figure 4(a).

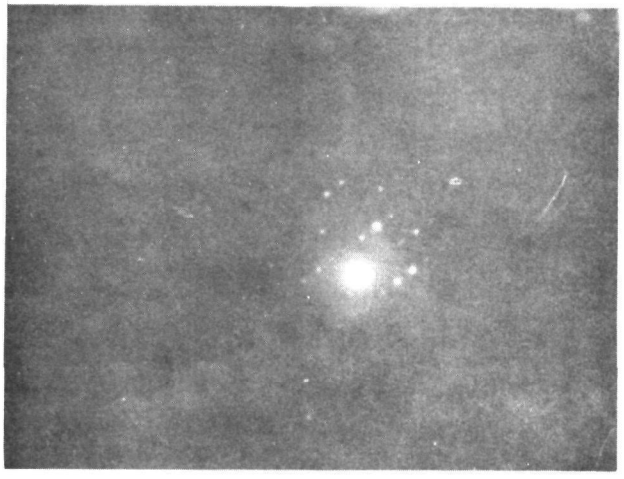
3.3 Transmission Electron Microscopic (TEM) Observation of Standard Asbestos

The BeO substrate specimen can be either used in a SEM in the 'semi-transmission' mode or in a TEM for selected area electron diffraction (SAD) analysis. Chrysotile asbestos fibers in aqueous enviroment may lose magnesium[27,45]; hence, there identification by E.D. x-ray fluorescence analysis in the SEM is not reliable. Under such circumstances, SAD analysis in the TEM complements SEM-E.D. x-ray analysis. Moreover, BeO substrate specimens can be used in new-generation TEMs in which E.D. x-ray analysis as well as SAD analysis can be carried out.[35,36]

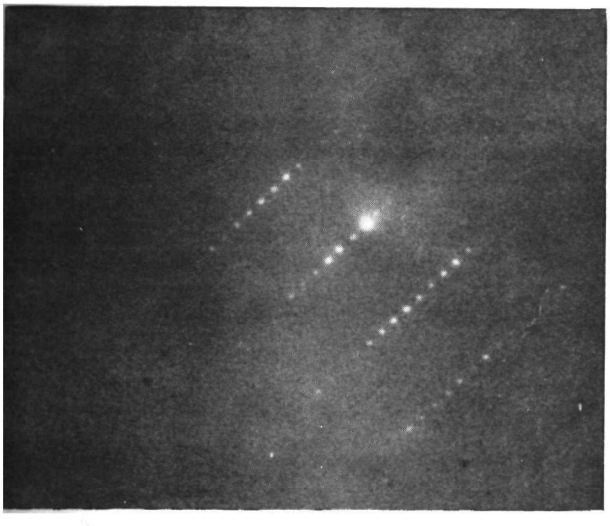
Selected area electron diffraction (SAD) patterns of standard asbestos fibers are unique[30,33,34] and can be used to identify unknown asbestos fibers, Figure 8. A BeO substrate specimen prepared according to Figure 1 is shown in Figure 9(a); the specimen contained U.I.C.C. Canadian chrysotile. An SAD pattern from the substrate is shown in Figure 9(b), which indicates that the substrate is crystalline; the substrate consists mostly of very fine grained BeO with some Be crystallites. However, the single crystal SAD pattern from a chrysotile fiber is observed distinctly, Figure 9(c), on the background of faint BeO rings. When an asbestos fiber occupies most of the selected area, the BeO rings (arising from a small fraction of the selected area) appear faint.



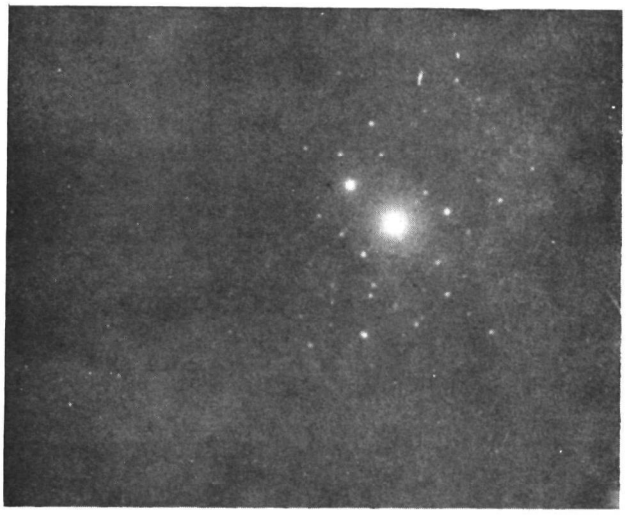
(a)



(b)

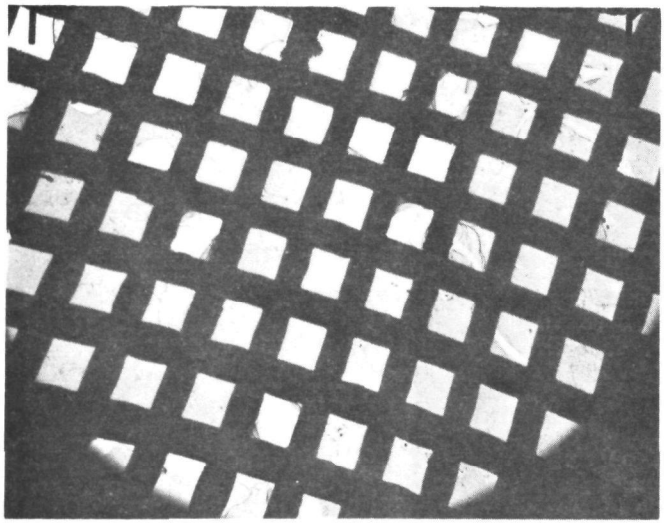


(c)

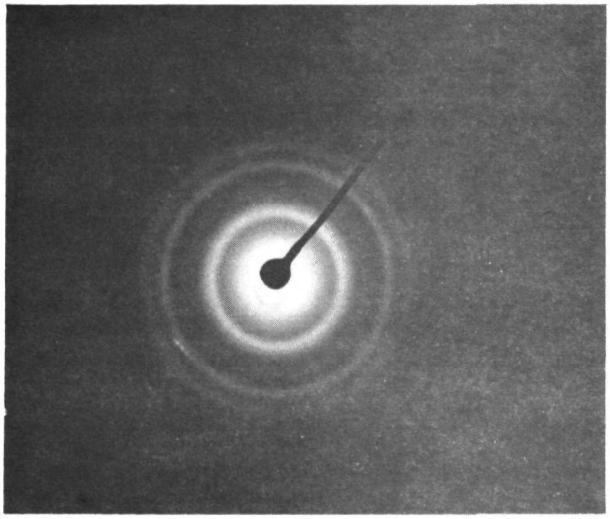


(d)

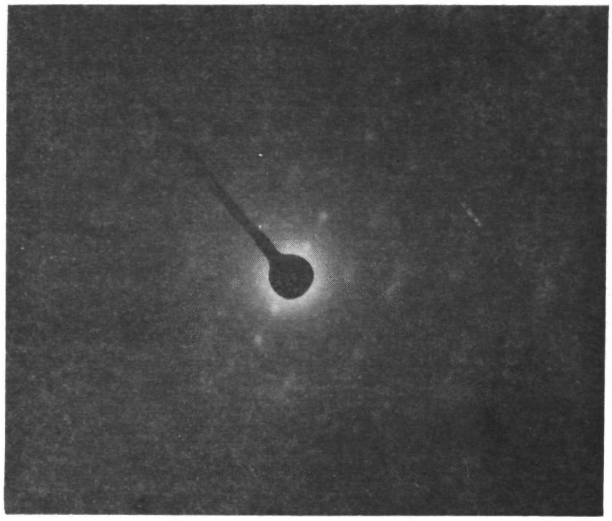
Figure 8. Selected Area Electron Diffraction Patterns from U.I.C.C. Standard Asbestos Fibers. (a) Chrysotile (b) Anthophyllite (c) Amosite, (d) Crocidolite.



(a)



(b)



(c)

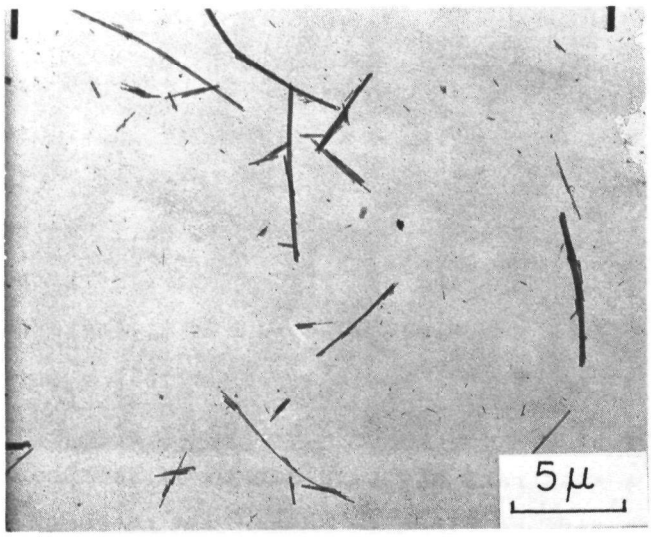
Figure 9. TEM study on BeO Substrates. (a) Low-Magnification Image of Copper Grid with BeO Substrates, Canadian Chrysotile Processed according to Figure 1. (b) SAD Rings Arising from Mostly Fine-Grained BeO. (c) SAD Pattern from Chrosotile Fiber.

The BeO substrate is, more or less, featureless and Canadian chrysotile fibers, as observed on such a substrate which has been processed thorugh the steps shown in Figure 1, are shown in Figure 10 at different magnifications. At a relatively high magnification, Figure 10(c), the substrate is not truly featureless but it is believed that it will not exclude image analysis[39,41]. Beryllium (Be) was evaporated onto a substrate kept at room temperature, Appendix A; this resulted in a film which is shown in Figure 10. It is expected that a more featureless BeO substrate can be prepared by depositing Be on a colder substrate. Additionally, the substrate may turn out to be amorphous which will result in a fewer diffuse rings in comparison to those shown in Figure 9(b).

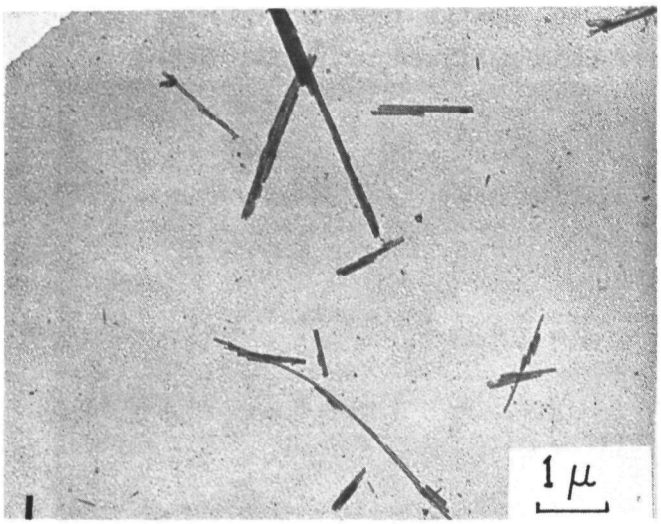
3.4 Analysis of Airborne Asbestos

Airborne asbestos samples, comprised of point-source (inside an asbestos manufacturing factory), near point source (outside an asbestos factory) and ambient air samples, have been analyzed using the FIRL technique. Specimens were prepared using the steps shown in Figure 1 whenever possible. Primarily the SEM-E.D. x-ray analysis was used for airborne asbestos analysis (Sections 3.1 and 3.2); occasionally, the TEM-SAD technique (Section 3.3) has been applied to some samples.

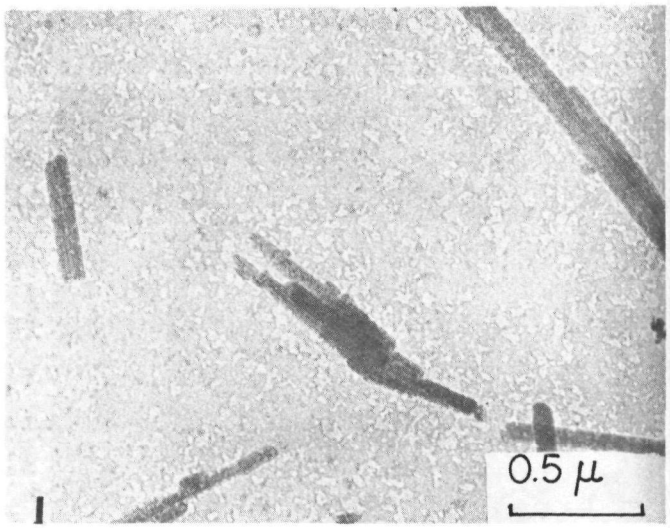
At the termination of this investigation an important variable, the magnification used for observing and counting of asbestos fibers, had not been finalized. A magnification of X3,000 is probably the most suitable for analyzing airborne asbestos samples which contain relatively large fibers as well as fibrils, Figure 3(c), although, a magnification X1,000 was used for some samples. Further investigations are necessary to clarify the influence of magnification on the statistical significance of the counts obtained.



(a)



(b)



(c)

Figure 10. TEM Micrographs of U.I.C.C. Canadian Chrysotile on BeO Substrate Processed According to Figure 1. (a) X3,000, (b) X9,000; (c) X35,000

The optimum magnification for counting asbestos fibers and determining the size distribution seems to depend on the type of samples being analyzed. The magnification chosen should be such that only a few fibers are seen on the viewing screen. For a sample containing relatively large fibers, a magnification of X1,000 is more convenient than X3,000; but the chances of missing fibrils obviously increases. The equations used for statistical analysis, Equations [1] and [2], (Section 2.2.4) are independent of magnification. Nevertheless, variable statistics have been obtained at different magnifications in preliminary tests. This result will not be presented here, as it meeds more exploration. The following results are based on an assumed insensitivity to the magnification used.

A number of point source and near point source samples had been analyzed in a previous investigation[42] on a preliminary basis, i.e., each fiber in them was not identified and the specimen preparation did not include the LT ashing step. The same samples have been analyzed in the present investigation systematically following all the steps shown in Figure 1 for the specimen preparation. The data is presented in Table 1 and representative SEM micrographs are shwon in Figure 11 to 15.

The point source samples, Figure 11 and 12, contain relatively large fibers with some fiber clumps. The near point source samples also contain some fiber clumps and single asbestos fibers, Figures 13 to 15. SEM micrographs and TEM micrographs of the same near point source sample are shown in Figure 14 and 15 respectively. In manual operation, the operator can make judicious judgement in counting the fiber clumps as to their sizes, which is necessary for the calculation of mass concentrations. Some of the chrysotile fibers appear to coexist with other particles, Figure 14(b). The E.D. x-ray analysis is carried out in relatively free portions of the fibers; a similar approach is applicable to SAD analysis. If the E.D. x-ray analysis is carried out on the fiber very near to other coexisting particles, then secondary x-ray fluorescence peaks usually appear from the extraneous particles.

