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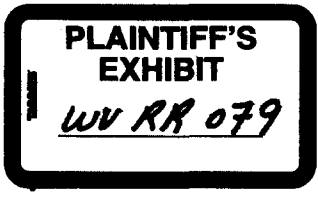
PROPOSED CRITERIA AND RECOMMENDED INTERIM STANDARD FOR ASBESTOS



U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service

Consumer Protection and Environmental Health Service

Environmental Control Administration

PROPOSED CRITERIA AND RECOMMENDED INTERIM STANDARD FOR ASBESTOS

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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Bureau of Occupational Safety and Health
Cincinnati, Ohio

PREFACE

Industrial experience has proved the need for criteria and standards to protect the health of workers exposed to an ever-increasing number of potential hazards at their work place.

In order to provide relevant data from which valid criteria and effective standards could be deduced, the Bureau of Occupational Safety and Health has projected a formal system of research with priorities determined on the basis of specified indices.

It is intended to present successive reports as studies are completed and standards are sufficiently crystallized so as to be feasible. The first report, which follows, concerns asbestos. Other reports will follow as the research and evaluation progresses. These standards are not considered definitive and will be reviewed in the light of additional data as research continues to keep protection of the worker's health as effective as the state of our technology requires.

I am pleased to acknowledge the contributions made by members of my staff, who developed this project, and the valuable constructive comments made by the "Ad Hoc Review Committee." A list of these contributors and reviewers appears on page ii.

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PROPOSED CRITERIA AND RECOMMENDED INTERIM STANDARD FOR ASBESTOS

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INTRODUCTION

This report presents the criteria and recommended interim standard which were prepared to meet the need for protecting the health of workers exposed to asbestos as delineated in "Position Paper on Asbestos" forwarded _____ to the Surgeon General of the Public Health Service. In addition, available relevant data is made available for use by the Secretary, Department of Health, Education, and Welfare, in the event that the Occupational Safety and Health Act of 1969 is enacted by Congress. Among other provisions, the Act requires the development of criteria by "The Secretary, Department of Health, Education, and Welfare...on the basis of such research, demonstrations, and experiments and any other information available to him..."

The Bureau of Occupational Safety and Health, after a review of all data and consultations with others, formalized a system for the development of criteria upon which standards can be established to protect the health of approximately 80 million workers from exposure to hazardous chemical and physical agents. Priorities in this system are based on five indices: (1) the number of workers potentially exposed; (2) the relative toxicity index of a particular substance or physical agent; (3) the incidence of illnesses (or death); (4) the quantity of the substance produced and used in the United States; and (5) the increase or decrease in the quantity used over a period of years.

The judgments of over 30 industrial hygienists from the states and private industry were considered in establishing a tentative priority list for over 90 chemical and two physical agents. Although an interim standard for coal dust was recommended to the Surgeon General in December 1968 as a result of work that the Bureau had already completed, the information contained in this report on asbestos is the first formal presentation of results from the use of the system.

RECOMMENDED INTERIM STANDARD

The U. S. Public Health Service recommends that occupational exposure to asbestos dust be controlled so that no person shall be exposed to a greater level than 12 fibers per milliliter based on a count of fibers greater than 5 μ in length as determined by the recommended method, which is described in this report.

The interim standard recommended is based on recent unpublished epidemiological investigations by the U. S. Public Health Service and the 1965 American Conference of Governmental Industrial Hygienists Threshold Limit Value. It will be subject to review and will be revised as necessary.

It is believed that adherence to this interim standard will reduce to an insignificant risk the occurrence of asbestosis, even among workers who may be exposed to asbestos dust for as long as 30 years.

DISCUSSION

REVIEW OF PROBLEM

Asbestos is a generic term that applies to a number of mineral silicates incombustible in air and separable into filaments. The most widely used in industry in the United States is chrysotile ($3MgO\ 2SiO_2\ 2H_2O$), a fibrous form of serpentine. Other types include amosite ($3MgO\ 11FeO\ 16SiO_2\ 2H_2O$); crocidolite ($Na_2O\ 3FeO\ Fe_2O_3\ 8SiO_2\ H_2O$); tremolite $[Ca\ Mg_3\ (SiO_3)_4]$; and anthophyllite $[(MgFe)_7\ Si_8\ O_{22}(OH)_2]$. Since chrysotile accounts for about 93 percent of the asbestos used in the United States,[1] the information on the relationship between asbestos dust exposure and its effects on workers is centered on the deleterious effects to workers from inhalation of chrysotile asbestos. and this "dose-response" relationship is one of the criteria used in setting a hygienic standard for asbestos.

