Environmental Health Perspectives
Vol. 9, pp. 95–109, 1974

Identification and Quantitation of Asbestos in Talc

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The currently used analytical methods for identification, characterization and quantitation of asbestos fiber in consumer talcum products include polarized light microscopy, x-ray diffraction analysis, transmission electron microscopy with selected area electron diffraction and electron microprobe techniques.

Light microscope methods have severe limitations imposed by the ultimate size resolution of the light-optical system. Small particles go unresolved; those marginally resolved may possess optical properties different from those properties cited in the literature; most optical properties, e.g., indices of refraction, are difficult to measure on small particles. In addition to these difficulties, talc fibers often possess optical properties different from those of talc plates, which further confound analysis. Light microscopy is recommended for use only as a preliminary tool on limited, large-sized, samples. Transmission electron microscopy is a good standard technique for visualization of contaminant asbestos fibers. Together with selected area electron diffraction, talc fibers may be easily differentiated from amphibole asbestos fibers on the basis of both morphological and structural characterization. Chrysotile fibers are easily distinguished on this basis as well. The amphibole asbestos minerals require chemical characterization to differentiate among the different fiber types. Probe analysis is mandatory for such fibers. The major drawbacks to electron beam instrumentation for the mineralogical characterization of talcum products are the time and effort required for data acquisition. These techniques do not lend themselves to routine study.

X-ray diffraction analysis, utilizing the step-scan method, offers a relatively rapid, quantitative technique for gross fiber analysis. Based on comparison with standard specimens the fiber content of talcs may be quantitatively determined. It is essential to employ a specimen preparation technique which yields homogeneously dispersed particles. Tremolite may be determined at levels as low as 0.10% by weight, chrysotile 0.25%, and anthophyllite at 2.0% by weight occurrence in talc. The variance of these values depends upon many factors, including the mass absorption coefficient of the fiber types as compared to talc and selected diagnostic reflections and their relative intensities.

Each of the above techniques is described in detail. A method for routine analysis of consumer talcum products is suggested.

Introduction

The mineral talc is a monoclinic, occasionally triclinic, hydrated magnesium sheet silicate with the ideal formula: $Mg_6Si_8O_{20}(OH)_4$. Although a magnesium silicate, it frequently contains small amounts of iron and other trace metals in the structure. It can occur in several crystal habits from plates to fibers. *(1, 2)*. In most talc deposits, plates tend to be far more common than fibers. The term "fibrous talc" implies, mineralogically, talc occurring with a fiber habit (form). As used in the medical literature, fibrous talc is synonymous for talcs containing any fiber, including asbestos.

Geologically, talc occurs in rock masses often coexisting with a large number of other hydrated magnesium silicate mineral species *(3, 4)*. This latter observation is based on mineralogical analysis of naturally occurring talc deposits and laboratory studies of talc crystallization. Frequently, these coexisting mineral phases are asbestos (Table 1).

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Table 1. Talc and its associated asbestos minerals.

	Talc	Tremolite	Anthophyllite	Chrysotile
Empirical formula	$Mg_6Si_8O_{20}(OH)_4$	$Ca_2Mg_5Si_8O_{22}(OH)_2$	$(Mg_5Fe)Si_8O_{22}(OH)_2$	$Mg_6Si_4O_{10}(OH)_8$
Common chemical substitutions	Fe for Mg Al for Si	Fe for Mg Mn for Mg Na for Ca	Fe for Mg Al for Si	Fe for Mg Ni for Mg
Structure and habit	Sheet silicate; plates common; fibers common; forms massive foliated aggregates; intergrowths on submicron scale; many talc fibers observed in platy talcs on submicron scale	Chain silicate; fibers common; often as massive aggregates; forms intergrowths in some talcs on submicron scale; fibers tend to short and stubby; size ranges from visible by eye to sublight microscopic	Chain silicate; fibers common; columnar or fibrous aggregates; forms intergrowths in some talcs; fibers tend to be long and thin; size ranges from visible by eye to sublight microscopic.	Sheet silicate; curved sheets form fibers; often as compacted fibers in pseudo-plates (foliated masses), especially in serpentine rock; forms interplanar (interlaminar) contaminant in talc plates; fibers in talc tend to be sublight microscopic in size
Crystal system	Monoclinic; *triclinic*	Monoclinic	Orthorhombic	Monoclinic *orthorhombic*
Cleavage	*Parallel to plate; (001)* perfect; prism terminations	*Parallel and across* fiber axis; (110) perfect	*Parallel and across* fiber axis; (110) perfect	*Parallel to fiber axis;* (001) for clino variety
Optical properties				
n_x	1.539–1.550	1.581–1.615	1.596–1.654	1.532–1.549
n_z	1.589–1.600 Indices higher for fibers	1.601–1.641	1.625–1.666	1.545–1.556 Indices lower for low-iron chrysotiles
Mass absorption coefficients ($CuK\alpha$ = 1.542) [a]	~1032	~1335	~1072	~717
Occurrence	Generally present as the major mineral in commercial talc	Common contaminant in many talcs (in carbonate rocks)	Often a contaminant in talcs (in carbonate and serpentine rocks)	Occasional contaminant in talcs (especially in serpentine rocks)
Other minerals commonly in talc:	Carbonates (e.g., calcite); micas (e.g., phlogopite); clays (e.g., montmorillonite); chlorite; feldspars (e.g., andesine); quartz; serpentine (e.g., antigorite); spinels (e.g., magnetite)			

[a] All coefficients calculated on the basis of the empirical formula for each.

Talc rocks, those commercially worked for ore material, may form as the result of two major geological processes: hydrothermal alteration of preexisting mafic (Mg–Si–rich) rocks and low-grade hydrothermal metamorphism of siliceous dolomite (silica-bearing, Mg–Ca–rich) rocks. These processes are geologically referred to as steatitization and serpentinization. They involve slightly different original bulk chemical compositions and end mineral products. Both may produce significant amounts of asbestos minerals, chrysotile in serpentinization and amphibole asbestos minerals in steatitization. The metamorphism of siliceous dolomites almost invariably results in the formation of the asbestos mineral tremolite *(2)*.

During geological alteration of rocks, new mineral phases are frequently created from preexisting ones. Most commercial talc deposits are formed as the result of such processes. These deposits may consist of fine-grained, intimate mixtures of minerals, especially talc and asbestos. In addition to the mineral complexities of talc deposits, these ore bodies are often zoned. That is, the mineral composition and assemblage (reflecting changes in bulk

chemistry) varies over short distances, several feet to several inches. This invariably means that the mined talc ore consists of mineral mixtures, since mineral phase separation is difficult if not impossible to achieve during mining. The complexity of mineral deposits may be illustrated by a recent paper on the mineralogy and mineral paragenesis of the New York State talc deposits in the Gouverneur district *(5)*.

Because commercial talc deposits consist of natural admixtures of minerals, a number of mineralogically different materials have been used as commercial talc. The mineral talc is naturally soft and may be physically reduced in size with little mechanical effort because of the weak bonding forces between adjacent unit sheets. The material possesses a number of properties making it useful in hundreds of applications *(6)*. Many of these applications, however, require small particle sizes, high surface areas, and good surface sorption characteristics. Therefore, many of the talc products must be fine-grained, but need not be pure. The result is a requirement for a talclike rock rather than pure talc. Therefore, talc as used in industry does not refer to the mineral species talc, but rather to a property *(7)*. A number of materials have been used as synonyms for talc: asbestine talc, steatite, soapstone, tremolite talc, French talc, fibrous talc. All of these materials may contain quantities of asbestos fiber.