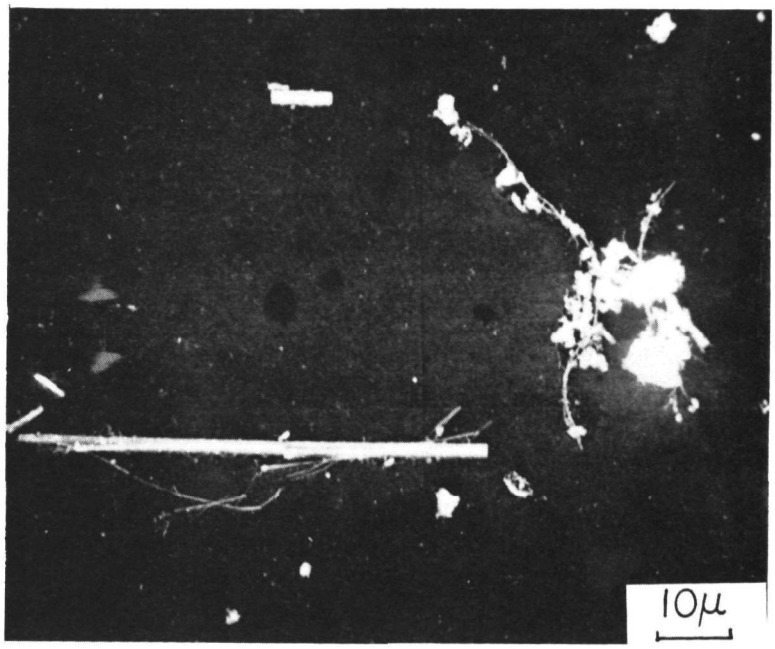
TABLE 1

ANALYSIS OF AIRBORNE ASBESTOS SAMPLES

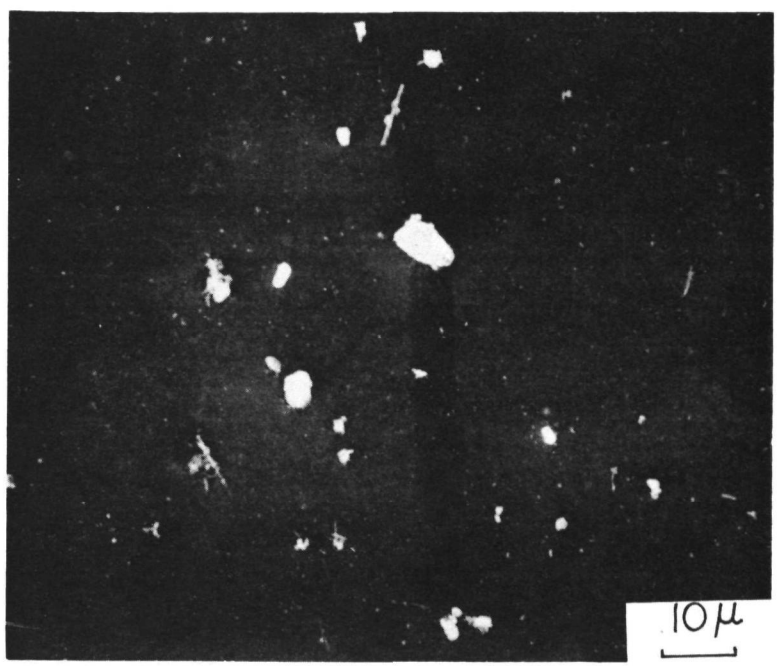
Sample*	Type**	Volume of Air (m^3)	Magnification Used	Number of Asbestos Fibers Counted	Fiber Concen. ($\#/m^3$) x 10^3	Fiber Concen. (gm/m^3) x 10^{-9}	Fiber Type
A-228	PS	0.135	X1,000	97	3,800	200,000	Chrysotile
A-224	PS	0.090	X3,000	24	1,900	530	Mostly Chrysotile
A-227-1	PS	0.135	X3,000	88	5,100	795,000	Chrysotile
A-227-2	PS	0.135	X3,000	72	7,800	478,000	"
A-226	NPS	0.135	X1,000	60	2,200	14,300	Mostly chrysotile, some tremolite
A-223	NPS	0.135	X1,000	56	400	153,000	Equal amounts of chrysotile and tremolite
	Demolition Site	0.96	X1,000	9	11	4,000	Chrysotile and tremolite
	Ambient Air (Philadelphia)	10.3	X3,000	6 + 2 lumps	2	67	Chrysotile

*Different designations like A-228, etc, refer to different places inside or outside the factory and to different times and dates.

**PS: Point Source (Inside factory)
NPS: Near Point Source (20 feet from factory)

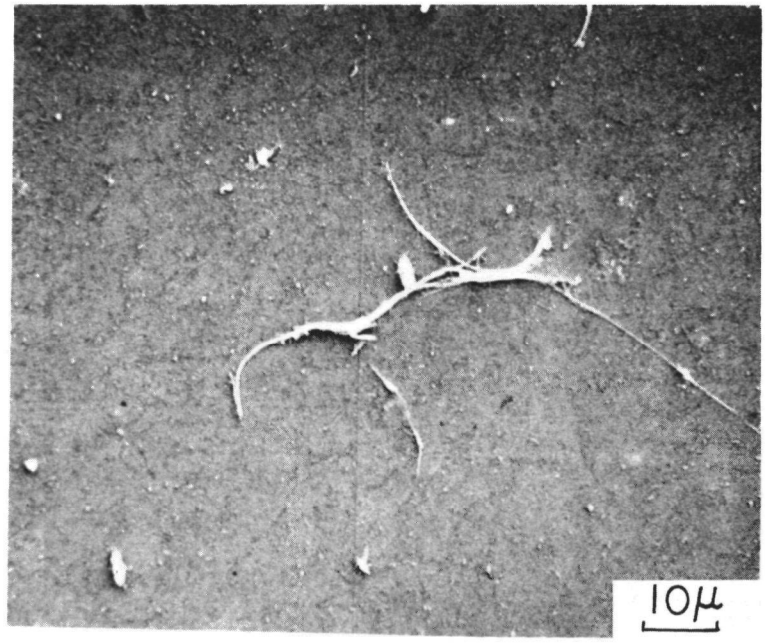


(a)

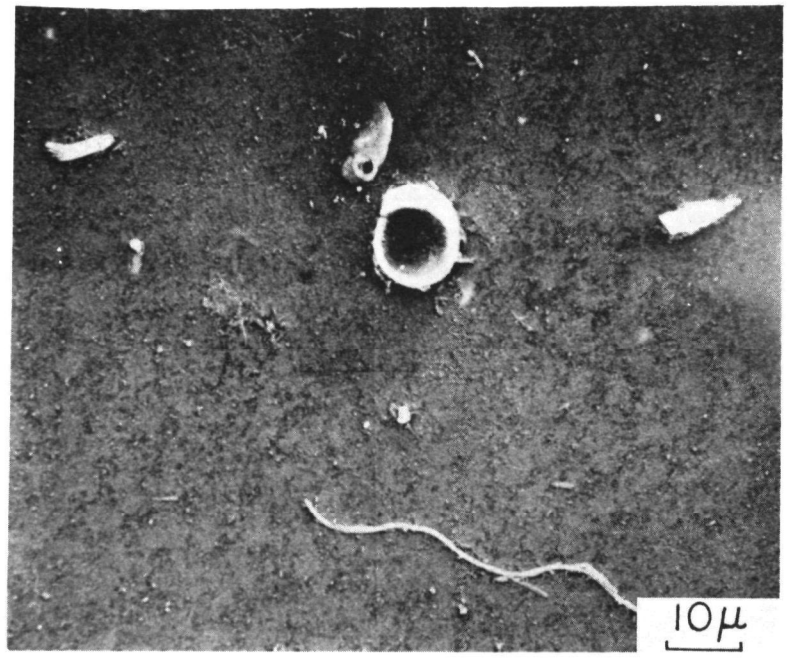


(b)

Figure 11. SEM Micrographs of Point Source Sample, #A-228, X1,000 ((a) and (b) refer to different areas)

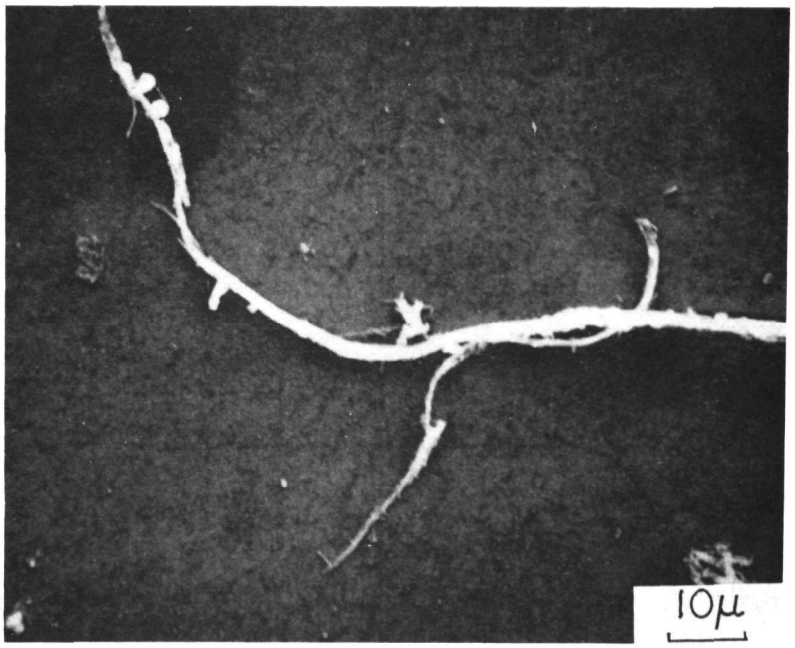


(a)

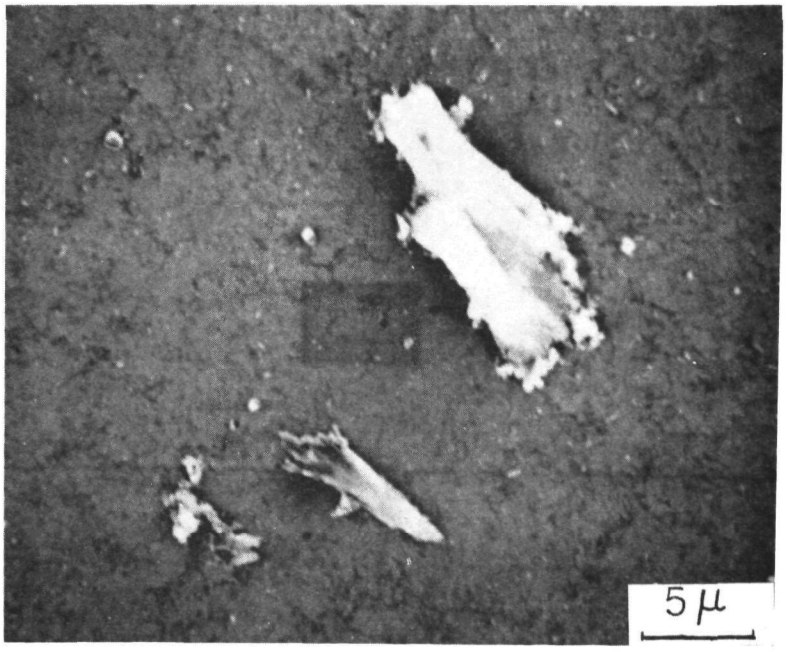


(b)

Figure 12. SEM Micrographs of Point Source Sample, #A-224; X1,000.

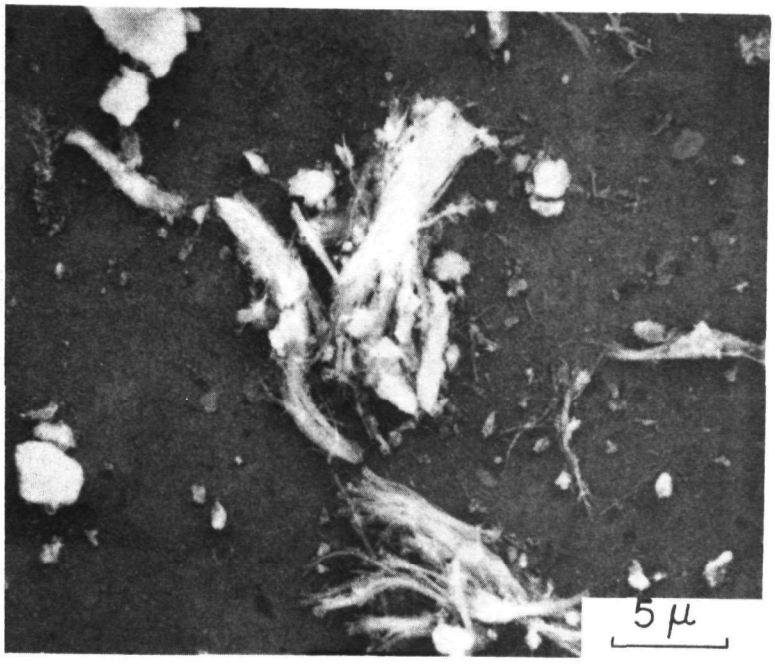


(a)

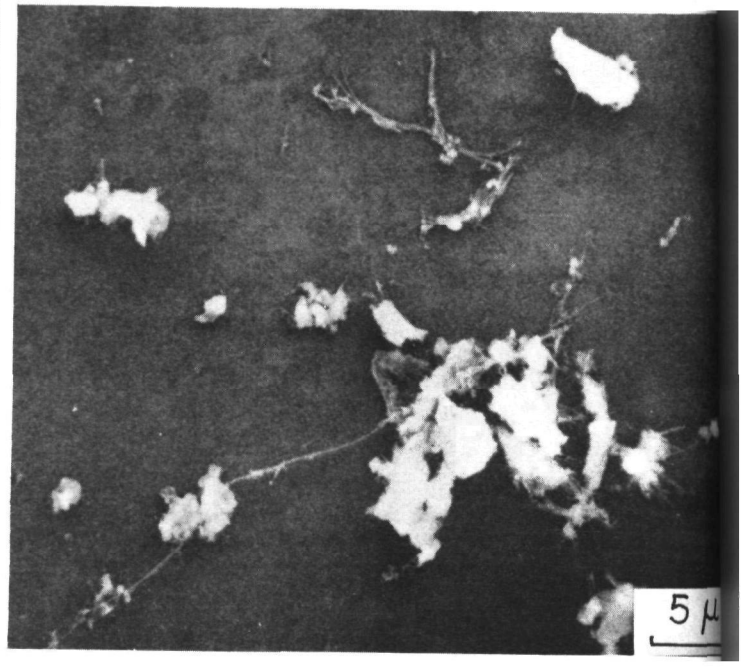


(b)