Uses of Asbestos

Almost one million tons per year of asbestos are used in the United States.[1] Approximately 66 percent of the asbestos is used in cement products (building materials); 2 percent is used in manufacture of asbestos textiles; friction materials such as brake linings and clutch facings consume 4 percent; asbestos paper, 7 percent; floor tile. 10 percent; paints, roof coating, and caulks, 3 percent; plastics, 1 percent; and miscellaneous uses account for 7 percent.[1]

Exposure to Asbestos

The domestic mining and milling of asbestos is a limited industry employing fewer than a thousand workers. Heavy dust exposures to workers in this industry, particularly to those milling the asbestos, have been observed.

Heavy exposures to asbestos dust also occur at uncontrolled or poorly controlled operations in the manufacture and application of asbestos-containing products. In the use of asbestos, potentially high dust exposures occur in the mixing process in which asbestos is combined with other materials (cement, asphalt, vinyl, etc.).

There are approximately 40,000 insulation workers who are exposed to asbestos dust. These workers also cause secondary exposures to an estimated three to five million other construction workers involved in the construction of commercial and industrial buildings. These same insulation workers also create secondary exposures in shipbuilding, where up to 60,000 workers may have secondary exposures.[2] The dust exposure of workers in the construction (three to five million workers) and shipbuilding (250,000 workers) industries is extremely variable. Because of this variation and the small numbers of asbestos workers at any one location, asbestos dust exposures to these workers have never been satisfactorily estimated.

An estimated 50,000 workers are involved in the manufacture of asbestos-containing products. This figure does not include secondary manufacture of products which contain asbestos as electrical or thermal insulation, or products which include previously manufactured components containing asbestos.[2]

Early Indications of Hazard

As a result of the increasing use of asbestos minerals, there has been an undercurrent of concern over their role as factors in human disease. When asbestos dust is inhaled in excessive amounts, a lung disease termed asbestosis may develop.[3] This disease entity will be discussed in the medical section of this document. The first record of a case of asbestosis was made by Montague Murray in 1900.[3] The first complete description of the disease and of the "curious bodies" seen in lung tissue and sputum appeared in 1927 when Cooke[4] and McDonald[5] reported two cases of asbestosis and listed their reasons for believing that asbestos bodies originate from asbestos fibers that reached the lungs. Publication of their papers aroused general interest in the subject and additional reports appeared soon afterward. Hoffman[6] was the first American to call attention to the magnitude of the asbestosis problem. In 1918 he reported that 13 deaths from asbestosis had occurred among asbestos textile workers, and about the same time Pancoast, Miller, and Landis[7] reported on 17 cases of

asbestosis. Mill's publication[8] was the first pathological report on asbestosis published in the United States, and in that same year, 1930, Lynch and Smith[9] reported on asbestosis bodies found in the sputum of the asbestos workers.

In Merewether's abstract review,[10] emphasis is placed on the relation of asbestosis to working conditions. The clinical aspects of this disease are well documented. Gloyne's discussion of the pathology of asbestosis[11] is particularly helpful. Middleton's Milroy lectures on pneumoconiosis[12] contain a section of asbestosis. Egbert[13] in his summary of the literature reports on 26 fatal cases of asbestosis stated: "Active pulmonary tuberculosis was present in 6 instances of the total 26 cases; the fatal outcome was primarily the result of tuberculosis in 3 instances." The Annals of the New York Academy of Sciences presents a very excellent and lengthy documentation on the "Biological Effects of Asbestos.[1]

Development of Standards

The industrial experience associating exposure to asbestos with the development of a potentially disabling pneumoconiosis in man has amply demonstrated the need for a standard to limit allowable exposures to asbestos dust.

The first standard recommended was a threshold limit of 5 mppcf for asbestos dust recommended by Dreesen et al.[3] in 1938 after they had

studied 541 employees in four asbestos textile plants where massive exposures occurred. They found numerous well-marked cases of pneumoconiosis at concentrations of dust above 5 millions of particles per cubic foot of air (mppcf), but only three doubtful cases at concentrations under 5 mppcf.

Believing that the 5 mppcf limit recommended by Dreesen et al. was inadequate to give complete working-life term protection against all forms of asbestos, the Committee on Hygienic Standards of the British Occupational Hygiene Society reviewed medical evidence from the United Kingdom and epidemiological data from the United States Public Health Service. In 1968 they stated criteria for limiting exposure to chrysotile asbestos and recommended the following:[14]

Dust Category	Concentration Averaged over 3 Months (Fibers/cm^3)
Negligible	0 - 0.4
Low	0.5 - 1.9
Medium	2.0 - 10.0
High	over 10.0

(Note: 10 fibers/ml is equivalent to slightly less than 2 mppcf.)