In 1973, there were 38 major talc producers in the United States; talc was mined in 10 states. The geological rock types from which these materials were mined covered the entire spectrum of geological possibilities. For example, in St. Lawrence County, New York State, 30% or less of the materials recovered as "talc" is the true mineral talc *(5,6)*. In this deposit the amphibole asbestos minerals, tremolite and anthophyllite, as well as serpentine (including the mineral chrysotile) occur throughout *(5)*. Therefore, the purity of any commercially available talc in the United States is related to both the nature of the original talc deposit and the extent to which the rock is upgraded to eliminate contaminant minerals. This latter process is often referred to as beneficiation.

Some mineralogical analyses have been made of commercial talcs. One such study showed of the 51 talcs studied, none was 100% talc *(7)*. The asbestos content of these materials ranged from 0 to 87%. Studies of New York State talc deposits and their asbestos contents have been carried out. Mineralogical analyses of these materials indicated all samples were predominantly asbestos *(8)*. In another study, in which 22 available consumer talcum products were examined, it was found that fibrous constituents were present in all of the samples *(9)*.

Biological Consequences of Talc Dust Exposure

Exposure to talc dust, in intensity equivalent to an occupational exposure, has been shown to be associated with a diffuse interstitial lung scarring which has been termed talcosis *(10-16)*. However, even in these studies, some questions were raised as to the specific pathogenic agent in the talc itself. For example, asbestos bodies were frequently observed in the lung tissues of individuals who died of talcosis *(11, 13, 17)*; clinical and radiological similarities existed between the disease asbestosis and talcosis *(12, 13, 18)*; and "fibrous" talc appeared to be more pathogenic than "platy" talc *(19)*. Several investigators using the individual mineral components of fibrous talc (made up of mixtures of tremolite asbestos and platy talc) observed different biological responses to the components in animals. They observed that the asbestos component induced a greater fibrogenic response in the animals *(20)*. One investigator has also reported an increased incidence of neoplasia amongst talc miners and millers exposed to asbestos-containing talc dusts *(21)*. Lung tissues from workmen exposed to talc dust have been analyzed in our laboratory. Both amphibole and chrysotile asbestos fibers were observed in these tissues by electron microscopy *(22)*.

Several recent studies, involving experimental animals and observations on human materials, have shown that exposure to asbestos and talc may be associated with tumors of the ovary and cervix *(23, 24)*. In addition, the use of such talcum products as lubricants, drying agents, and excipients in a number of food and food packaging products may pose a hazard in terms of an increased neoplastic risk in the gastrointestinal system through ingestion *(25)*.

Asbestos Content of Consumer Talcum Products

Because the mining of talc almost invariably includes the mining of asbestos as well, this natural asbestos contaminant in talc may be carried over into the consumer product. Since asbestos has been suspected as the pathogenic agent in talc workmen, low levels of asbestos in consumer talcs have been the focus of many recent studies. These data and observations lead to an important public health question: is asbestos present in consumer talcs, and, if present, which fiber type and in what concentrations?

Instrumental Methods of Identification of Asbestos in Talc

There are a number of standard mineralogical techniques which may be used for identification and quantitation of asbestos fibers in talc. These include light optical methods, electron optical techniques, and x-ray diffraction techniques.

Light Microscopy

The most widely used and inexpensive instrumental technique for the analysis of mineralogical specimens is optical microscopy. A microscope which employs polarized light optics has been a standard technique for identification of minerals for the past century. When used with immersion oils, not only may phases be identified, but the bulk chemistries of the phases may be determined with remarkable accuracy. The field of optical mineralogy has been properly termed optical crystallography, in that the information obtained may be elegant and quantitative. The analyses of the light visible mineral phases within talcs may be made with this method.

We have examined numerous talcs by means of light microscopy. Powders from different sources (ca. 0.5 mg) both natural and man-made, were placed on precleaned glass slides and immersed in mounting n_D = 1.500, 1.550, 1.600. Several splits from each sample were examined for their optical properties. The microscope employed in all cases was equipped with bright field illumination and polarized light optics. An overall view of various properties of the material was obtained at this level of investigation: relative relief, birefringence, gross morphology, and extinction angles of fibers were observed or measured. The relative purity of each sample was observed, and the general size distributions of the mineral phases were determined (Fig. 1). The identified mineral phases tended to be coarse-grained. However, when the talc samples are fine-grained, and contain talc fibers, some problems are encountered. Specifically, the normal birefringence characteristics may not be present (for the fibers); indices of refraction are difficult to measure (differentiation of internal reflectance and Becke line when viewed with central illumination); talc fibers have higher indices of refraction than talc plates, and may be confused with amphiboles (especially small fibers of tremolite); fibers are difficult to routinely resolve from talc plates when the latter are oriented on edge (especially at high magnifications); many fibers are too small to see by light microscopy.

In summary, light microscopy, employing polarized light optics, has severe limitations for critical analysis of talc specimens for asbestos fibers. The inherent limitation of optical microscopic resolution may so restrict the analysis that large numbers of small fibers may go undetected. It is a paradox, however, that optical microscopy is well suited for determining the presence of other contaminants in talc, e.g., the carbonate minerals and other silicate phases (quartz, feldspar, micas, etc.). Also, it is remarkably sensitive for the determination of trace mineral phases, if they are present in sizes resolvable by light optical systems. This method, although limited, is recommend as a preliminary tool of investigation *(26)*.

X-Ray Diffraction

One of the standard mineralogical techniques used in the analysis of solid crystalline phases is x-ray powder diffractometry. With this method, those phases with crystallite sizes greater than 2000 Å may be subjected to x-ray bombardment and made to reflect from their atomic planes an x-ray spectrum characteristic of their interatomic distances and chemical makeup. This, in effect, is a structural "fingerprint" and serves to identify, in most cases uniquely, the nature of the phases present in the sample. Additional information may be obtained by x-ray powder dif-