Figure 13. SEM Micrographs of Near Point Source Sample, #A-223; (a) X1,000 (b) X3,000



(a)



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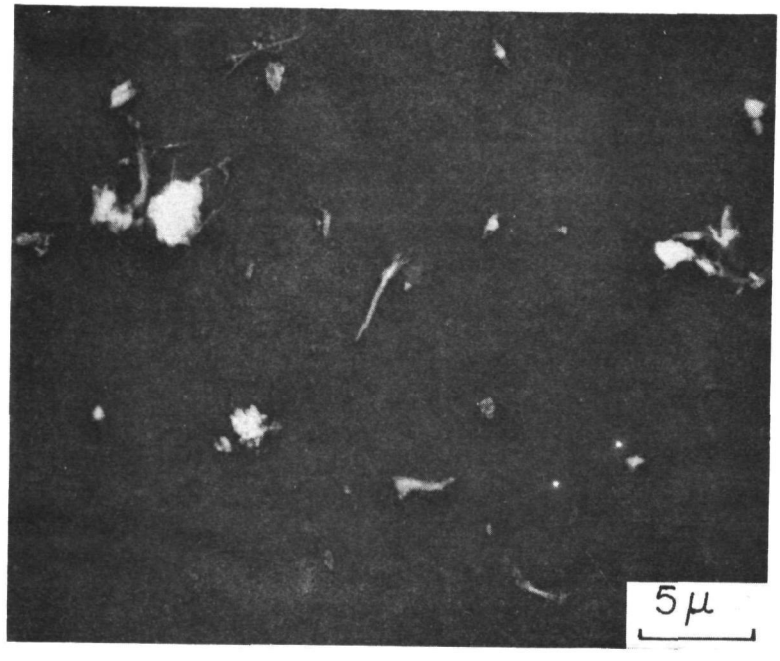
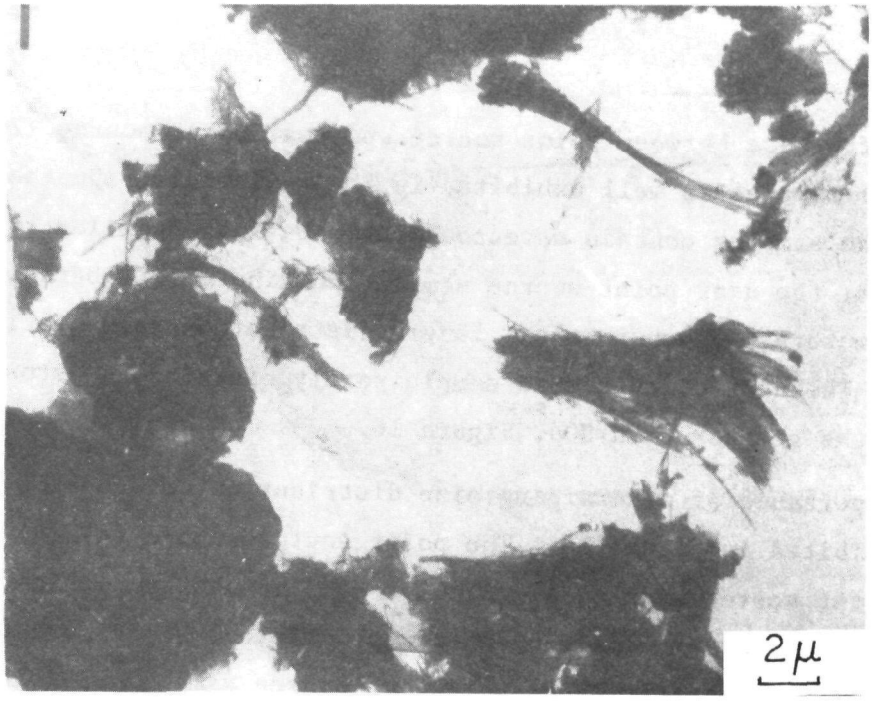
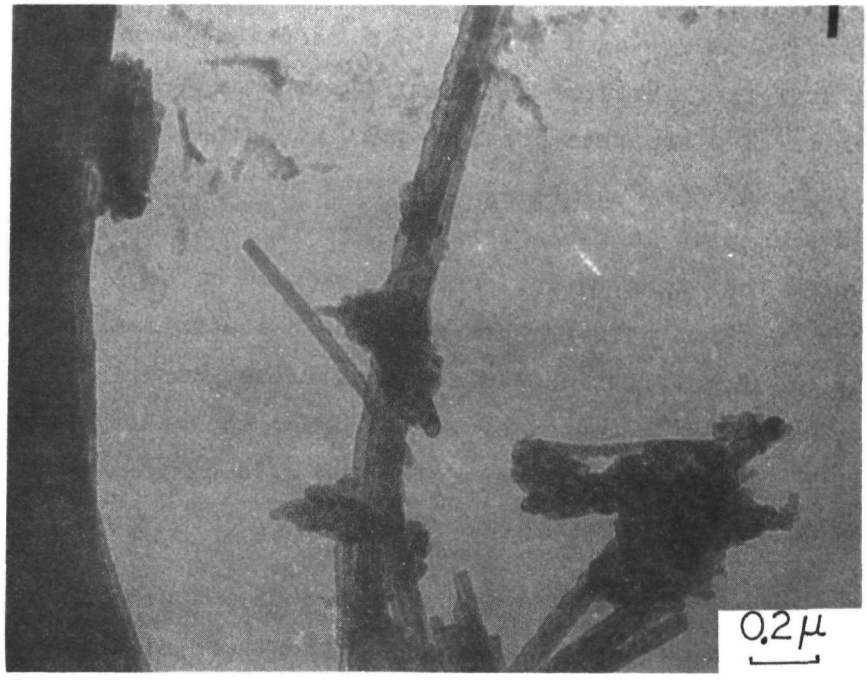


(c)

Figure 14. SEM Micrographs of Near Point Source Sample, #A-226, X3,000.



(a)



(b)

Figure 15. TEM Micrographs of Near Point Source Sample, #A-226. (a) X4,000, (b) 45,000

The difference between point source and near point source (20 ft. from the factory) samples is well exhibited in their size distribution, Figure 16. Both the samples contain asbestos fibers having a similar range of diameters; the near point source sample contains more fibers with smaller diameters. However, their length distributions are distinctly different. The near point source sample rarely contains asbestos fibers having lengths greater than 30μ, Figure 16.

The importance of determining size distribution of asbestos fibers is also exhibited in Figure 16. The point source sample (A-228) and the near point source sample (A-226) have similar number of fibers but significantly different mass concentrations, Table 1 and Figure 16. This arises from the observation that the point source sample has relatively larger fibers, both in diameter and length. Hence, a complete analysis should include the number and the mass of asbestos fibers per unit volume and the fiber size distribution.

In order to study variation in the statistical counting of asbestos fibers from different parts of a filter, the sample A-227 was sectioned into four parts. Two separate portions were prepared on two different beryllium studs and statistical counting was carried out. The data so obtained are presented in Table 1 and Figure 17 as A-227-1 and A-227-2. It is concluded that some variations are observed between two portions of the filter, without carrying out systematic statistical analysis. Observations of such variations in the same filter have led Bartosiewica[48] to design an aerodynamic funnel system in order to obtain a more uniform distribution of particles (air was collected with an open-ended funnel in the present investigation).

An airborne asbestos sample was obtained from a demolition site in Philadelphia City and representative SEM micrographs of this sample are shown in Figure 18. Relatively large chrysotile and tremolite fibers have been observed in this sample. In addition, the sample contained large extraneous particles since air was collected at street level. The particle and mass concentration for this sample are presented in Table I.

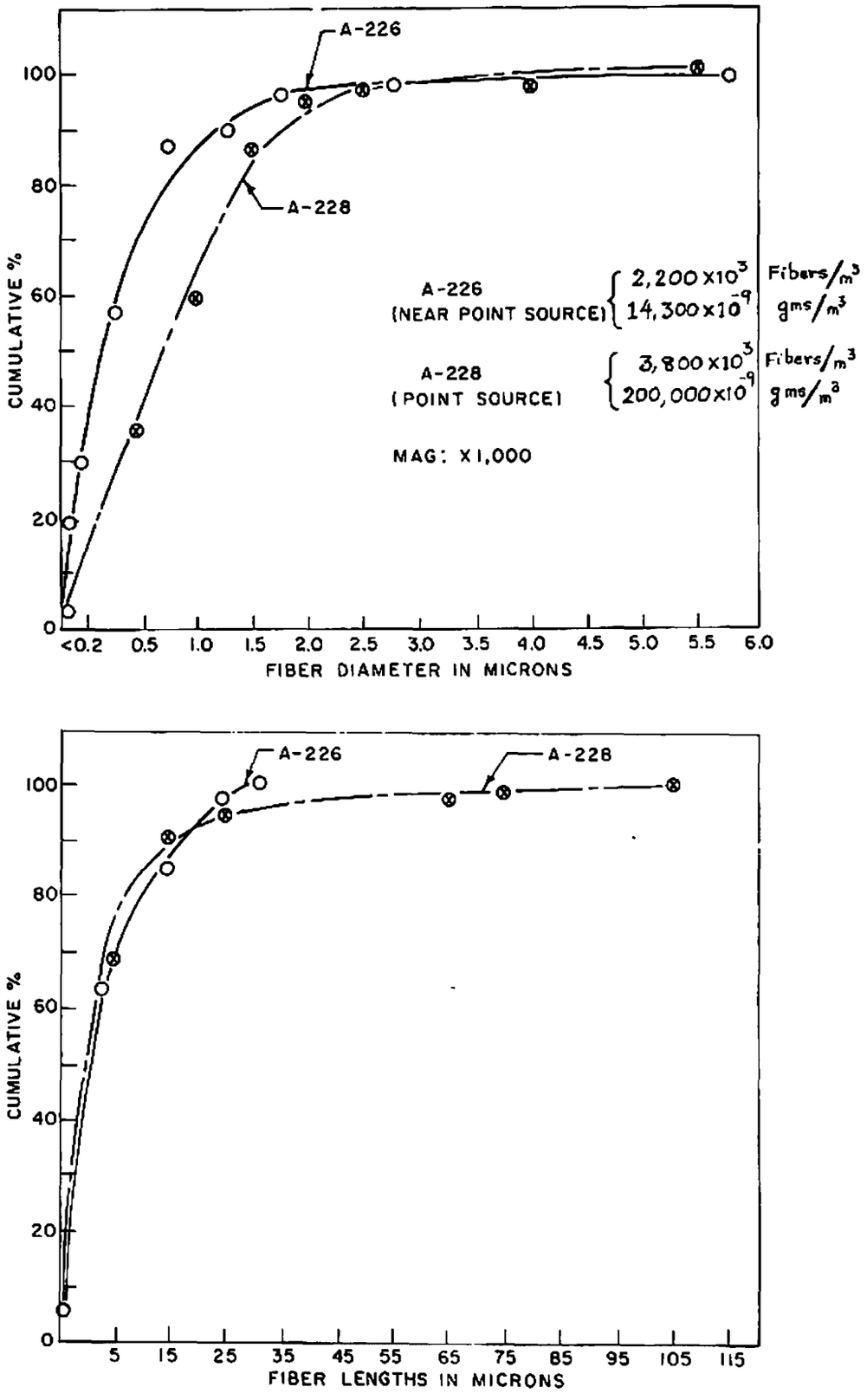


Figure 16. Cumulative Distribution of Asbestos Fiber Diameters and Lengths for Point Source and Near Point Source Samples.