Prior to establishing an asbestos standard based on American experience and applicable to American industry, researchers evaluated the health experience in asbestos plants. They found that the 5 mppcf limit was not sufficiently low to protect the workers who were exposed for 30 years. Balzer and Cooper[15] reported asbestosis among insulation workers exposed at levels not exceeding the time-weighted average of 5 mppcf.

As a result of its own recent epidemiological investigations considered with the work of others, the U. S. Public Health Service recommends an interim standard for asbestos of 12 fibers per milliliter greater than 5 microns in length. The membrane filter method of measurement used is that in which only fibers greater than 5 microns in length are counted. The British define a "fibre" as a particle longer than 5 μ and having a ratio of length to breadth greater than 3:1.[14] It is believed that this limit will reduce to an insignificant risk the occurrence of asbestos disease among workers even those who may be exposed to asbestos dust for as long as 30 years. However, the following must be emphasized:

1. One limit for "all types" does not reflect the differences in biologic activity of the different types of asbestos;
2. The interim standard does not recognize differing biologic activities of different forms of each type of asbestos;
3. The limit does not take into consideration differences in trace metal content that may result in display of genetic differences in susceptibility; and
4. The interim standard gives no assurance that it will protect against malignancies.

MEDICAL ASPECTS OF ASBESTOS

Asbestosis is a diffuse, pulmonary disease in which fibrosis is the dominant reaction to the prolonged retention in the lung of asbestos fibers and/or dust.[18] It is now widely accepted that asbestos dust inhaled in sufficient quantity as occurs in those occupationally exposed, in the absence of dust control, may be carcinogenic to the human lung.[19] In rats the inhalation of chrysotile has been associated with a 35 percent prevalence of lung cancer.[20] The question of the significance of the relationship of asbestos to lung or other cancer in the occupational neighborhood is unsettled at present.

Asbestos is not a systemic poison. No minimum lethal dose has been established and no distinct blood or urine derivatives have been found.

The principal pulmonary lesions caused by asbestos are described as regional atelectasis; interstitial, mucosal, and focal fibrosis; and bronchiolar fibrosis. This diffuse non-nodular fibrosis involves the primary framework of alveolar wall, interlobular septa, and visceral pleura with a consequent alveolar-capillary block.[16] Either distortion, distention, or stenosis of the bronchi with a fine diffuse emphysema along with the fibrosis are additional factors causing respiratory disability.

The perivascular fibrosis observed in most cases contributes to the development of cor pulmonale or right heart failure. Usually the disease

process is dispersed throughout the lung , but is more accentuated sub-pleurally and at the bases of the lungs where the amplitude of the breathing movements is greatest. Many alveolae may contain asbestos fibers surrounded by a protein capsule giving an indication of exposure, but not necessarily a diagnosis of asbestosis. Asbestos fibers may concentrate around lesions such as inactive tubercular lesions or bronchiectic areas.

The progressive alveolar capillary block initially results in a slightly decreased vital capacity, but a normal lung volume at rest. There is fairly normal maximal breathing capacity with normal distribution of inspired gases, hyperventilation first on exercise and later at rest and slightly reduced oxygen saturation of arterial blood at rest. There is a progressive reduction of arterial oxygen saturation on exercise as well as a decrease in oxygen diffusion capacity. The arterial oxygen saturation may stay within normal limits until late in the disease process. or it may precede radiological manifestations. The gaseous diffusion across the alveolar-capillary membrane may occasionally be only slightly abnormal.

Breathlessness associated with a cough occurs relatively early and becomes progressively worse. The symptoms begin insidiously with dyspnea of the exertional type and crackling rales later followed by exercise cyanosis and dyspnea. Symptoms of airway obstruction are often absent.

Clubbing is present in advanced cases. Severely impaired ventilation and reduced pulmonary capacity are often found in the advanced disease. The late complications of asbestosis include acute and chronic right heart failure and progressive cardio-respiratory failure, both of which are the most frequent terminal sequalae. In contrast to other pneumoconiosis, asbestosis is relatively infrequently complicated by bronchitis, bronchopneumonia, or pneumonia.

X-rays, when positive, show a ground glass appearance and occasionally the finest stippling. A honey-combing effect in the lungs with pleural plaques and pleural thickening are also present. The cardiac silhouette may be blurred. Concurrent exposures to other dusts may give a coarse pattern.