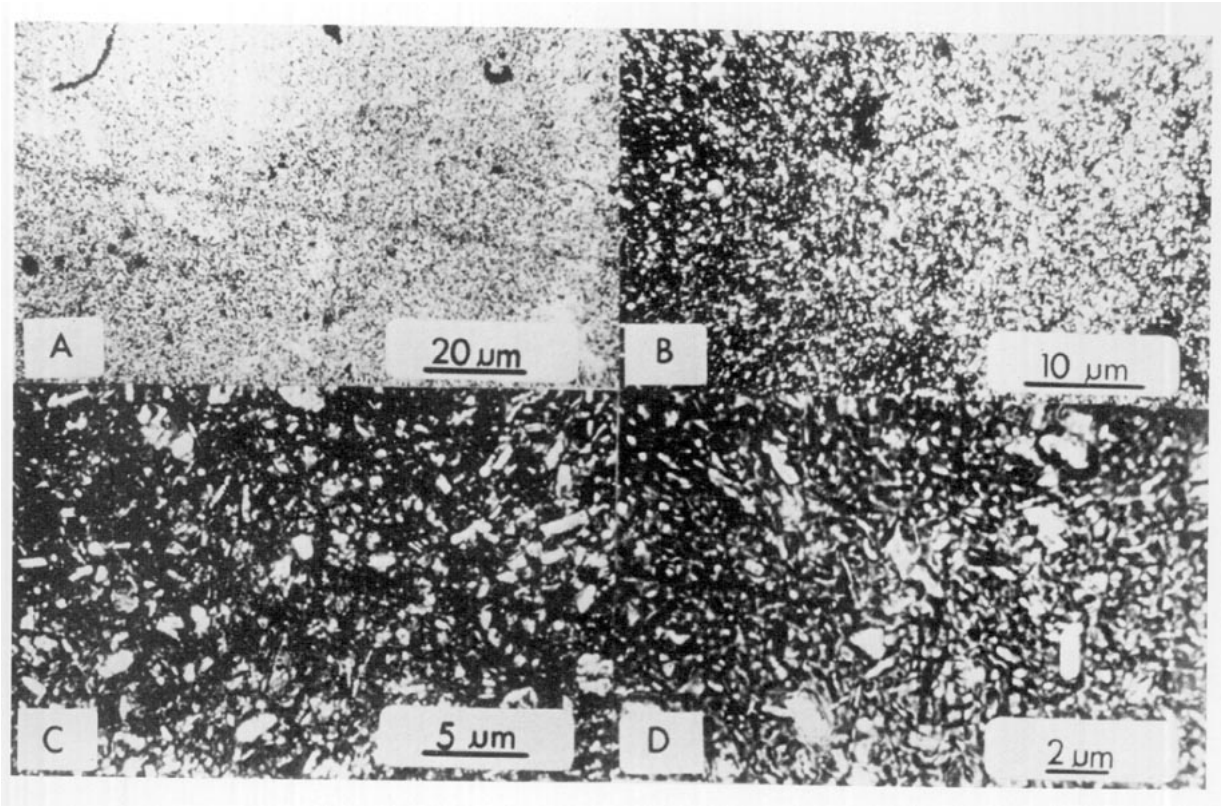

FIGURE 1. Photomicrographs of a talc sample from New York State: *(A)* talc in plane polarized light) shows "granularity" and small size of pulverized sample; *(B–D)* consecutive photos of pulverized samples between crossed polars) show the presence of prismatic crystals. Several on-edge plates may be confused with fibers. Some of the larger crystals, on the basis of their optical properties, were identified as tremolite.

fractometry, including quantitation of the individual phases present in a crystalline matrix and their average particle size. *(27)*.

X-ray diffraction is considered to be a more sophisticated tool than the polarizing microscope. Although less sensitive than the electron microscope for the detection of trace quantities of materials present in a matrix, this instrumental technique is commonly used for the analysis of talcs. The difficulties and nuances involved in the x-ray analysis of talc for trace asbestos fiber are many. We describe these below and outline what we consider to be an acceptable analytical technique. This technique consists of the preparation of talc standards (talc matrices admixed with known quantities of fiber), the selection of characteristic x-ray reflections to be scanned, sample preparation to insure homogeneity and reproducibility, and instrumental technique.

Preparation of Standard Dilution of Asbestos Minerals in Talc for the Purpose of Quantitative X-Ray Analysis

The identification and quantitation of asbestos fiber in talc by x-ray diffraction techniques may be achieved by comparison of known dilutions (fiber type and quantity) of asbestos in a talc matrix with unknowns. The preparation of standard (known) dilutions of asbestos minerals in talc for quantitative analysis requires: (1) a talc matrix completely free of contaminating asbestos minerals; (2) pure asbestos fiber as the sought contaminant phase; (3) a preparation method for insuring homogeneity and reproducibility of the standard dilution material, i.e., identical aggregate

geometry; (4) selection of diagnostic x-ray reflections with no superimposed interferences.

Selection of the Talc Matrix Mineral: Various types of talc were tested for possible use as pure reference material, including pharmaceutical, excipient, and additive talcs (acknowledged high purity grade). Screening of talcs was made by x-ray powder diffraction analysis. For each of the talc samples, a continuous scan from 3 to 60°, at the rate of 1° 2θ/min, was made in order to rapidly identity the major mineral phases, particularly asbestos minerals. If no asbestos phases were detected, the material was re-examined in the step-scan mode with a step-scanning rate of 0.02° 2θ in the diagnostic asbestos reflection regions (Table 2). If no asbestos was detected by this method, the absence of asbestos was further verified by transmission electron microscopy. Typically, specimens were scanned at 42,000 direct screen magnification to insure the detection of chrysotile fibrils. By using these screening techniques, a talc which was apparently free of asbestos was selected as the matrix material.

During the course of this screening, it was found that many talcs contain varying amounts of the hydrous iron–magnesium silicate mineral, chlorite. The presence of this mineral interferes with the detection of small amounts of chrysotile. The presence of chlorite is indicated by strong x-ray basal reflections [14.2 Å (001); 7.1 Å (002)]. This latter reflection occurs in the same general area as does the (002) reflection of chrysotile (7.3 Å). Therefore, a higher-order reflection was chosen for the purpose of resolving these mineral phases.

Selection of the Asbestos Fibers: In addition to selecting a talc of high purity, it was necessary to obtain asbestos mineral samples which were themselves free of contamination. This would ensure a high quality talc-asbestos dilution. The reference asbestos minerals of the International Union Against Cancer (UICC) were found to be generally suitable for this purpose *(28)*. The reference anthophyllite and tremolite were micropulverized and analyzed for purity by step-scanning x-ray analysis and by transmission electron microscopy in accordance with the procedures previously described for talc. The fibers were found to be free of interfering contaminants. The chrysotile specimen used in making the talc-chrysotile dilutions was a triple air jet milled sample from the Jeffrey Mine, Quebec (provided chrysotile, Johns-Manville Corp.)

Sample Preparation: Among the problems of specimen handling for diffractometer analysis are the effects of particle size, preferred orientation and surface flatness. In the preparation of the asbestos-talc standards, particular care was taken to ensure that the samples had a uniform size distribution and an effective crystallite dimension on the order of five microns or less. This was done in order to reduce the mean deviation of reflection intensities to a value of about 1% *(29)*.

The reproducibility of reflection intensities is strongly influenced by the degree of cleavage of crystalline powders. Talc, which possesses perfect cleavage parallel to its basal plate (Fig. 2*A*), will tend preferentially to orientate parallel to this direction when the sample is packed into the holder (Fig. 2*C*). This will occur even when crystallite size has been greatly reduced by grinding *(27, 29)*. In addition to plate orientation, one can easily envisage how admixed fibers can orient with their fiber axis parallel to the plates (Figs. 2*B*, 2*D*).

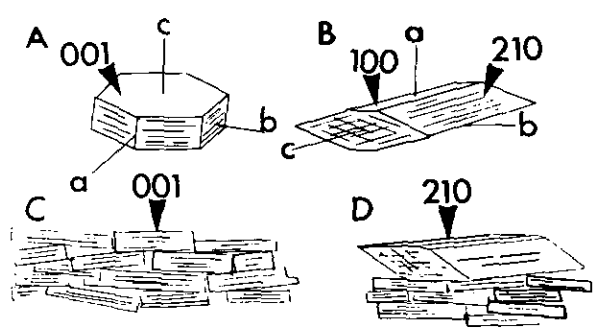

FIGURE 2. Preferred orientation *(A)* talc plate (001) and *(B)* anthophyllite fiber (210); *(C)* prepared talcs tend to align themselves parallel to their basal plates, the (001) cleavage; *(D)* anthophyllite fibers in talc matrices tend to align themselves with their (210) surfaces parallel to talc (001) cleavages. Crystallographic axes marked *a*, *b*, *c*. *C* and *D* looking parallel to talc plates.