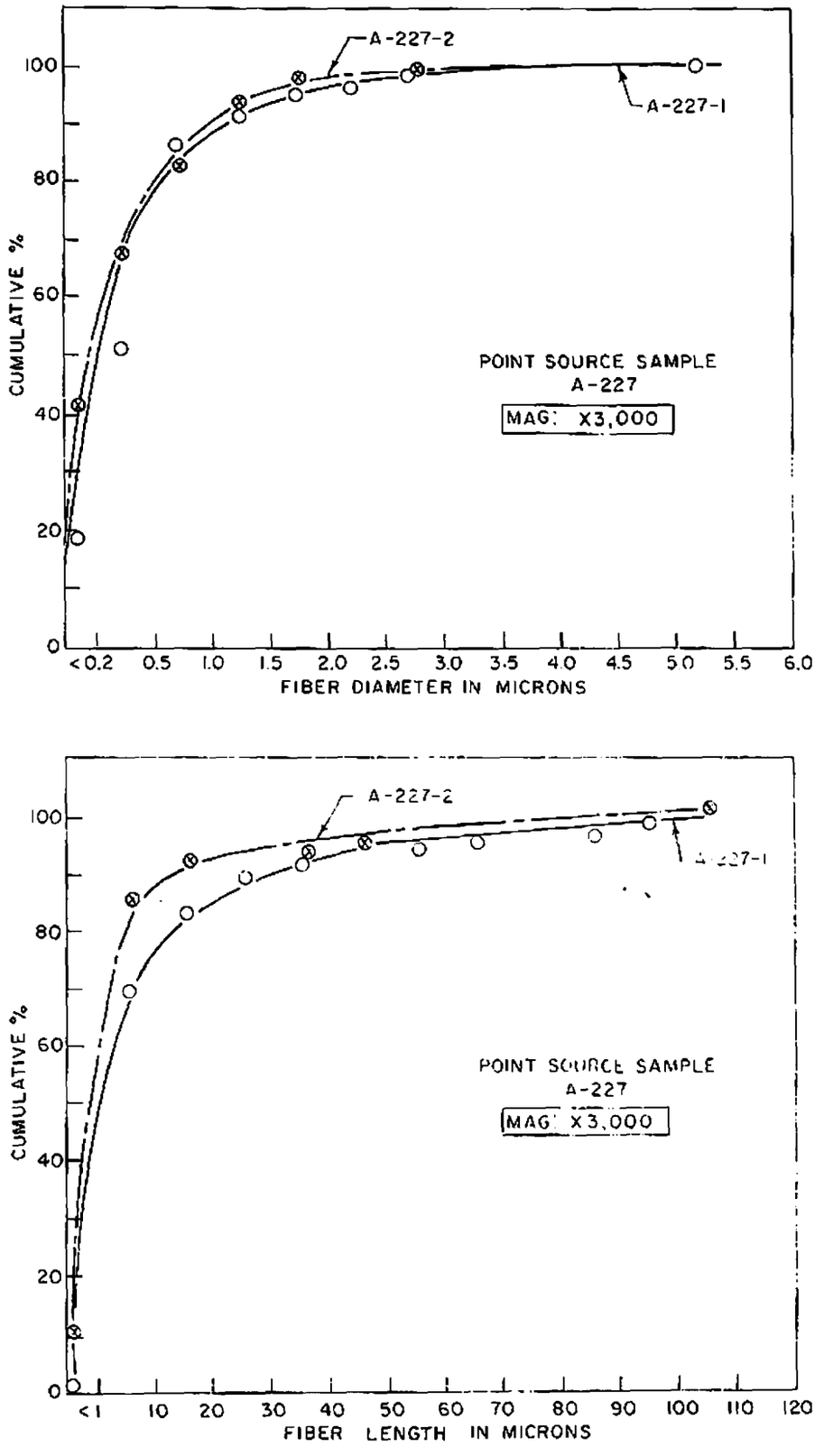
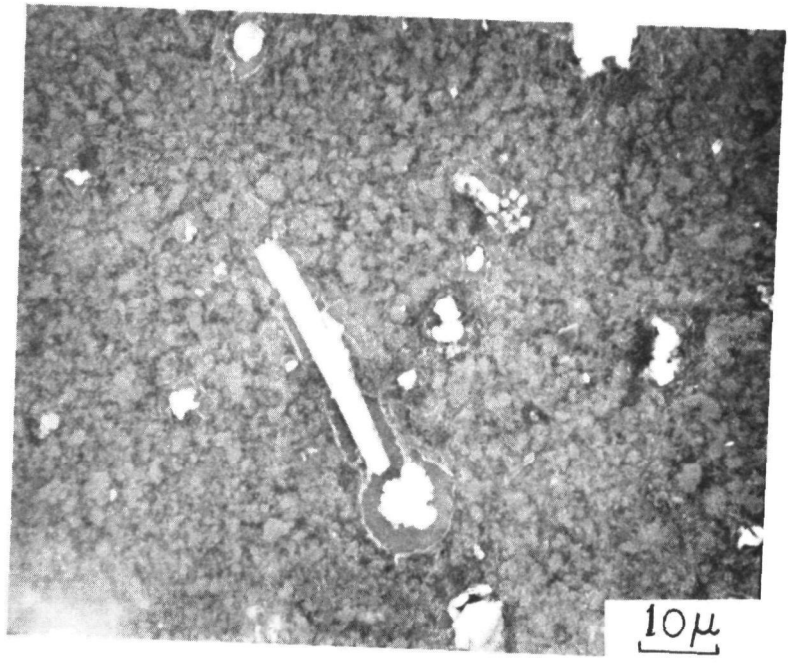
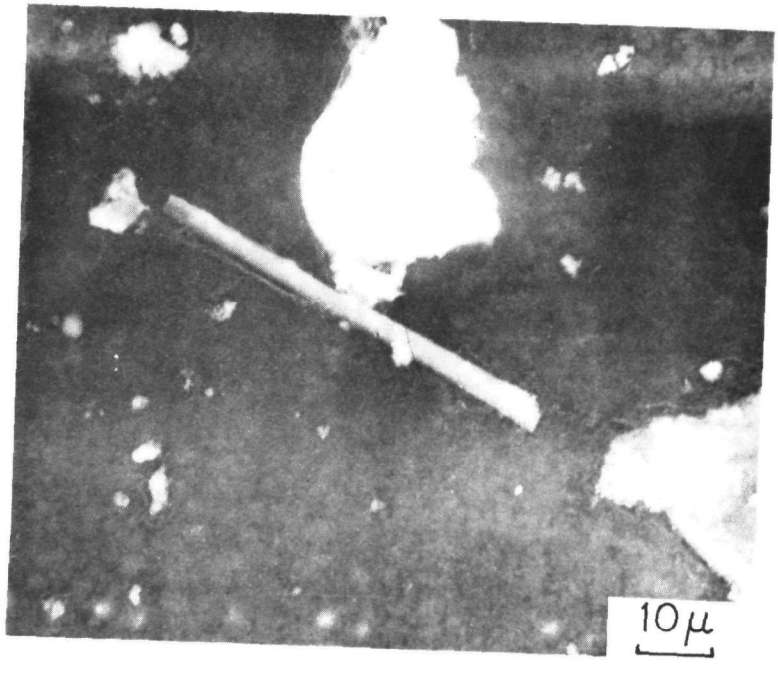


Figure 17. Cumulative Distribution of Asbestos Fiber Diameters and Lengths for a Point Source Sample, #A-227 (A-227-1 and A-227-2 refer to different portions of the filter)



(a)



(b)

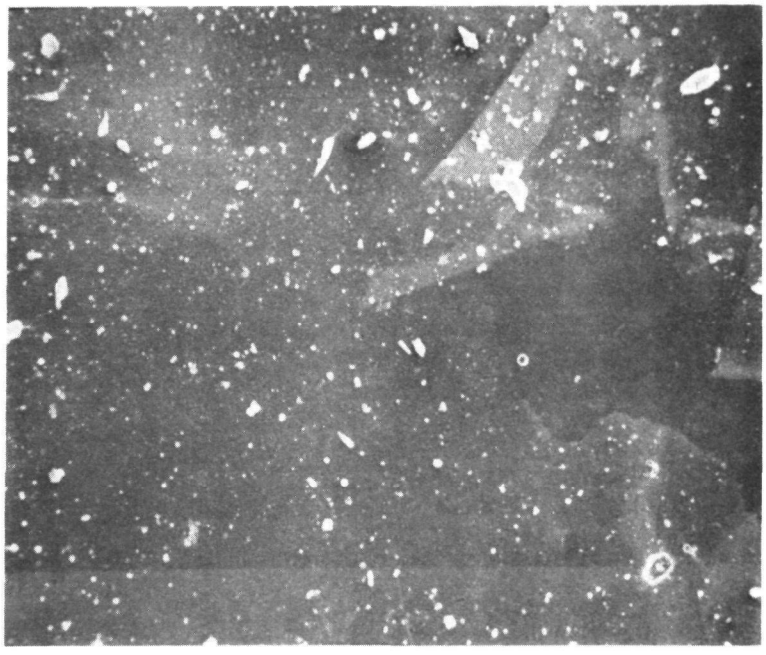
Figure 18. SEM Micrographs of Demolition Site Sample, X1,000.

A few ambient air samples, collected at the FIRL, have been analyzed. The sample collected at the street level had numerous relatively large particles, most of which were inorganic in origin. The fraction of organic particles was negligible since no reduction in particle concentration was observed after LT ashing.

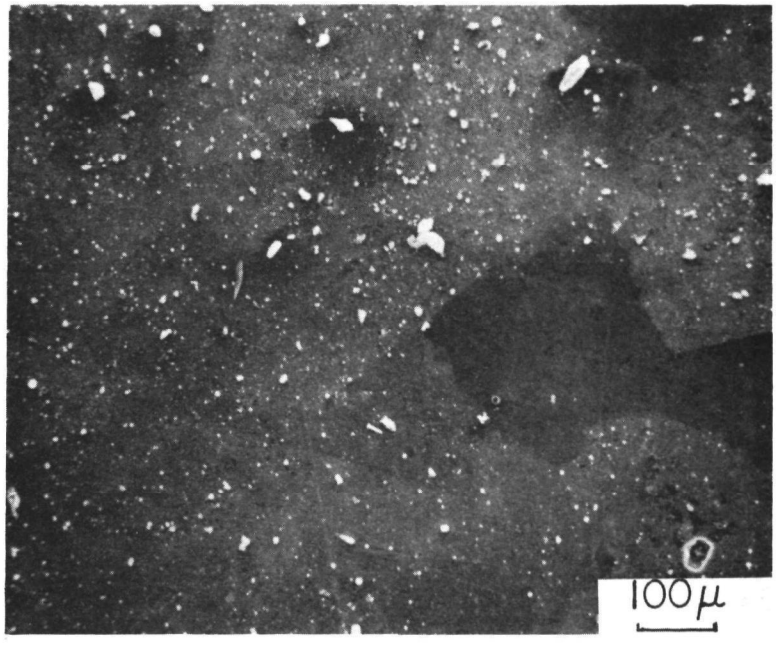
One ambient air sample, collected at the roof of the four-storied FIRL building, was systematically analyzed. The specimen was observed before and after LT ashing step in order to study the effectiveness of the LT ashing as a concentration step. SEM micrographs of this sample are shown in Figures 19 and 20. Observation of Figure 19 indicates that most of the particles are inorganic in nature. However, small particles and fibers, which were embedded in the carbon extraction replica, Figure 20(a), are freed and appear distinctly after LT ashing, Figure 20(b). The specimen was ashed while the oxygen plasma was directly flowing over the particles. There is no evidence of any loss of small particles by the plasma stream and the particle distribution is not disturbed significantly.

A certain amount of difficulty was faced when carrying out statistical counting of asbestos fibers in the ambient air sample. A random viewing of the sample, following a square grid pattern as was done for point source and near point source samples, showed no asbestos fibers. Later, the 25mm beryllium stud specimen was scanned in a more rigorous manner, i.e., viewing every area without leaving out any of them. Following such steps, many chrysotile asbestos fibers were identified including some fiber clumps, Figure 21. A statistical count could be carried out and the result is presented in Table I. Chrysotile fiber clumps in ambient air samples have also been observed by Holt and Young[28]. TEM micrographs of the same sample are shown in Figure 22. A few chrysotile fibrils were observed after thorough viewing of the BeO substrate specimen.

A few point source and near point source airborne asbestos samples had been obtained from the project officer. The airborne particulates had been collected on MF type Millipore filters with a nylon backing;

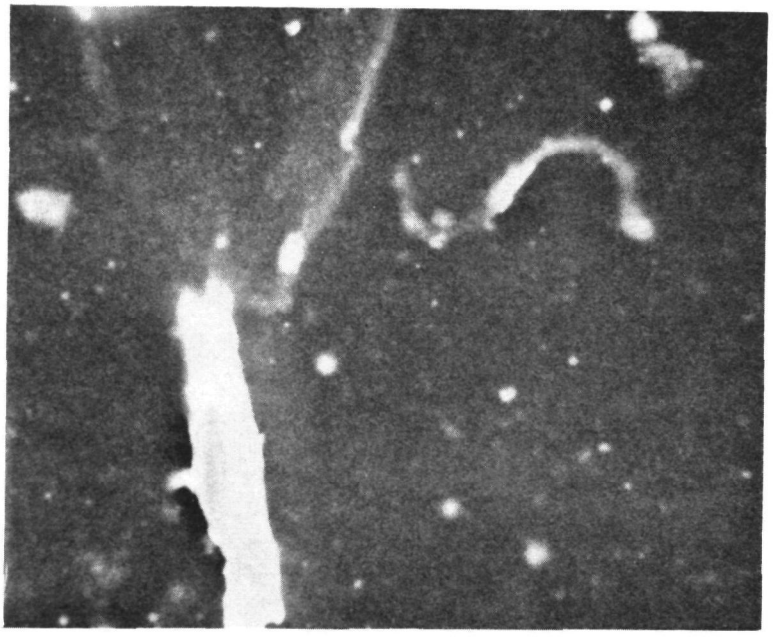


(a)

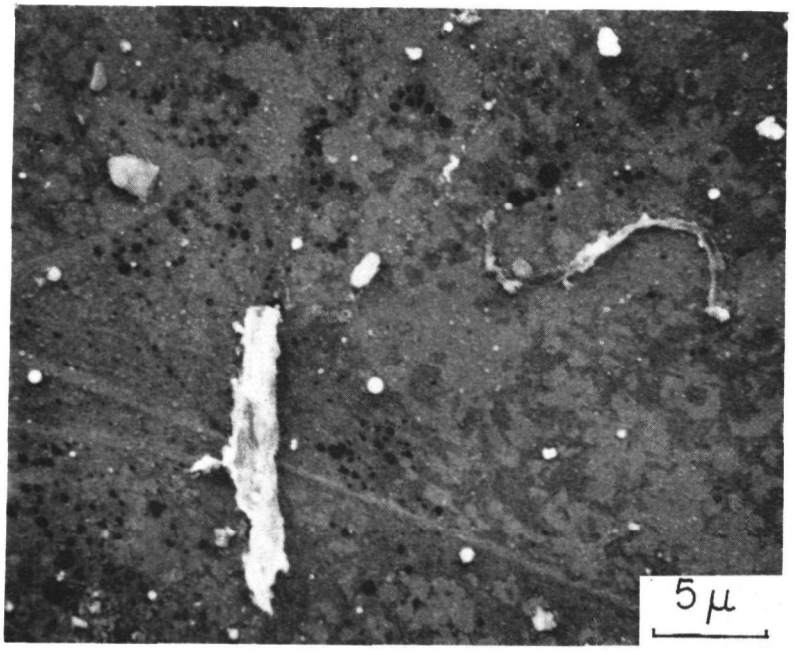


(b)

Figure 19. SEM Micrographs of the FIRL Ambient Air Sample, Roof Level, 0.165m^3 of Air; X100. (a) Before LT Ashing, (b) After LT Ashing.

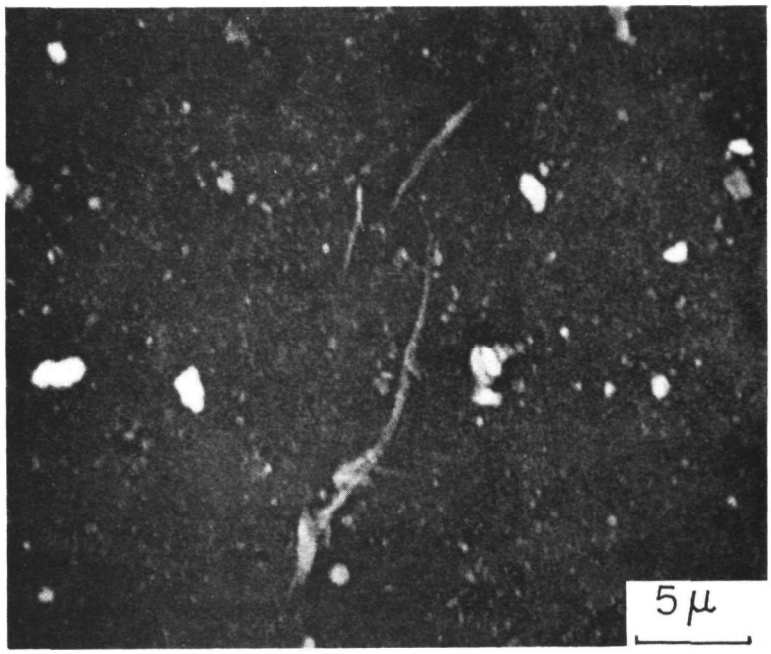


(a)

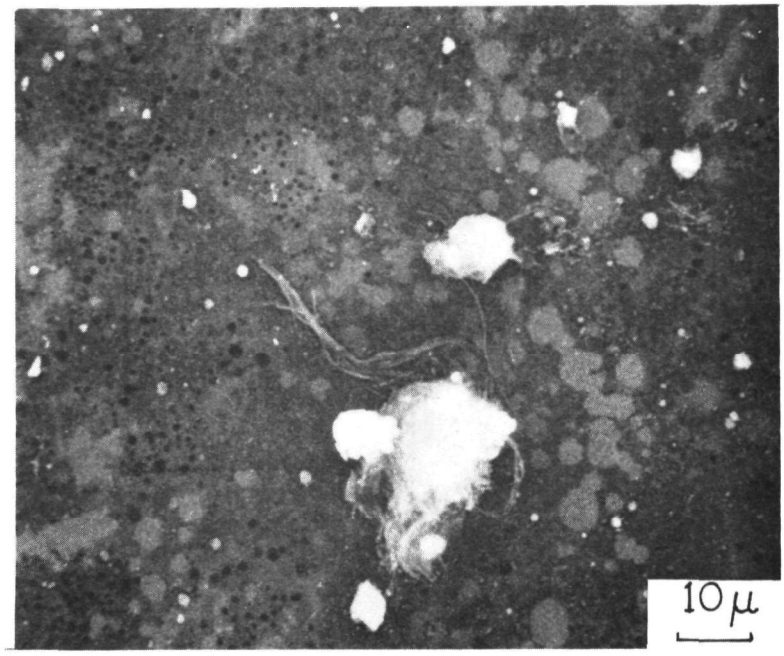


(b)

Figure 20. SEM Micrographs of the FIRL Ambient Air Sample, Roof Level, 0.165m^3 of Air; X3,000. (a) Before LT Ashing; (b) After LT Ashing (Note: Even very small particles are in place after LT ashing).