Other diseases definitely related to occupational exposure to asbestos include:[2]

(1) Bronchogenic Carcinoma - A cancer originating in the bronchi of the lung.

(2) Mesothelioma - A cancer originating in the lining of the pleural and peritoneal cavities.

(3) Asbestos Wart - A benign fibrotic nodule in the skin resulting from implantation of asbestos spicules.

The epidemiological evidence, or the incidence and prevalence of these diseases, in the American worker is not known.

It was not appreciated that exposure to asbestos dust could produce mesotheliomas, as well as gastrointestinal cancers, until Selikoff studied a cohort of 632 asbestos workers in the insulation trade. His report firmly established that work in this asbestos industry is associated with excessive incidence of asbestosis, lung cancer, pleural and peritoneal mesothelioma, and possible gastrointestinal cancer (1/2 stomach and 1/2 colon).[17] In an asbestos workers union in the New York area with 632 members in 1942, there were 349 deaths by the end of 1968; only 251 were to be expected according to mortality patterns representative of the general population.[17] The excess was attributed to asbestosis and lung cancer. Lung cancer accounted for one death in five, seven times the expected rate. No deaths from mesothelioma were expected; yet twenty were observed. The incidence of gastrointestinal cancer was three times the expected.

Smokers who work in the asbestos insulation trade face over 92 times the risk of lung cancer as compared with non-smokers in other industries.[17]

EPIDEMIOLOGY

Two major epidemiological surveys have been performed relating asbestos dust levels with asbestosis. The 1938 United States Public Health Service survey by W. C. Dreesen et al.[3] observed that "clean-cut" cases of asbestosis were found only in dust concentrations exceeding 5 mppcf. Only five persons were exposed over 10 years to asbestos dust concentrations from 0 to 4.9 mppcf. The longest exposure was 16 years to any concentration. None of the 39 persons exposed to dust concentrations below 2.5 mppcf had a case of asbestosis. Only six persons had been employed more than five years. Three doubtful cases of asbestosis fell in the range 2.5 to 4.9 mppcf. This study was conducted when dust concentrations were high and before industry initiated control methods. Few of the workers studied were exposed for long periods of time to low levels of asbestos dust,[3] which is the environmental condition most prevalent today.

The British Occupational Hygiene Society's study "Hygiene Standards for Chrysotile Asbestos"[14] related airborne fiber levels with incidence of asbestosis. According to this report, approximately one percent (no more than three percent) of the workers would exhibit early clinical signs of asbestosis at an accumulated exposure of approximately 100 fiber years per cubic centimeter. This parameter relates concentration of fibers with the duration of exposure. The figure of 100 fiber years per cubic centimeter

could represent an average exposure of two fibers per cubic centimeter for 50 years, or four fibers per cubic centimeter for 25 years, or 10 fibers per cubic centimeter for 10 years.

A third study was initiated in 1964 by the United States Public Health Service and is scheduled for completion in 1972. This study will relate the quantities of asbestos dust breathed by the workers to the harmful health effects attributed to asbestos; most particularly cancer. Other environmental factors such as worker smoking habits will be evaluated.

The primary purposes of this study were to determine the dust levels at which asbestosis occurs and the level at which no excess cancer occurs. Trace metals, as well as the carcinogenic oils in asbestos dust, may be important in the mechanism of causation of cancer and asbestosis and are included in this investigation.

METHODOLOGY

AIR SAMPLING METHODS

The original epidemiology of asbestos by Dreesen et al.[3] used midget impinger count data as an estimate of dust exposure. All of the dust particles seen, both grains and fibers, were counted since too few fibers were seen to give an accurate measurement. The resulting count concentration was a measure of overall dust levels rather than a specific measurement of the asbestos concentration. This method was satisfactory at that time since exposures were massive and the control measures installed to reduce overall dust levels also reduced the asbestos dust levels.

As dust levels were reduced, it became necessary to measure the biologically appropriate attribute of the dust cloud. At equal levels of overall dustiness, the concentration of asbestos could vary considerably from textile manufacture (75-85% asbestos) to insulation (5-15% asbestos). Furthermore, if the limit were lowered below the 5 mppcf used previously and dust counts taken by the impinger technique, it would be necessary to consider the effect of background dust, which could be as high as 1 mppcf.

A number of methods for measurement of asbestos dust concentrations have been used in the United States Public Health Service epidemiological study of the asbestos product industry.[21,22,23,24] Based on the data the preferred index of asbestos exposure is the concentration of fibers longer

than 5 μ counted on membrane filters at 430X with phase contrast illumination.[25,26] This method has been adopted as the standard field sampling method by the United States Public Health Service.