A number of techniques have been developed for reducing preferred orientation effects, including binder and slurry mounted methods, sifting and backloading dry powders, and

various other techniques *(27–31)*. Several such preparation methods were tested for use in the present study. None were found to give satisfactory reproducibility, as indicated by the variation (deviation) of reflection intensity of duplicate dilution standards which had been uniformly prepared and mounted. The lack of success in this regard was taken to indicate that, in mixtures of minerals with platy or fibrous habit, a statistically random distribution of orientations is extremely difficult, if not impossible, to achieve.

Accordingly, a technique was developed which was intended to obtain a high degree of sensitivity for substances present in minute quantities, and more important, which had a greater degree of reproducibility of reflection intensities. Binary systems of chrysotile, tremolite, and anthophyllite in talc were prepared at varying levels of dilution on a weight per weight basis. The following per cent concentrations of fibers in talc were initially prepared for each binary system: 5.0, 4.0, 2.0, 1.0, 0.5, 0.25, 0.20, 0.10%. The standard weight of the total sample was 50 mg.

The weighed talc-asbestos mixtures were prepared in 10 ml of filtered water (to avoid any possible contamination) utilizing a surfactant and ultrasonic energy to disperse the phases homogeneously. This slurry was poured immediately into a 30-cc hypodermic syringe and filtered through a 37-mm diameter, 0.22 μm effective pore size membrane filter. [A standard filter holder for attachment to a hypodermic syringe is available (Fig. 3) from the Millipore Co.] In the course of filtering, the syringe is held in a horizontal position and is frequently rotated and shaken. This action helps to prevent size and density separation of the suspended particles. The residue forms a cake of uniform thickness of about 0.5 mm on the membrane filter, and the resulting surface of the filter cake is flat. The cake is allowed to dry and then is glued to a glass microscope slide for x-ray powder diffraction analysis. X-ray analysis of the dried cake on repeated preparations shows that the mineral phases are homogeneously distributed throughout. This technique has the advantage of uniformly preparing, mounting, and measuring the talc-asbestos dilutions under identical conditions. The reproducibility and sensitivity of the technique is demonstrated by a comparison of the measured areas of index reflections for a number of samples (Table 3).

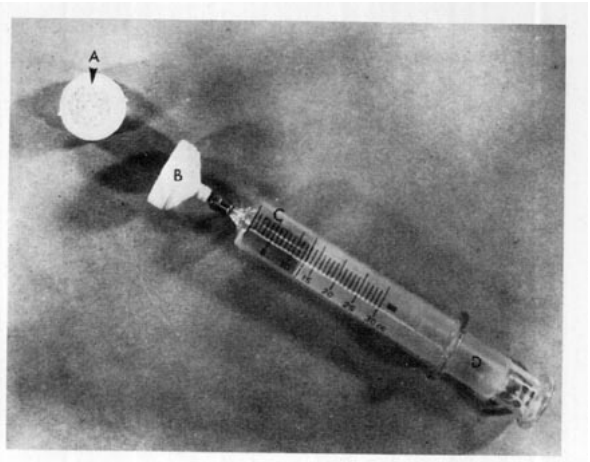

FIGURE 3. Device used to prepare filter cakes of standard dilutions of asbestos fibers in talc: *(A)* holder which accommodates the membrane filter; *(B)* holder and gasket attachment to syringe; *(C)* syringe; *(D)* plunger.

Selection of X-Ray Reflections: In order to detect the weak reflections of dilution components it was necessary to scan in a stepwise manner across a preselected area of the x-ray profile. Because of structural similarities in the minerals under examination, there was much "overlapping" or interference in many reflections (Table 2; Fig. 4). The similarities in crystal structure and the consequent overlapping and interference of the x-ray diffraction reflections of talc, chrysotile, anthophyllite, and tremolite have been mentioned. This condition made it necessary to select a reflection or set of reflections for each mineral component which could be used unambiguously as an index or indices of

Table 2. Diagnostic reflections of asbestos minerals used in standard dilutions.

Mineral	d, Å	hkl	I/I_1	2θ	Scan 2θ
Anthophyllite	8.26	(210)	55	10.65°	10.1–11.1°
Chrysotile	3.66	(004)	80	24.31°	23.5–27.5°
Tremolite	8.38	(110)	100	10.55°	10.0–11.1°

[a] For each characteristic interplanar spacing given, the Miller Index, relative intensity, Bragg reflection angle, and step-scan interval are included.

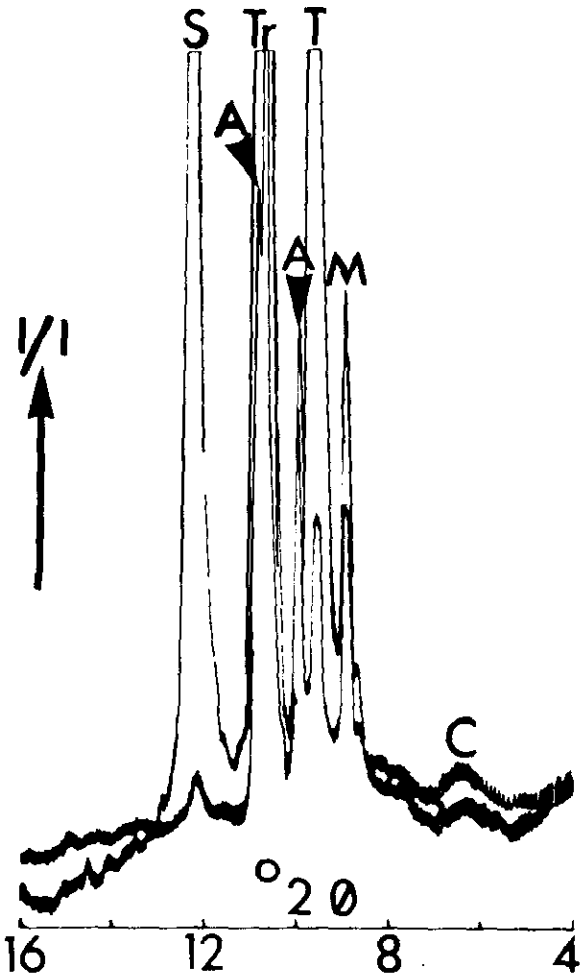

FIGURE 4. X-ray diffraction tracings of fibrous talc samples from New York State, in the 8–16° 2θ region of reflections: *(S)* serpentine (includes the minerals *chrysotile, lizardite, antigorite*); *(A)* anthophyllite; *(Tr)* tremolite; *(T)* talc; *(M)* mica (phlogopite); *(C)* chlorite. Note that the anthophyllite peak at 8.9 Å (020) is often masked by a strong talc peak at 9.3 Å (002); the anthophyllite 8.26 Å (210) peak is often masked by the tremolite 8.38 Å (110) peak. The tremolite peak in this figure masked almost 5% anthophyllite. I/I_1= intensity.