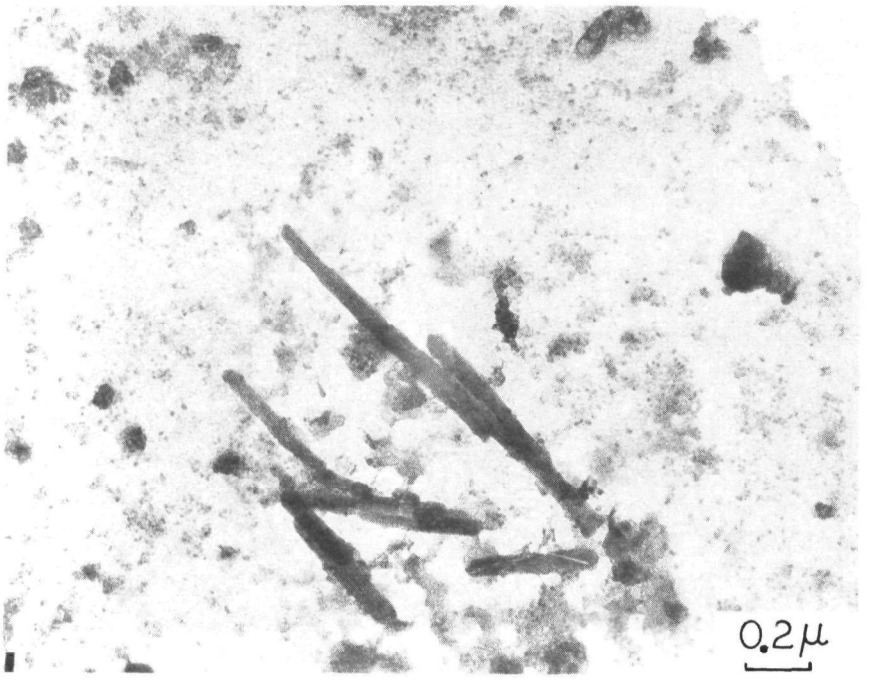


(a)

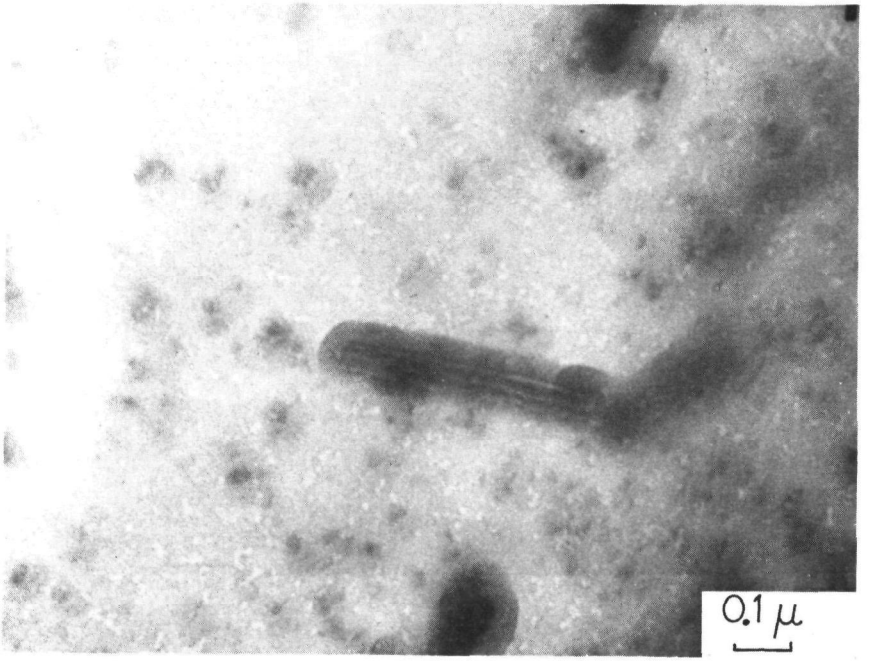


(b)

Figure 21. SEM Micrographs of Chrysotile Asbestos Observed in One of the FIRL Ambient Air Sample, Roof Level, 10m^3 of Air; (a) Single Asbestos Fibers; X3,000; (b) Fiber Lump, X1,000.



(a)



(b)

Figure 22. TEM Micrographs of the FIRL Ambient Air Sample, Roof Level, $10m^3$ of Air on 0.45μ Millipore Filter, BeO Substrate. (a) Non-asbestos Fibers, X38,000, (b) Chrysotile Fibril, X76,000.

this type of filter is not well suited for preparing specimens following the steps shown in Figure 1. Hence, certain modifications had to be incorporated in order to handle these specimens.

A fraction of the specimen, #1000367 (Table II), was oven ashed at 450°C for four to eight hours. The resultant ash was dispersed in 250cc of distilled water in an ultrasonic bath for 10 minutes and filtered through a 0.22μ MF Millipore filter. Minimum time to disperse the ash ultrasonically was used since extensive ultrasonification is commonly used to break down chrysotile fibers into fibrils[24,25]. It is believed that a ten minute ultrasonification only disperses the ash without breaking down fibers into smaller fragments; however, breaking down fiber clumps into single asbestos fibers is not ruled out.

All such specimens, Table II, were oven ashed at 450°C followed by dispersion and filtration. The MF Millipore filter is then dried and processed through the specimen preparation steps shown in Figure 1. Only a fraction of the available filter, for specimen #1000367, was ashed and the resulting specimen is shown in Figure 23. Chrysotile asbestos fibers and other inorganic particles (bright areas) are seen in a dull background of the resulting ash which arises primarily from the nylon grid. Identification of asbestos fibers could be carried out on specimens similar to that shown in Figures 23 and 24 and the statistical results are presented in Table III. The ash generally gives rise to an extra sulphur x-ray fluorescence peak.

The size of the nylon-backed Millipore filter that is ashed plays an important role in the final specimen preparation. A larger filter gives rise to a greater amount of ash. If the ash content is high, small fibers and fibrils are embedded under the ash. Such was the case with specimens #1000376 and #1000378, Table III, and the resulting final specimen was not very conducive to statistical analysis.

Usually no asbestos fiber clumps were observed in specimens listed in Table III. The fiber clumps are probably broken down to single fibers by the ten-minute ultrasonification. The size distribution of asbestos fibers observed for the specimen #1000367 is shown in Figure 25.

The significance of these results will be discussed further in Section 4.2 as to the reliability, advantages and limitations of the FIRL technique.

TABLE II

Details of Samples Analyzed in Table III

Number	:	Collection Site
1000367	:	#7, Nicolet Settling Pond, Pennsylvania, Date: 10/17/73
1000274	:	#3D Vermont, Date: 9/29/73
1000210	:	#8A, Vermont, Date 9/28/73
1000376	:	#10 Herald Construction Yard, Pennsylvania, Date: 10/16/73
1000378	:	#9 Hopewood Residence 212 Chestnut, Pennsylvania, Date: 10/16/73

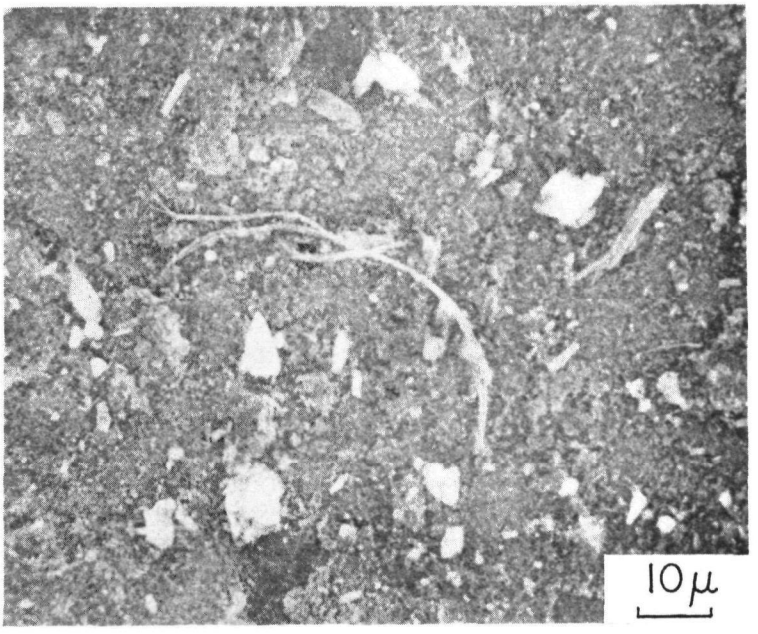
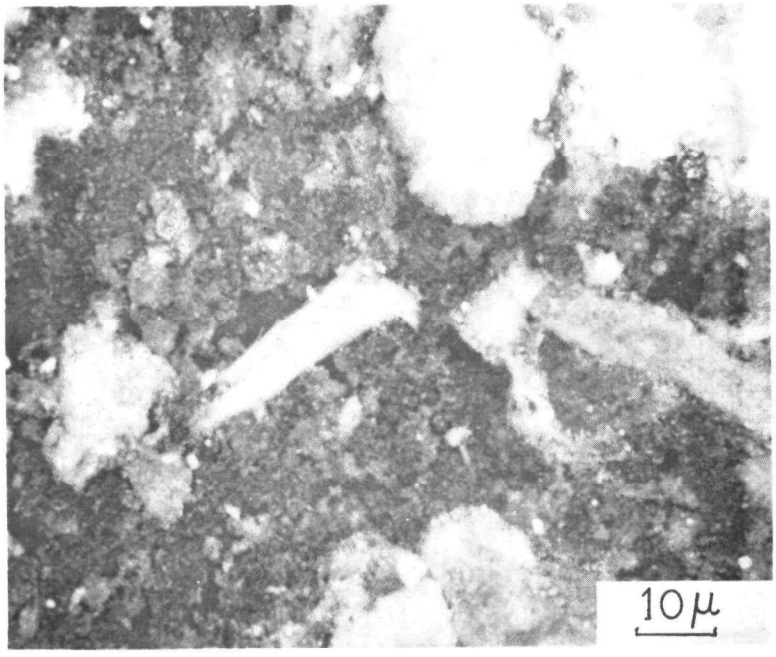
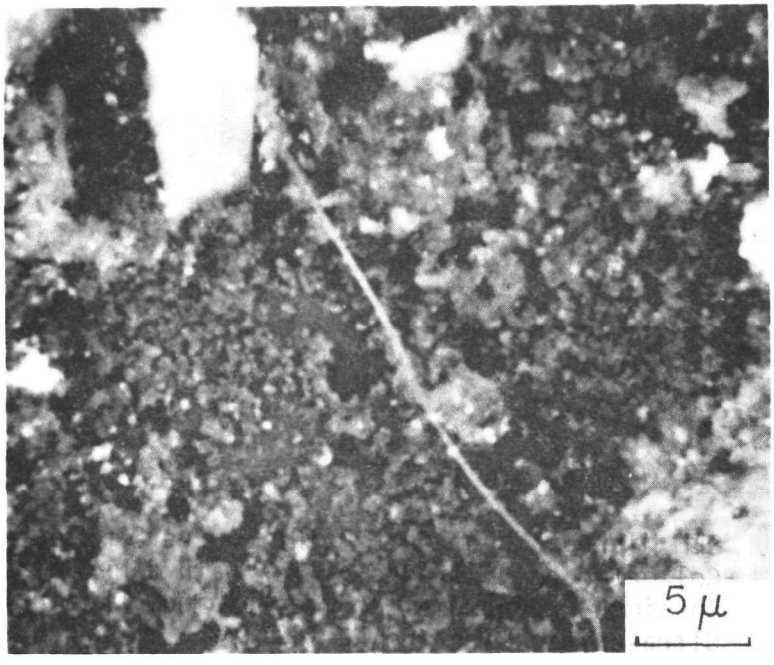


Figure 23. SEM Micrograph of Near Point Source Sample, #1000367 Collected on Millipore Filter with a Nylon Backing. Specimen Prepared after Oven-ashing, Dispersion by Mild Ultrasonification and Re-filtering through a Millipore Filter (Note: Ash in the background), X1,000



(a)



(b)

Figure 24. SEM Micrographs of Near Point Source Sample, #1000274, Particles Originally Collected on Millipore Filter with a Nylon backing; (a) X1,000, (b) X3,000

TABLE III

Analysis of Airborne Asbestos Samples*

Sample**	Volume of Air (m^3)	Magnification	Number of Asbestos Fibers Counted	Fiber Conc. ($\#/m^3$) x 10^3	Fiber Conc. (gm/m^3) x 10^{-9}	Fiber Type
1000367	6	X3,000	46	2.5	3,400	Mostly chrysotile
1000274	25	X1,000	74	123	3,000	Chrysotile; a few crocidolite
1000210	22	X3,000	68	1900	2,100	Chrysotile
1000376***	44	X1,000	11	7.3	3,500	Chrysotile
1000378	172	X3,000	9	13.2	15	Chrysotile

*Asbestos fibers had been collected on Millipore filters with a Nylon backing - Such filters are not well suited for the FIRL technique. Hence, the data should be viewed accordingly.