the amount of that mineral present in a mixture. This was done by a comparison of the ASTM X-Ray Powder Data File for each of the minerals and by indexing the diffractograms of each of the UICC asbestos minerals and the reference talc. When this data was assembled and compared, it was possible to select reflections unique in *d* spacing and strong enough in intensity to be used as quantitative indices

Table 3. Replicate measurements of areas of diagnostic peaks of chrysotile in chrysotile–talc dilutions.[a]

Specimen	Peak areas, in.[2] A	Peak areas, in.[2] B
99.5% Talc–0.5% chrysotile	2.20	2.19
	2.17	2.17
	2.18	2.19
Avg.	2.18	2.18
99.75% Talc–0.25% chrysotile	0.84	0.88
	0.88	0.88
	0.84	0.88
Avg.	0.84	0.88
99.9% Talc–0.10 chrysotile	Not detected	Not detected

[a] Measured with compensating polar planimeter; peaks plotted on same scale on step-scan runs under constant settings (2×10^3 cps; 0.02° 2θ; 45 kV/20 mA).

(Table 2). In this way, certain diagnostic or index reflections for each of the dilution components were selected and these angular intervals were x-ray step-scanned at 0.01 and 0.02° 2θ. A digital printout of elapsed time in a fixed-count determination was used to prepare precise positions and profiles of the diagnostic reflections. In the fixed count mode, the diffractometer scans equal angular intervals (0.02° 2θ), accumulating fixed counts at each point with equal accuracy. Although weak reflections require longer times than higher intensity reflections, all points are determined with equal precision. In this method the statistical accuracy of any measured count depends only on the total number of counts recorded. The number of counts was calculated by taking the reciprocal of counting times. The counting rates were selected to give a uniform percentage probable error of about 2.0%. When the number of counts is plotted as a function of 2θ a profile of the diagnostic reflection is found (Fig. 5). The area above background, determined with a compensating polar planimeter, is taken to be proportional to the reflection intensity.

Factors Affecting the Limits of Detectability of Substances by X-Ray Diffraction

In a mixture of powders, the resulting x-ray diffraction pattern consists of the superposition

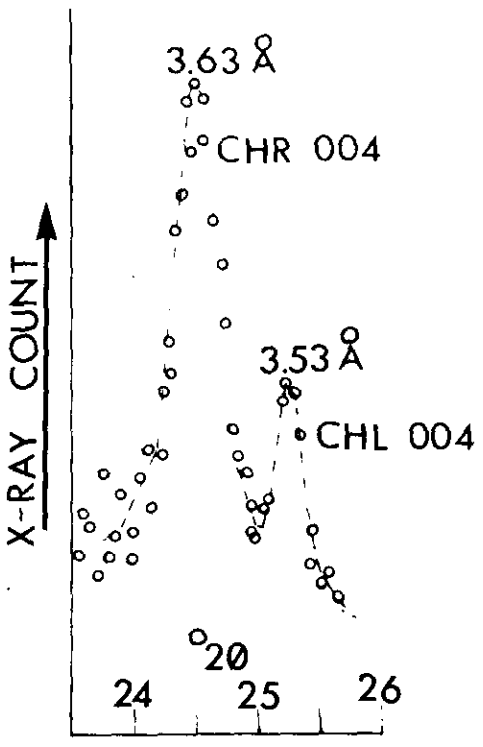

FIGURE 5. Step-scan profile obtained on a standard dilution of 1% chrysotile in a 99% talc matrix. Note the contamination of talc with a trace of chlorite (3.53 Å reflection). Step-scan obtained at 0.05° 2θ for 2000 counts.

of diffraction patterns of the constituent compounds (Fig. 4). The intensity of each compound's pattern is proportional to, but not necessarily a linear function of, its concentration *(29)*. Aside from instrumental factors (e.g., change in x-ray output from target tube) which may influence the profiles of diffraction maxima, there are a number of other factors to be considered. These are related primarily to the material, including sample homogeneity, chemical makeup, particle size, preferred orientation, sample thickness and flatness, and absorption characteristics.

General Factors: The components of a mixture and their relative amounts may be determined by the intensity measurements of the diffraction patterns, if all these factors are considered. However, it is necessary that certain conditions be satisfied. The component sought must be homogeneously mixed in its matrix and consist of randomly oriented small particles to insure that a large proportion of them will satisfy the Bragg geometry for reflection. It has been shown that with materials of intermediate atomic number (Z=12–30), particle sizes in the range of 2–10 μm will give a reproducibility of greater than 1% *(27, 29)*. A uniformly small particle size will also help to minimize particle orientation and microabsorption effects. Comparative intensity measurements also require that the porosity of the specimen is constant and that the specimen is thick enough to diffract x-rays with maximum intensity.

The powdered materials used in this study and the filter-mounting technique of specimen preparation were selected in order to fulfill these basic requirements of quantitative x-ray diffraction analysis.

Special Factors: An important factor which affects the ability to detect small amounts of material by x-ray diffraction analysis is specimen x-ray absorption. This occurs when two substances with different mass absorption coefficients are mixed. The mass absorption coefficient (μ/ρ) is a measure of the fraction of the energy in the incident x-ray beam absorbed when a beam of unit cross section traverses a unit mass of material. It is useful because it is characteristic of the chemical elements in the absorbing material and is essentially independent of their chemical or physical aggregate state. It is a function only of the wavelength of the absorbed radiation and the atomic number of the absorbing element. The sensitivity of detection of a component may vary considerably, depending on μ/ρ for the component relative to that of the matrix. The mass absorption coefficients of talc, chrysotile, anthophyllite, and tremolite for the wavelength of copper x-radiation (1.542 Å) are given in Table 1. Chrysotile has the lowest μ/ρ of the four minerals, about 717, which is about 7/10 that of talc, 1032. Thus, the sensitivity of detection of chrysotile in talc is greater than that of the other two asbestos minerals, neglecting the effects of such variables as particle size and degree of crystallinity which may have equal or greater influences on the sensitivity of detection.

The precision (reproducibility) of intensity measurements obtained in x-ray diffraction analysis can be optimized by a suitable counting strategy. If an accumulated count of

$4\times10^5-5\times10^5$ is obtained, the precision of the relative intensity measurement due to counting statistics alone is $N^{1/2}$. The determination is also related to specimen preparation reproducibility. With specimens having an average particle size of 1–2μm, the range in intensity measurements is from 0.1 to 0.5%. The overall precision of quantitative x-ray analysis will probably lie in the range of 0.5 to 1.0% *(27)*.

The accuracy of x-ray analysis depends in large measure on the degree of preferred orientation of particles in the sample. The materials used in this study, sheet silicates and fibers, can be expected to have a high degree of preferred orientation. This inescapable physical limitation is the main factor in controlling the level of accuracy.

Standard Dilutions

Chrysotile in Talc: The presence of chlorite in the talc standard used in preparation of chrysotile-talc dilutions may preclude the use of the (002) reflection of chrysotile as a diagnostic reflection. The chlorite reflection at about 12.6° 2θ overlaps and masks the latter reflection. When the intensities of these two reflections are about the same, the peaks can be resolved with a step-scanning rate of 0.01° per degree 2θ. Except for this special condition, the peak-to-background ratio of the chrysotile (002) does not permit it to be measured with precision. If chrysotile and chlorite are both present in the sample, but chrysotile predominates, then the (002) peak of chrysotile can be used as an indicator of the relative amount of chrysotile present.

Another mineral which may interfere with the detection or quantitation of chrysotile is kaolinite. This mineral is the most common member of the kaolin group of hydrous aluminum silicate clay minerals. Although kaolinite has not been reported in talc or serpentine rock, particularly because the modes of formation and geochemical environment are quite dissimilar, this fact does not preclude the presence of kaolinite in industrial or consumer talcum by admixing. The mechanical and physical properties of kaolinite would be in harmony with those of talc. In fact, it has been identified as a component of some cosmetic talcum products. Because there are close structural similarities between chrysotile and kaolinite, their x-ray diffraction patterns are similar in many respects. The first-order basal reflection of kaolinite at 7.15 Å may thus overlap or mask the chrysotile (002) reflection at 7.24 Å. Depending on the relative amounts of these two minerals present, chrysotile may be neither detectable nor quantitatively determined with precision by use of the 7.24 Å reflection. It has been found that the 3.63 Å (004) reflection of chrysotile at 24.3° 2θ is more useful than the (002) reflection for detecting the dilutions of that mineral in talc matrices. This chrysotile reflection is better resolved from reflections of associated minerals, particularly from the 3.53 Å (004) reflection of chlorite at 25.1° 2θ. The peak-to-background ratio of the chrysotile (004) line, which has an intensity of about 8/10 of the (002) reflection, is thus used to determine the minimum detectable amount of chrysotile in talc standard samples. The samples are step-scanned at a rate of 0.02 per degree 2θ from an angle of 23.0 to 27.0° 2θ in order to achieve maximum peak and minimum background intensities in the same region of the spectrum. A minimum of 0.25% by weight of chrysotile in standard talc has been detected consistently. Chrysotile at lower levels of dilution cannot be detected.

Tremolite in Talc: A few specimens, labeled as tremolite, were prepared for x-ray powder diffraction analysis and continuously scanned from 3° to 60° 2θ at a rate of 1°/min. When these spectra were indexed, it was found that only one tremolite sample was free of contaminants. That is, the positions and relative intensities of all of its reflections compared exactly with the data given for an ASTM reference tremolite (American Society for Testing Materials standard powder diffraction file, #13-437). As indicated in Table 2, the 8.38 Å reflection of tremolite, which has a relative intensity of 100, was selected as the diagnostic reflection for the tremolite-talc dilution series. The 3.12 Å tremolite reflection, which also has a relative intensity of 100, was not used because it overlaps with the 3.12 Å reflection of talc. Dilution levels from 99.0% talc–1.0% tremolite through 99.95% talc–0.05% tremolite were prepared and step-scanned under constant instrumental conditions. The diagnostic reflection of tremolite was detected at all levels of dilution up to, and

including, the 99.9% talc–0.1% tremolite level. Less than 0.1% tremolite was not detected above background. Replicate dilution mixtures at the 0.1% and 0.05% tremolite levels were prepared and step-scanned to confirm these observations. The results were consistent and reproducible.

Anthophyllite in Talc: The anthophyllite used in preparing dilution mixtures of fiber in talc was from the UICC standard asbestos reference mineral collection, previously characterized *(28)*. A specimen of this material was continuously scanned by x-ray diffraction from 3° to 70° 2θ at 1°/min. When the peaks on the diffraction pattern were assigned d spacings, it was found that the anthophyllite was contaminated by talc, chlorite, and phlogopite. However, these intrinsic contaminants do not preclude use of the material as a dilution standard. A more serious limiting condition pertains to the similarities between the diffraction patterns of "pure" anthophyllite and talc (see Fig. 4). Among the most intense reflections of anthophyllite are the 3.05 Å (obscured by the superposition of the talc 3.12 Å, I/I_1 = 40); the 4.50 Å (obscured by the 4.53 Å, I/I_1 = 12 and the 4.56 Å, I/I_1 = 45 both of talc) and the 3.23 Å (obscured by the 3.33 Å mica contaminant of talc, I/I_1 = 100). Since the peak-to-background ratio of the most intense reflections of the powder pattern is the most important single factor in determining the minimum detectable amount of a substance, the interference between similarly spaced strong reflections of talc and anthophyllite significantly diminishes the possibility of detecting minute amounts of anthophyllite asbestos in talc. The 8.26 Å reflection of anthophyllite, with the relative intensity of 55, was selected as the most useful diagnostic reflection for the anthophyllite—talc dilution series. Dilution mixtures ranging from 95.0% talc–5.0% anthophyllite through 99.5% talc–0.5% anthophyllite were prepared. When step-scanned under constant conditions, anthophyllite was not detected at concentrations below 2.0% in repeated samples. With continuous scanning, anthophyllite was not detected at or below the 4.0% dilution level when the 8.26 Å reflection was used as an index (see Fig. 4).

Preparation and Analysis of Chrysotile–Talc Dilution Samples by Electron Microscopy

Aliquot portions of various chrysotile–talc dilution levels which had been analyzed by x-ray diffraction were prepared for transmission electron microscopy by a "rubout" procedure *(32)*. Standard weights (0.01 mg) of each of the dilution standards are dispersed in a nitrocellulose film and mounted on Formvar-coated electron microscope grids. The dispersal is accomplished by mounting the sample in a drop of nitrocellulose–amyl acetate solution on a microscope slide and grinding it with the edge of a clean watch glass to reduce the sample into submicron-sized particles. This procedure breaks apart the fiber bundles of chrysotile, already greatly comminuted by triple air jet-milling and sonification, into unit fibrils or into small fiber bundles. At the same time, large aggregates of talc particles are reduced in size and dispersed to allow all asbestos fibers to be seen and counted.

After dispersing the sample, a drop of amyl acetate is placed on a second clean side. The two slides are placed in contact and the ground residue and nitrocellulose solution is further dispersed. The residue is typically spread over the slide for a length of 5 cm. The two slides are then pulled apart, leaving two films with the powder uniformly distributed in them. The films quickly dry. The edges of the slide with attached film are scraped with a scalpel blade; then by dipping the slide into water, the film can be floated onto the surface of the water. Electron microscope grids are placed on top of segments of the film and covered with a strip of filter paper. The grid is retrieved by lifting the filter paper out of the water. After drying, the grids can be picked off the filter paper and mounted in the electron microscope for scanning.

Typically, three grids are prepared for each dilution level of chrysotile–talc and six squares of each grid are scanned at about 10,000× magnification to obtain a number of representative fields for study. A large number of fields are photographed and enlarged prints are then made. From the photographic enlargements the number of long unit fibrils per field are counted

and the results are tabulated. When multiple fibril bundles are encountered, the number of unit fibrils in the bundles is estimated by counting the number of visible central capillaries and by judging the optical density of the fiber bundle. The electron microscopic fiber counts show a fairly good correlation with levels of chrysotile dilution. For example, the average number of chrysotile fibrils per field, scanned at 7100× magnification was counted at the following dilution levels: 5% chrysotile–95% talc, 92 fibrils per field ± 10%; 1% chrysotile–99% talc 22 fibrils per field ± 10%; 0.5% chrysotile–99.5% talc 8 fibrils per field ± 10%; 0.25% chrysotile–99.75% talc 6 fibrils per field ± 10%. It is evident that there are considerable numbers of chrysotile fibers present in talc even at very low dilution levels. By using the fiber count data for the various dilution levels it is possible to calculate the number of fibrils contained in a unit weight of sample.