**For details, see Table II

***For 1000376 and 1000378, data is not reliable

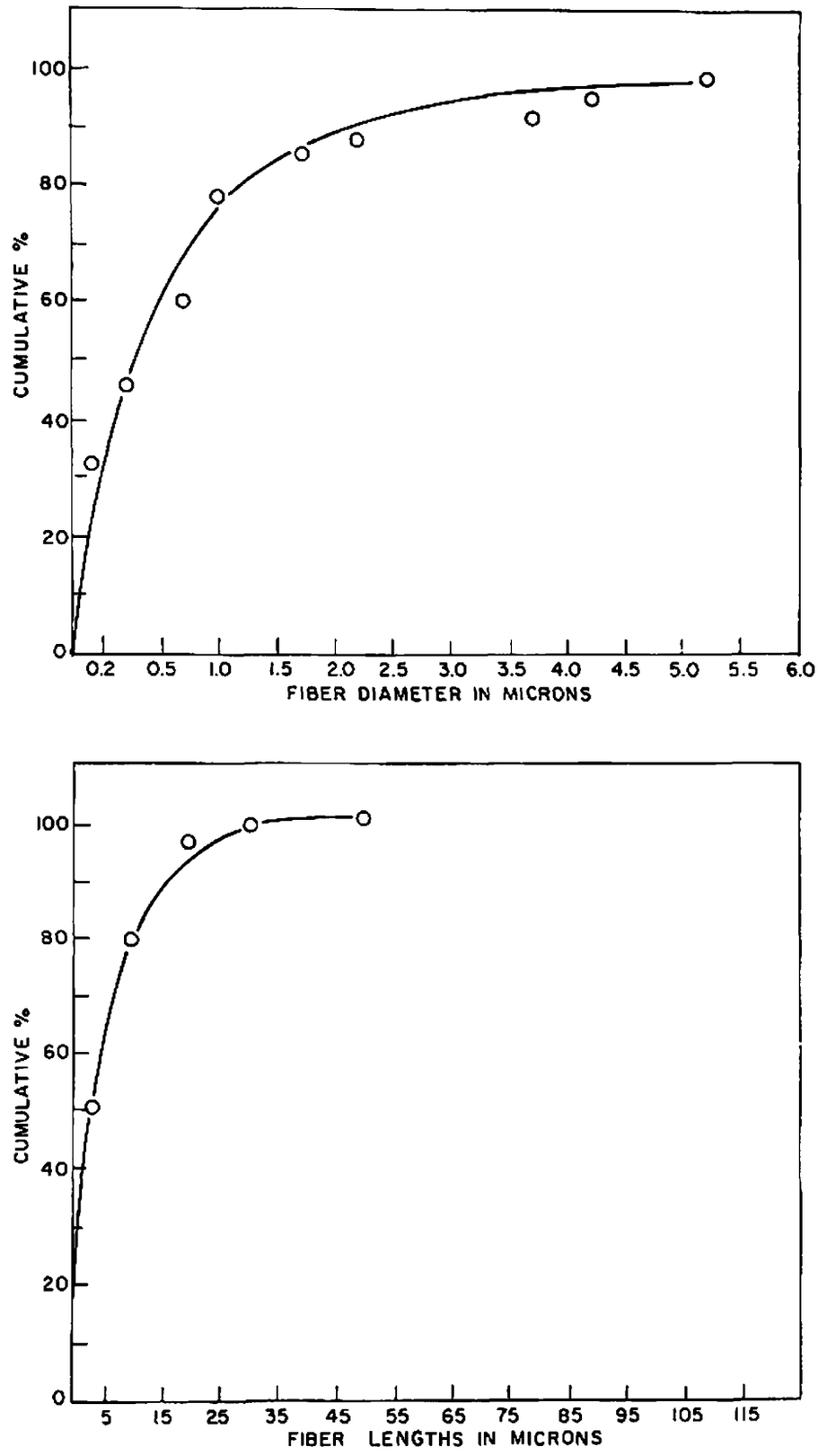


Figure 25. Cumulative Distribution of Asbestos Fiber Diameters and Lengths for the Sample #1000367

4. DISCUSSION

4.1 E.D. X-Ray Fluorescence Analysis of Standard Asbestos Using a Field Emission SEM

The present investigation has been carried out using a JSM-50A which is a conventional SEM with a tungsten hair-pin filament. Recently, SEM's have been commercially available with a field emission source. An x-ray fluorescence spectrum from a small fiber depends on beam voltage and current density, i.e., current per unit area. The field emission source gives a higher current density than the thermionic emission source when the electron beam size is smaller than 1000Å[49]. Hence, one would expect to obtain a better asbestos x-ray spectrum using a field emission SEM than a conventional one, particularly for asbestos fibrils which have diameters of ≈ 300Å. A study has been carried out on amosite fibers and fibrils in the true transmission mode of operation using a field emission SEM[37].

It was of interest to know what improvements are obtained by using a field emission SEM on the specimens prepared by the FIRL technique. A Be-stud specimen and a BeO substrate specimen were prepared from U.I.C.C. Canadian chrysotile following the FIRL specimen preparation technique, Figure 1. Both the specimens were observed in a CWICSCAN* field emission SEM; the Be-stud was observed in the normal mode and the BeO substrate in the 'semi-transmission' mode.

X-ray fluorescence spectra obtained from Canadian chrysotile fibers on a Be-stud specimen are shown in Figure 26. A comparison between Figures 26 and 6 leads one to conclude that the field emission SEM is superior to conventional SEM in the identification of small asbestos fibers. The smallest fiber that was analyzed for the Be-stud specimen was 0.1μ in diameter, Figure 26; however, even smaller than 0.1μ, say, 0.05μ, might be identified using the field emission SEM. The x-ray spectrum from the 0.1μ fiber, Figure 26, is better delineated than the

*Trade name for field emission SEM manufactured by Coates and Walter, Sunnyvale, California

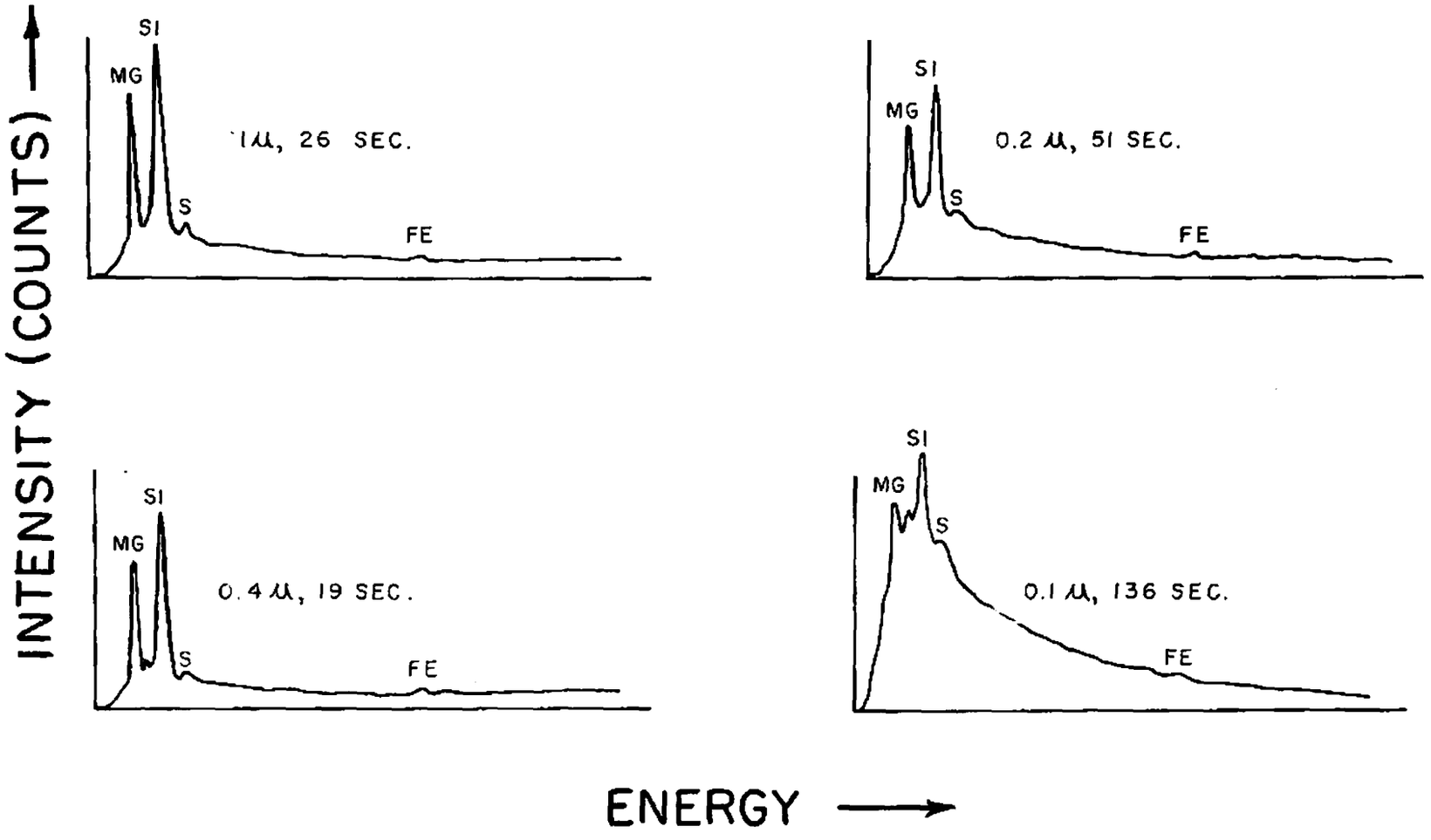


Figure 26. X-Ray Fluorescence Spectra from U.I.C.C. Canadian Chrysotile on Be-stud Obtained in a Field Emission SEM with E.D. Analysis at 18Kv and 3×10^{-9} amp.

similar spectrum in Figure 6. Sulphur appears as an impurity peak from the ash which is a result of LT ashing.

X-ray fluorescence spectra from the BeO substrate specimen are presented in Figure 27. Extra copper peaks appear from the supporting copper grid. A comparison of Figures 27 and 7 again leads one to conclude that the field emission source SEM is superior to conventional SEM for asbestos fibril identification. In fact, a chrysotile fibril of 0.03μ (300Å) was analyzed in 83 secs., Figure 27. The times spent in identifying the asbestos fibers in Figures 26 and 27 are close to the minimum possible for reliable spectrum generation.

Field emission SEM micrographs of the 300Å chrysotile fiber that was analyzed, Figure 27, are shown in Figure 28. The spectrum for the 300Å fibril shown in Figure 27 was obtained in a 'picture-mode' since the 'reduced picture (or scan)-mode' of operation was not available in the system that was used for the present investigation. However, even better x-ray spectra than shown in Figure 27 can be expected if 'reduced-scan-mode' is used as was the case for conventional SEM observation, Figures 6 and 7. Reduced-scan-mode of operation reduces the background spectrum considerably.

In summary, the field emission SEM is superior to conventional SEM as far as identification of asbestos fibrils are concerned. The detection limit of chrysotile asbestos fibers by the two types of SEMs is as follows:

Specimen	Conventional SEM	Field Emission SEM
Be-stud	>0.1μ	<0.1μ
BeO-substrate	$\lesssim$0.1μ	$\lesssim$0.03μ

4.2 Analysis of Airborne Asbestos - Overall View

Many electron microscopic techniques have been developed for the analysis of airborne asbestos[24-29] in addition to the FIRL technique. Some laboratories prefer transmission electron microscopic techniques, in which the asbestos fibers are identified by their SAD patterns and some laboratories prefer scanning electron microscopic techniques, in which the asbestos fibers are identified by their x-ray fluorescence peaks.

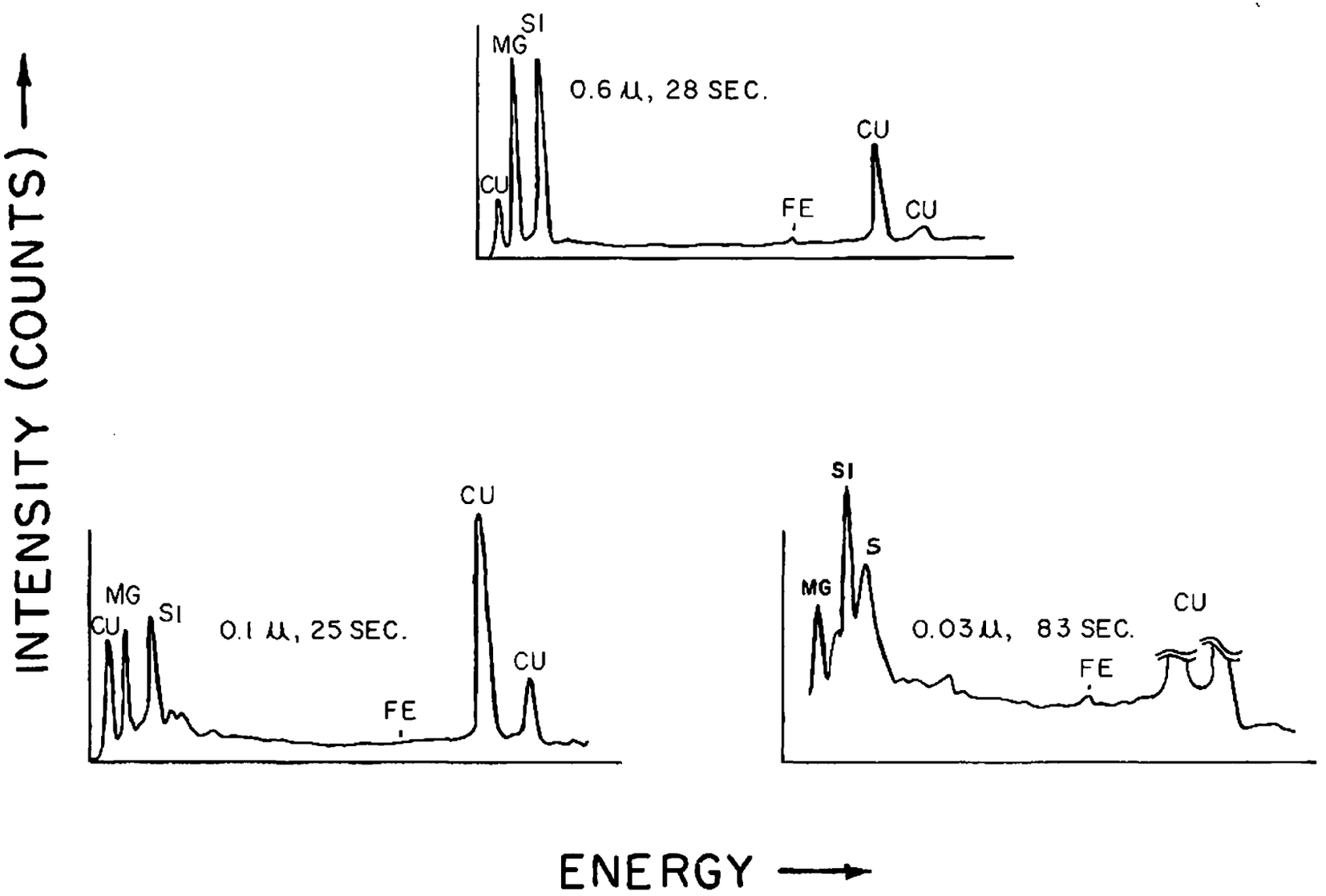
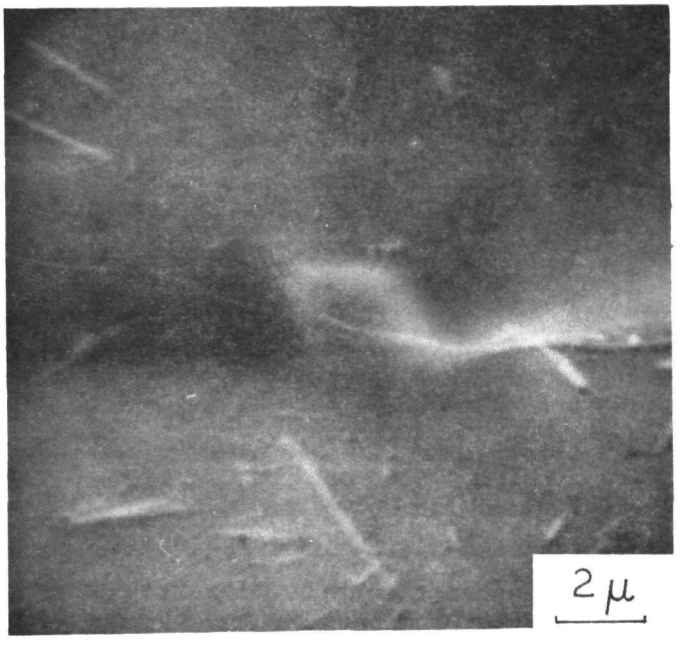
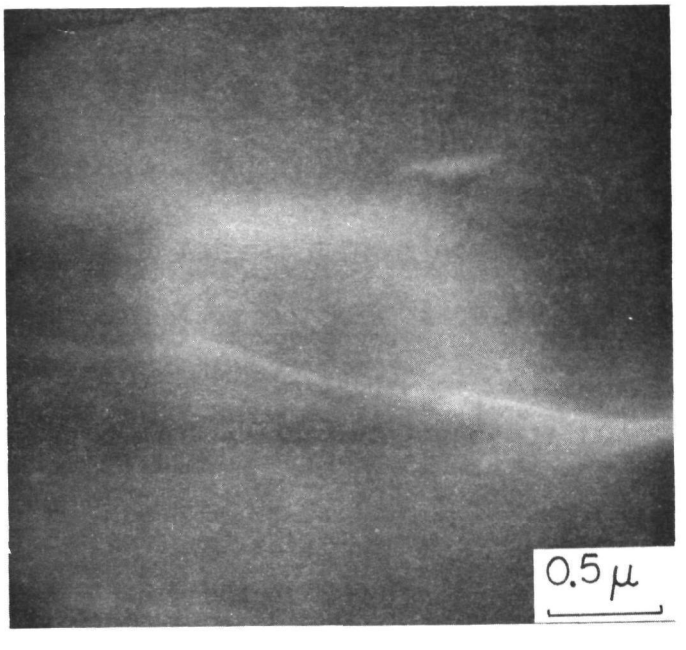