The area of the nitrocellulose film is known, as is the magnification factor. From these and a measurement of the area of the photographs, a conversion factor is calculated. Allowing for an error as large as one magnitude the calculations show that there are $2N \times 10^8$ fibrils/mg of sample, the value N being the average number of fibrils per field. Thus, in a 1% dilution of chrysotile in talc, there would be about 4×10^9 fibrils/mg. At the lowest level of detection of chrysotile by x-ray diffraction, i.e., 0.25%, there would be about a 10^9 fibrils/mg.

It is clear that in issuing regulations specifying the absence or absolute limits of asbestos in talc, close attention must be paid to the capabilities of the analytical technique used for determining whether, or how much, asbestos is present. X-ray diffraction can provide positive answers to these questions only at the 0.25% level for chrysotile which has been shown to be a crude and inaccurate measure of the potential contamination and possible hazard involved. In addition, as much as 2.0% of anthophyllite in talc may not be detected by this method. On the other hand, electron microscopic analysis can be a sensitive tool for detecting extremely minute amounts of chrysotile and other asbestos minerals in talc.

Application of Transmission Electron Microscopy Methods (Including Selected Area Electron Diffraction) in Detection of Asbestos in Consumer Talcs

Consumer talcs have been prepared and examined by means of transmission electron microscopy. Representative sample aliquots were sonically dispersed in filtered water and pipetted onto Formvar–carbon 200-mesh copper electron microscope grids. After these preparations were dry they were again carbon coated to insure a thermally and electrically stable preparation. Samples were scanned at magnification in excess of 20,000 and examined for their fiber content. A representative platy and fibrous talc is shown in Figure 6. The asbestos content of talc may be directly estimated utilizing transmission electron microscopy. Each fiber type may be identified. For example, chrysotile asbestos is morphologically unique. Its internal capillary, fibril dimensions, susceptibility to electron beam damage, and unique electron diffraction pattern, all make the fiber easily recognizable *(33)*.

Fibers which are electron-dense and which possess the morphological characteristics of amphiboles, were examined by selected area electron diffraction for confirmation. We have done this on many particles in numerous samples and are able to differentiate fibrous talc from fibers of asbestos quite easily (Fig. 7) *(33)*. However, this method is not sufficiently sensitive to distinguish among the amphiboles. Here, microchemical characterization is necessary *(34)*. Electron microscopy is an excellent qualitative tool for determining the presence or absence of asbestos fibers in talc.

Microchemical Analysis by Electron Microprobe Analysis

By means of microchemical analysis, it is possible to differentiate among the amphibole asbestos fiber types. We have examined talc samples obtained from a mill in which anthophyllite and tremolite fibers occurred within the talc. These samples were examined on an ARL electron microprobe analyzer equipped with crystal spectometers. The instru-

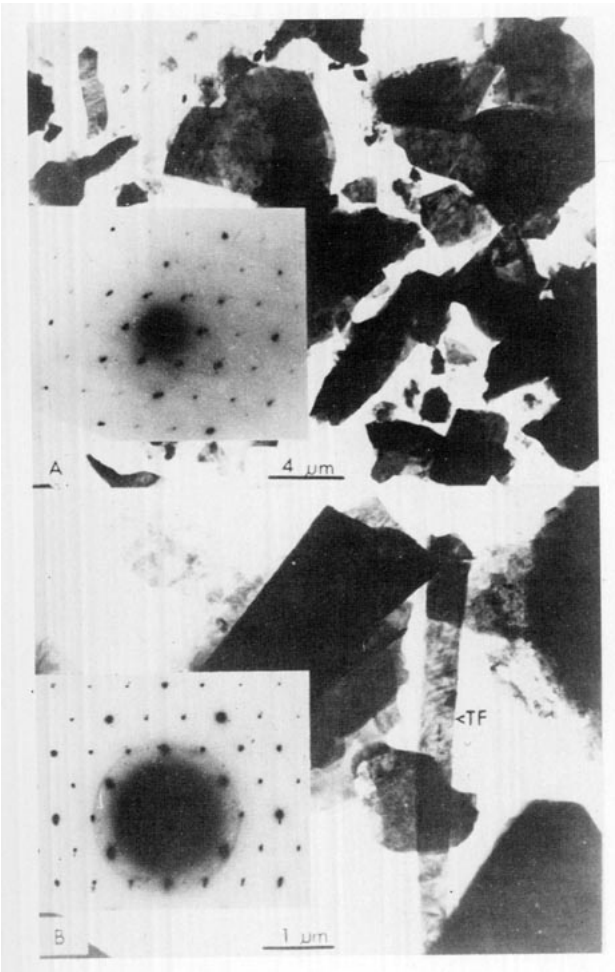

FIGURE 6. Transmission electron micrographs of *(A)* a "platy" talc and *(B)* a "fibrous" talc. The platy talcs tend to be made up of a mixture of well-formed polygonal and "ragged" edged sheets. Fibers visible are talc fibers. The fibers in *(B)* are made up of tremolite, anthophyllite, and talc. Fibrous components and non-fibrous objects are common. Magnification for *(A)* and *(B)*, as marked.

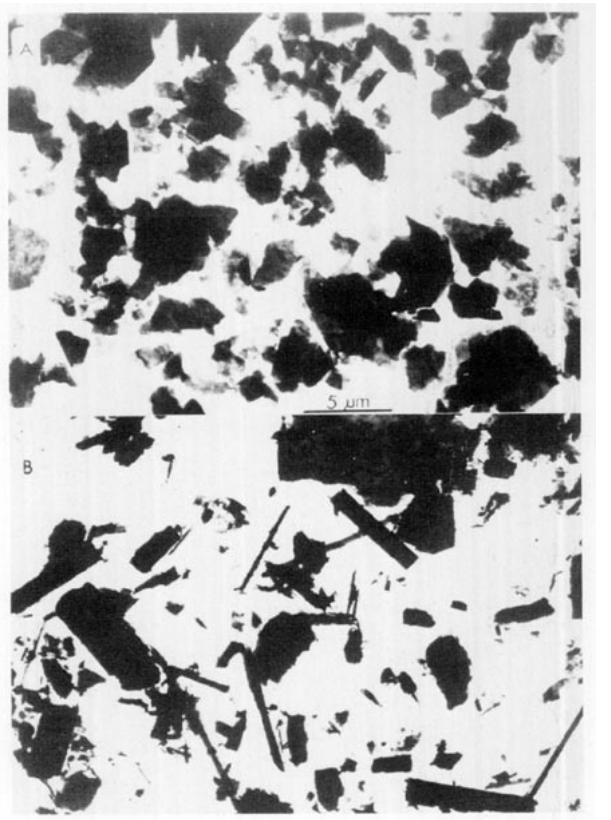

FIGURE 7. Selected area electron diffraction patterns obtained on *(A)* a talc plate and (marked TF in *B*) a talc fiber. Talc fibers are not confused with amphiboles. They are often curvilinear, possess irregular diffraction contrast contours as do talc plates, tend towards prismatic truncations, and have identical diffraction patterns as compared with plates.

ment and technique have been described elsewhere *(30, 31)*.