Figure 27. X-ray Fluorescence Spectra from U.I.C.C. Canadian Chrysotile on Be0 Substrate Obtained in a Field Emission SEM with E.D. Analysis at 18Kv and 2 x 10-9 amp.

F-C3779



(a)



(b)

Figure 28. Field Emission SEM Micrographs of U.I.C.C. Canadian Chrysotile on BeO Substrate, Prepared According to Figure 1. (a) X6,000, (b) 300A Chrysotile Fibril from which x-ray spectrum, shown in Figure 27, was obtained in the "scan mode", X30,000.

A special advantage in the use of TEM for chrysotile asbestos is that such fibers can also be identified by their tube-like unique morphology.

The SEM - E.D. x-ray analysis is faster than the TEM-SAD analysis but each technique has advantages and disadvantages which are discussed below specifically for *airborne* asbestos analysis.

SEM-E.D. X-RAY ANALYSIS

(1) The resolution of the SEM is ∿100Å compared to ∿5Å for TEM. Hence, there is a greater chance to miss very small asbestos fibrils, Figure 22(b), when these are situated among numerous other particles.

(2) The difficulties involved in identifying asbestos fibers by E.D. x-ray analysis increase with decreasing fiber size. In conventional SEM's asbestos fibers up to ∿0.1μ in diameter can be identified using thin substrate specimens. However, even the smallest chrysotile fibril can be identified if a field emission SEM is used.

TEM-SAD ANALYSIS

The major disadvantage of this technique is that identifiable SAD patterns can only be obtained from asbestos fibers having a limited range of diameters. Very small fibers and large fibers do not give rise to usable SAD patterns.

Apart from the experimental difficulties involved, there are many other factors which have to be considered in the enumeration of airborne asbestos. Many of the electron microscopic techniques[24,25] destroy the original asbestos fiber size distribution and give only a mass concentration of asbestos fibers. Such techniques are *probably* necessary[50] for ambient air samples in which the concentration of asbestos fibers is rather low. Techniques employing steps to preserve the original fiber size distribution[28], including the present technique (Section 3.4), have not proved very successful for ambient air samples.

However, reliable statistical counting of asbestos fibers can be performed on point source and near point source samples, while preserving the original fiber size distribution, Section 3.4. The present technique has proved very successful in this regard except for one problem which needs further discussion. Point source and near point source samples very often contain fiber clumps, Figures 11(a), 14(a) and (b), and 15. It is difficult to specify the size of a clump simply and to estimate the number of fibers in a clump. It therefore seems desirable to report a clump of asbestos fibers as a clump but estimates of mass concentration will be inaccurate if a sample has a significant number of clumps.

One way to overcome the problem arising from fiber clumps is to specify:

(1) fiber concentration/m^3 and clump concentration/m^3

(2) fiber size distribution (free fibers only)

without an estimate of mass concentration. It is unlikely that fiber clumps can be inhaled and can reach the lungs. A different approach should be taken if automated counting is to be developed - this is discussed in Section 4.3.

4.3 Feasibility of an Automated Counting System

The present technique has been developed for a possible automated counting system for airborne asbestos. The specimen preparation techniques are such that asbestos fibers are observed on a featureless background which is essential for image analysis[39-41]. The feasibility of an automated system consisting of an SEM, E.D. x-ray analyzer and an IMANCO image analyzer (Quantimet 720 system) has been established[42] even though many peripheral problems remain to be investigated.

The present investigation included analyzing point or near point source airborne asbestos samples. Reliable statistical data have been obtained for such samples, Section 3.4. A previously unexpected problem has arisen as far as automated image analysis is concerned and this needs further discussion.

Automated image analysis will be unreliable for samples containing fiber clumps, Figures 11(a), 14, 15 and 21 , and fibers in close proximity with other particles or fibers clumped with other particles, Figures 11(a), 14(b), 15(a) and 21(b). Hence, if automated image analysis is being contemplated, then some specimen preparation steps should be investigated to free the asbestos from either asbestos fiber clumps or heterogeneous clumps without disturbing the original fiber size distribution (or, disturbing the size distribution to a minimum).

FUTURE WORK

The following steps should be investigated for freeing the asbestos fibers from clumps if automated image analysis is to be developed.

(1) The Millipore filter with collected airborne asbestos is ashed in a LT asher. The LT ashing is preferable to oven-ashing.

(2) The ash is dispersed in filtered distilled water in an ultrasonic bath for 10 mins. Experience has shown that a 10-minute ultrasonification is only necessary to disperse the particles uniformly. It is expected that fibrillation is minimal during the ten-minute ultrasonification.*

(3) Refilter the ash through a MF-type Millipore filter and then follow the steps shown in Figure 1.

*Ultrasonification is carried out for 4-12 hours to break all chrysotile fibers into fibrils[24,25]

5. CONCLUSIONS

The following conclusions have been drawn from the present investigation.

1. Further developments have been carried out in the specimen preparation technique that was developed earlier under an EPA research contract.

2. Specimens for the transmission electron microscope (TEM) are prepared simultaneously along with the specimens for the scanning electron microscope (SEM).

3. Both types of specimens exhibit featureless background for convenient observation of asbestos fibers and fibrils, and are suitable for automated image analysis.

4. The ∿25mm diameter Be-stud specimen is preferred for a truer statistical analysis in the SEM than the 3mm copper grid specimen meant for use in the TEM.

5. The specimen preparation technique preserves the *original* fiber size distribution with minimal loss of large particulates.

6. Asbestos fibers are identified in an automated manner by the programmed NS-880 E.D. x-ray analyzer interfaced with the SEM. Hence, less skilled operators are required for carrying out a statistical analysis.

7. The smallest chrysotile asbestos fiber that is confidently identified, using the Be-stud specimen, is ∿0.15μ in diameter while $\leq$ 0.1μ asbestos fibers can be identified using the BeO substrate specimen. The above limit of detection refers to a conventional SEM.

8. The field emission SEM is superior to conventional SEM as far as identification of small asbestos fibers are concerned. It is possible to identify the smallest chrysotile fibril (∿300Å) in the field emission SEM using the BeO substrate specimen.

9. Observation of small asbestos fibers in the presence of a large number of other particulates is made easier by the use of TEM in comparison to SEM.

10. Identification of asbestos fibers needs to be carried out in the TEM if a change in the chemical composition of the fibers has taken place. This is applicable more to waterborne asbestos and to asbestos in foods, drugs and tissues than to airborne asbestos. A chemical change for the airborne asbestos is very unlikely.

11. The present technique is applicable to point source and near point source airborne asbestos samples satisfactorily and less satisfactorily to ambient air samples.

12. Asbestos fiber clumps have been observed in point source, near point source and even in ambient air samples. In a manual mode of operation, this problem can be dealt with. However, problems are foreseen in a completely automated counting system. The automated image analyzing system may not be able to identify and count an asbestos fiber clump as a 'clump'.

13. It is recognized that a step involving mild ultrasonification is necessary to free asbestos fibers from adhering non-asbestos particulates and possibly to break down a fiber clump into asbestos fibers (without fibrillation). This step will be necessary if automated image analysis is being contemplated.

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Appendix

APPENDIX A

BeO Substrate Preparation

APPENDIX A

BeO Substrate Preparation

The optimum substrate for selected area diffraction and microscopy would be amorphous and featureless. For x-ray fluorescence analysis the substrate should contribute no characteristic peaks in the energy range of interest. Moreover, the substrate should be stable under low temperature oxygen plasma ashing which is a critical step in the preparation of samples.

Initially SiO substrates were prepared and were successfully used in the specimen preparation. The only disadvantage of SiO substrate is that Si from the substrate hinders identification of asbestos fibers which are uniquely identified by their Mg, Si, Ca and Fe x-ray fluorescence peaks. BeO is an ideal candidate since neither Be nor O is detected by E. D. x-ray analysis. BeO substrates have been successfully prepared in this laboratory after some initial set-backs. BeO is brittle and initially the substrates exhibited cracking as the copper grid curled during oxidation in the LT asher. The normal TEM copper grids have a ring at the periphery and this seemed to cause the distortion. The successful technique uses grids punched out of a sheet of copper mesh.

SUBSTRATE PREPARATION STEPS:

1. 3mm diameter copper grids are punched out of 300 mesh sheet.
2. The blank grids are preoxidized overnight at 175°C in air.
3. The copper grids are ultrasonically cleaned in acetone to remove non-adhering oxide.
4. A cleaned microscope slide is coated with a thin layer of dehydrated Victawet*.
5. A weighed amount of Be is evaporated onto the glass slide. The Be vapor oxidizes to BeO in the evaporator and deposits as BeO film.
6. The glass slide is scratched with a razor blade to form a square grid pattern on the BeO film.

*Victawet - Available from Ladd Research Industries, Vermont, U.S.A.

7. The BeO is floated onto the surface of deionized water containing a few drops of detergent. Small squares of BeO film are picked up on preoxidized copper grids and dried.

BeO substrates prepared in the above manner survive LT ashing and the stresses that are encountered during different steps of the specimen preparation, Figure 1.

The properties of the BeO substrates have already been described, Section 3.3. It is a crystalline film but is featureless for present purposes.

However, it is believed that the quality of the BeO substrate could be improved by depositing Be on a colder substrate. Amorphous BeO substrates should be possible. The present BeO substrates were adequate for this investigation.

TOXICITY OF BeO

It is well known that beryllium (Be) and its vapor are toxic. In the solid state, Be studs can be handled without much danger from its toxicity; however, care should be taken when Be vapor is encountered, which is the case in the preparation of BeO substrate. The following precautions are taken at the FIRL whenever BeO substrates are prepared.

(1) While evaporating Be in an evaporator, a somewhat temporary enclosure, made of thick aluminum foil, is made around the tungsten filament and the glass substrate. The specially tailored enclosure still allows viewing of the filament for controlled evaporation.

(2) A glass beaker of suitable size is put upside down above the aluminum foil enclosure. Hence escape of Be vapor to the outer chamber is minimal.

(3) After completion of evaporation, the aluminum foil is discarded safely and the glass beaker is thoroughly washed under an exhaust hood.

(4) The evaporator is also cleaned thoroughly using acetone and tissue papers after evaporation. Then the tissue papers are discarded safely.

The FIRL has had extensive experience in the preparation and handling of beryllium. Routine analysis of beryllium in the air of the beryllium laboratories of the FIRL is carried out according to environmental standards.

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Appendix

APPENDIX B

Computer Program for the Identification

of Asbestos Fibers

THE FRANKLIN INSTITUTE RESEARCH LABORATORIES
THE BENJAMIN FRANKLIN PARKWAY · PHILADELPHIA, PENNSYLVANIA 19103

APPENDIX B

Computer Program for the Identification of Asbestos Fibers

The JSM-50A scanning electron microscope at the FIRL is equipped with a computerized NS-880 E.D. x-ray analyzer. The associated minicomputer is programmed for various applications and x-ray fluorescence spectra can be stored on magnetic tapes. Recently, a system called Flextran*, has been developed for the NS-880 system; with Flextran, the computer can be programmed using Flextran language. New programs can be readily written by the user for specific applications. The following program has been developed for the identification of asbestos fibers.

Common asbestos fibers can be identified by the three-element ratio analysis[8,9]. The elements of interest are Mg, Si and Fe and their ratios are calculated according to the following formula:

$$A_i = \frac{I_i / I_i^s}{\sum_i I_i / I_i^s} \qquad \text{(B-1)}$$

where, i refers to Mg, Si, and Fe

- A : Element ratio
- I_i : Intensity of x-ray fluorescence peak from element i in an asbestos fiber
- I_i^s: Intensity of x-ray fluorescence peak from element i from a standard sample consisting of pure element i.

The A_i ratios are plotted on a ternary-type diagram, Figure B-1. The A_i ratios are not unique for a particular type of asbestos and the spread observed depending on fiber size and composition for the U.I.C.C. asbestos standards is shown in Figure B1. This diagram can be used for identifying unknown asbestos fibers. Similar approach was used by Langer et al.[8] while using an electron microprobe with a wavelength

*Tracor-Northern, Inc., Middletown, Wisconsin 53562

dispersive spectrometer. Their ternary-type diagram (Figure 5 of ref. 8) is similar but not identical to Figure B-1 since the ratio A depends on many factors, particularly the sensitivity of the detection system.