Tremolite may be easily differentiated from fibrous talc on the basis of its high calcium content and Si-Mg ratio, but anthophyllite, depending on its iron content, may not be (Fig. 8). These latter amphiboles may be differentiated from fibrous talc only on the basis of electron diffraction characteristics. Also, where fiber ends are visible, it is possible to differentiate talc from anthophyllite morphologically. Talc fibers tend to have prism truncation, whereas anthophyllite does not (Fig. 7). Microchemical techniques may be of limited use because of the time involved in analysis. Samples with a large number of fibers may be subjected to microchemical analysis to define the types of particles present. This requires the definition of standards and the analyses of several hundred representative fibers in the sample. The technique is excellent for characterization, but is not recommended as a routine analytical method *(34)*.

Summary and Conclusions

Talc because of its composition, conditions of formation and geological occurrence, is frequently contaminated with asbestos fibers. The presence of fibers may be determined by a number of instrumental techniques. Some in-

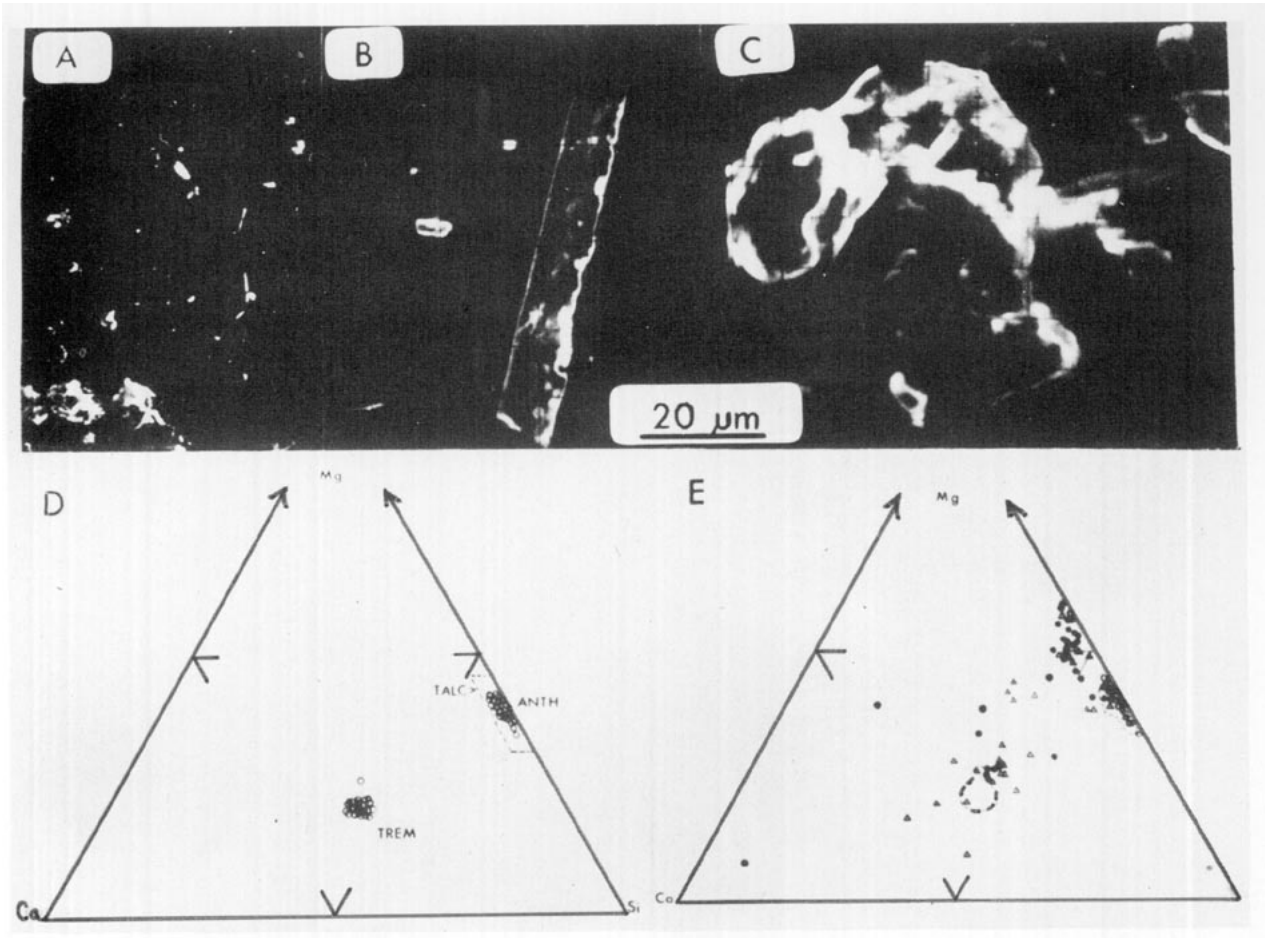

FIGURE 8. Electron microprobe analyses of 95 particles observed in a fibrous talc from New York State. *A-C* represent scanning micrographs (obtained monitoring backscattered electrons) of a fibrous talc dust: *(A)* an amphibole fiber in the dust; *(B)* analyzed as tremolite; and *(C)* a "talc" grain. The complex intergrowth of many phases invariably yields an analysis outside of the ideal compositional fields: *(D)* talc, anthophyllite, tremolite emission fields in the system Ca-Si-Mg. These analyses are scattered about these fields. Chemical analysis based on elemental emission, termed "pseudo-analysis" by Rubin and Maggiore *(34)*, show the presence of talc, tremolite, anthophyllite, quartz, feldspar, and carbonate phases. Differentiation between amphibole minerals is easily achieved; talc and anthophyllite fibers generally require structural characterization by selected area electron diffraction as well.

struments provide direct visualization of the fibrous objects. Although light microscopy and electron microscopy are excellent tools for qualitative analysis, each has distinct disadvantages. Use of light microscopy is restricted to analysis of objects larger than 1 μm. Electron microscopy requires extensive sample preparation and instrument time. Both techniques require homogeneous sampling to achieve quantitation or even estimates of fiber content. Unique characterization of amphibole fibers by transmission electron microscopy (anthophyllite and tremolite versus fibrous talc) requires structural analysis (selected area electron diffraction) and microchemical characterization.

Quantitative analysis for fiber may be achieved by x-ray diffraction techniques employing step-scanning modes of operation on selected characteristic reflections. Preparation by slurry filtration yields "cakes" which provide homogeneous samples for analysis. Samples thus prepared yield reproducible x-ray counting results. Each fiber type has its own level of sensitivity related to matrix and x-ray sorbtion effects. Anthophyllite may be detected at levels of 2.0%; chrysotile, 0.25%; and tremolite at

0.10% by weight in a talc matrix. Quantitative analysis of mineral systems more complex than two phases in composition may be compared with binary standards, with limitations.

We recommend the use of both x-ray diffraction analysis by step-scan mode of operation and transmissin microscopy with selected area electron diffraction for analysis of consumer talcs for their asbestos fiber content.

Acknowledgement

The authors wish to acknowledge support under a NIEHS Center Grant, ES 00928. One of us (AML) wishes to acknowledge support under a NIEHS Career Scientist Award, ES 44812.

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