Presently the FIRL is working on a FDA contract to identify asbestos fibers in talc, food and drugs. Experience has led to the development of a new program which is based on a five-element ratio using the following equations:

$$A_i = \frac{I_i/I_i^{\,s}}{\sum_i I_i/I_i^{\,s}} \qquad \text{(B-2)}$$

where i refers to Na, Mg, Si, Ca and Fe. Expanding Equation B-2 for Mg gives:

$$A_{Mg} = \frac{I_{Mg}/I_{Mg}^{\,s}}{I_{Na}/I_{Na}^{\,s} + I_{Mg}/I_{Mg}^{\,s} + I_{Si}/I_{Si}^{\,s} + I_{Ca}/I_{Ca}^{\,s} + I_{Fe}/I_{Fe}^{\,s}} \qquad \text{(B-3}$$

etc.

It was observed earlier, Figure B-1, that these A numbers are not unique and they have a spread corresponding to different regions defining specific type of asbestos. Hence, A + ΔA (ΔA referring to the spread in numbers) values for different types of asbestos and talc are stored in the NS-880 computer memory. Similar A numbers are determined from an unknown spectrum and matched with the numbers for standards in the following manner. The following numbers are calculated:

$$(A_{Mg} \pm \Delta A_{Mg})_{known} - (A_{Mg})_{unknown} = |B_{Mg}| \qquad \text{(B-4)}$$

$$(A_{Si} \pm \Delta A_{Si})_{known} - (A_{Si})_{unknown} = |B_{Si}|$$

etc.,

$$C_i = \sum_i |B_i|$$

$|B|$: Absolute value of $\pm B$

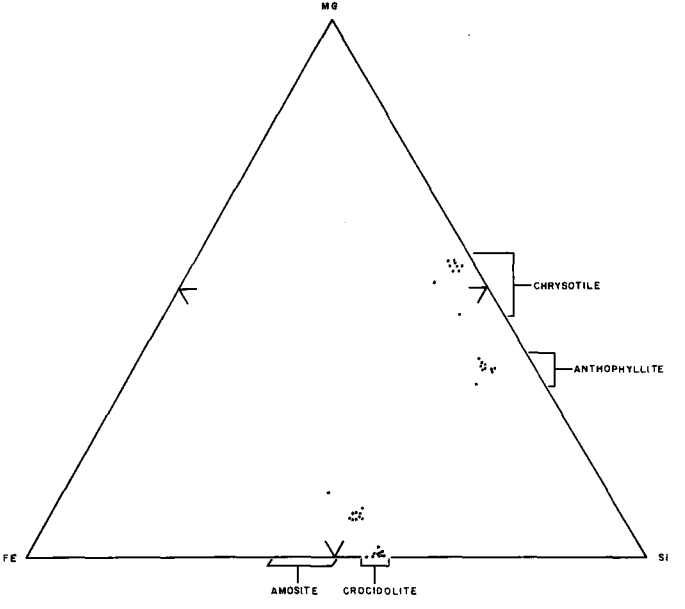


Figure B-1. Ternary Diagram of Mg-Si-Fe Kα Emission Ratios of Standard U.I.C.C. Asbestos

where, i refers to chrysotile, amosite and talc etc.

The C_i's are calculated for chrysotile, amosite etc., and the unknown fiber is identified to be that standard fiber which gives the least value for C.

Before the computer calculates the C values using Equation B-4, the fluorescence spectrum from the unknown fiber is stripped of the background spectrum then each peak is normalized with respect to standards.

A pseudo-ternary diagram illustrating the regions for different asbestos fibers is shown in Figure B-2. The 5-element space is shown projected onto the 3-element plane. The amount of sodium (Na) differentiates between the overlapping regions of amosite and crocidolite and hence there is no ambiguity.

Normalized A ratios with limits for different types of asbestos are presented in Table B-1. Standard asbestos fibers have been used to obtain the A ratios presented in Table B-1; the limits have been obtained carrying out x-ray analysis on a large number of fibers with different diameters and locations. A close scrutiny of the Table B-1 indicates that none of the asbestos variety has all the 5 ratios similar allowing unique identification. The uniqueness of identification is evident from Table B-1 and illustrated in Figure B-2 recalling that 5-element space is projected on the 3-element surface.

A schematic diagram of the computer program and logic is shown in Figure B-3. The program can be operated following two different routes:

(1) The fluorescent x-rays are accumulated as long as the operator decides and then, the computer is asked to identify the type of asbestos spectrum.

(2) The computer accumulates data for every 10 secs. and checks if the peaks are significant with respect to background and then tries to match the spectrum in order to identify.

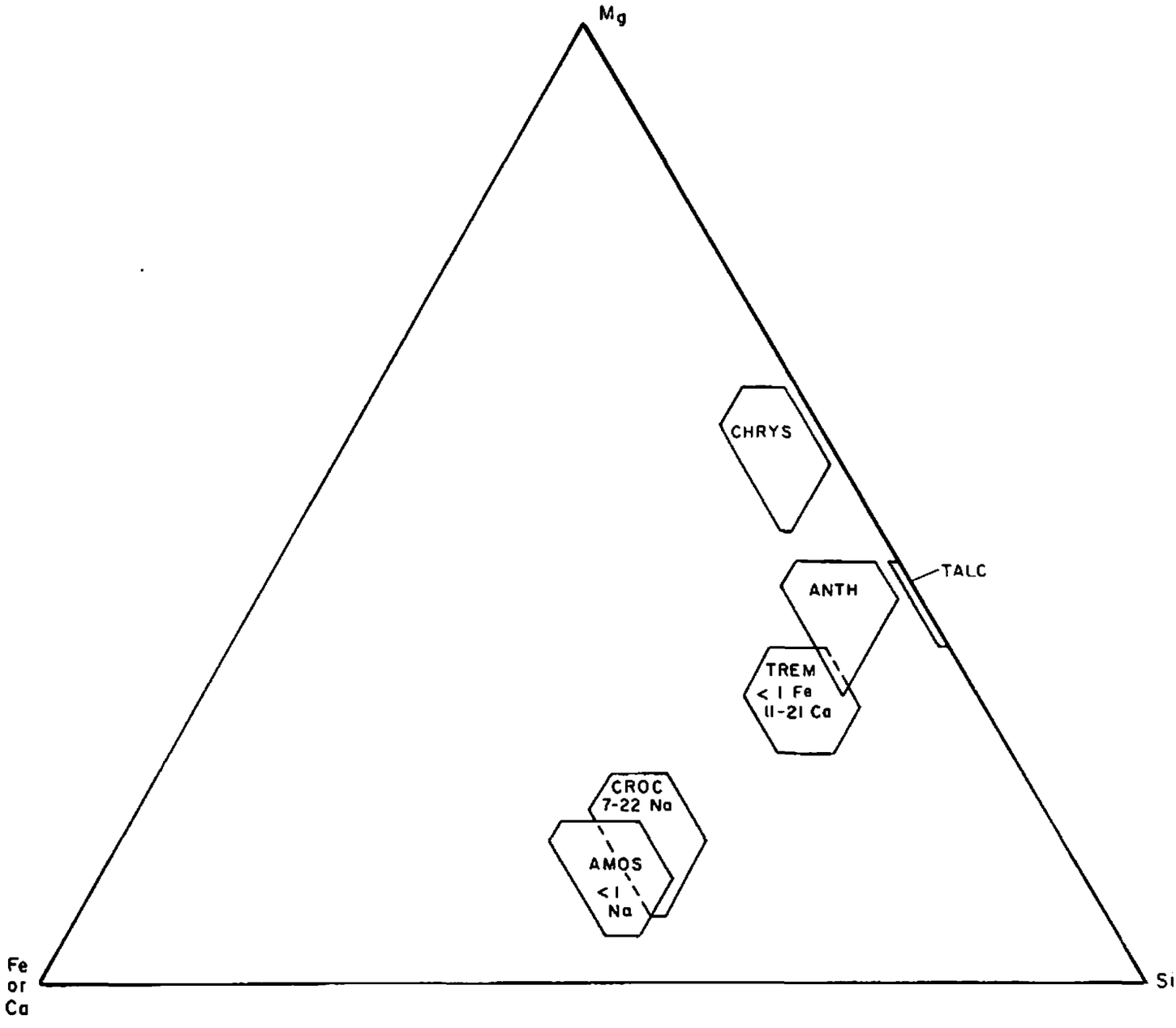


Figure B-2. Pseudo-Ternary Diagram of Na-Mg-Si-Ca-Fe Kα Emission Ratios of U.I.C.C. Standard Asbestos, Tremolite, and Talc.

TABLE B-1

NORMALIZED A-RATIOS FOR DIFFERENT ASBESTOS FIBERS

Limits of Peak Ratios

	Amos.	Crocid.	Chrys.	Anth.	Trem.	Talc
Na	<1	7 - 22	<1	<1	<1	<1
Mg	5 - 17	<4	47 - 62	30 - 44	24 - 35	35 - 44
Si	39 - 52	41- 53	33 - 45	47 - 58	49 - 60	54 - 62
Ca	<4	<5	<7	<5	11 - 21	<2
Fe	37 - 46	32 - 41	1 - 9	3 - 12	<1	<3

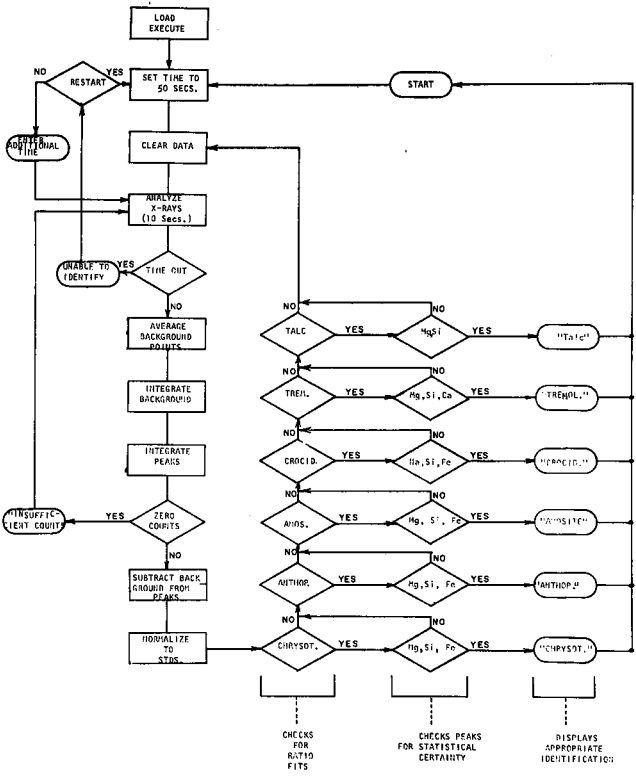
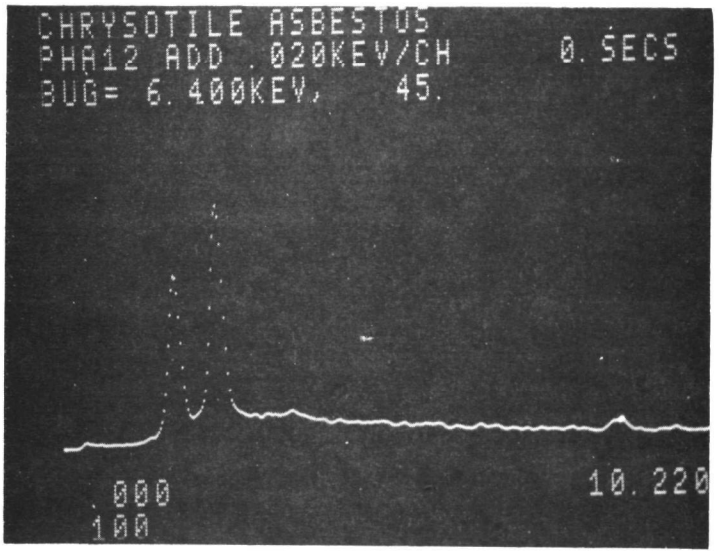


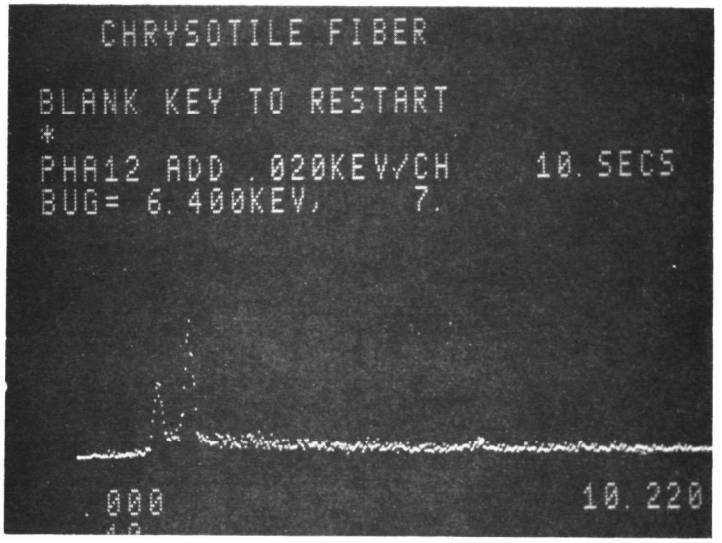
Figure B-3. Schematic Diagram of the Computer Program for the Identification of Asbestos

Route #2 takes the minimum time required to identify the asbestos fiber. During the execution of the program following either route #1 or route #2, the spectrum is displayed on the oscilloscope screen. The operator stops the automatic counting process if the spectrum contains elements that certainly do not belong to any asbestos type.

Examples of fiber identification by the route #1 is shown in Figure B-4(a) and by the route #2 in Figure B-4(b). The analysis was carried out on an asbestos fiber of 0.6μ in diameter. The spectrum was accumulated for 100 secs. in Figure B-4(a) whereas the spectrum in Figure B-4(b) was accumulated only for 10 secs.



(a)



(b)

Figure B-4. Oscilloscope Photographs of Identified Chrysotile Spectra
(a) Data collected for 100 sec. and then identified.
(b) Minimum time required (10 secs.) for the identification of the same fiber. (Total counts are different for (a) and (b)).

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16. ABSTRACT

The methodology that was developed at the Franklin Institute Research Laboratories (FIRL) under the EPA Contract No. 68-02-0544, for the determination of airborne asbestos has been perfected and developed further. Moreover, the newly perfected technique has been applied to point source, near point source and ambient air samples.

This report describes the analytical method which employs a scanning electron microscope equipped with energy dispersive x-ray analysis for the identification and counting of airborne asbestos. The specimens, prepared in a unique manner, are suitable for image analysis and for a possible automated counting system.

Results of the analysis on airborne asbestos are presented, and limitations and advantages of the present techniques are discussed.

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