Based on measurements in the asbestos textile industry, a concentration of 6 fibers/ml longer than 5 μ is approximately equivalent to 1 mppcf. If this relationship is used, the intended change in the Threshold Limit Values (TLV) adopted by the American Conference of Governmental Industrial Hygienists (ACGIH) of 2 mppcf based on the impinger methods is equivalent to 12 fibers/ml longer than 5 μ.[27] Although the British have refrained from standardizing on a single method of measurement, most recent measurements have been performed by a method essentially identical to the fiber count method described in detail below, and the British interim standards for chrysotile asbestos dust are stated in these terms.

When exposures are measured in industries other than asbestos textiles, the asbestos fiber concentration is generally lower than 12 fibers/ml when the impinger concentration is at 2 mppcf. Since the ACGIH TLV is concerned with asbestos exposure, it should be considered exceeded only when the fiber concentration is over 12 fibers/ml as the dust being counted in the impinger may include cement, resin, and other non-asbestos materials.

Collecting Sample

The recommended atmospheric sampling procedure is the method described by Edwards and Lynch.[25]

Breathing zone samples for count are collected on Millipore type AA filters in personal samplers operated by battery powered pumps and worn by the employees. The filters are contained in plastic filter holders and are supported on thick pads which also aid in controlling the distribution of air through the filter.

Several methods of admitting air to the filter have been attempted. With the face cap removed and the filter completely exposed, the air may enter the filter evenly, but large high velocity particles and foreign objects may also hit the filter and possibly cause damage.

As an alternative, the face cap may be left in place and the small plug removed. The passage of air through this 4 mm opening at a flow rate of 2.1 liters/min produces a velocity of 265 cm/sec. which yields an impaction parameter of 0.061 for a 1-micron (μ) unit density sphere. Although this impaction parameter would predict a very low collection efficiency of 1 μ particles by impaction, some larger particles would also tend to be impacted on the center of the filter. This was found not to affect count distribution, which is dominated by small particles; however, it does result

in obscuring a small portion of the filter, particularly if many large particles are present, as in friction product plants.

The third alternative was to drill 6 additional 4-mm holes in some face caps and to fit these perforated caps to the filter holder during sampling. This reduced the velocity to 38 cm/sec, thus eliminating the impaction problem while still protecting the filter from damage.

Mounting Sample

The mounting medium used in this method is prepared by dissolving 0.1 g of membrane filter per ml of 1:1 solution of dimethyl phthalate and diethyl oxalate. The exact proportions of the three components are not critical, but the medium must have as high a viscosity as possible without being difficult to handle. The index of refraction of the medium thus prepared is $N_D = 1.47$.

To prepare a sample for microscopic examination, a drop of the mounting medium is placed on a freshly cleaned standard (25 mm x 75 mm) microscopic slide, using a dropper or applicator. The volume of the drop is approximately 0.05 ml. A wedge-shaped piece about 1 cm x 2 cm is excised from the filter with a scalpel and forceps and placed dust side up on the drop of mounting solution. A No. 1-1/2 coverslip, carefully cleaned with lens tissue, is placed over the filter wedge. Slight pressure on the coverslip achieves contact between it and the mounting medium.

Clearing of the filter with this method is slow, requiring about 15 minutes. The sample may be examined as soon as the mount is transparent.

The transition of the dust-supporting substrate from the translucent solid, membrane filter, cellulose ester material to a transparent, optically homogeneous gel is very gentle, and at no time does a meniscus sweep across the dust deposit. Rather, the substrate slowly softens beneath the dust, and there is no opportunity for the washing away or redistribution of the dust.

The optical homogeneity of the resulting mount is nearly perfect, with only a slight background granularity under phase contrast, which disappears within one or two days.

Stability

Observers noted a reduction with time in apparent concentration for samples mounted with only dimethyl phthalate and diethyl oxalate. Observation indicated that this loss was due to the migration of the dust particles outward from the center through the gelatinous material of the fixed mount, with a decrease in concentration in that area. The cause of this migration was not determined, but may be related to a disordering or distortion of the membrane filter polymer caused by partial solution.

To determine the magnitude of this loss, a group of samples was mounted using 1:1 dimethyl phthalate and diethyl oxalate only, and counted at

one- to three-day intervals for periods ranging up to 76 days. Counts were displayed as fractions in percent of the original, or first day counts. At the end of one week, samples mounted by this method yielded only 75 percent of their original values. By 30 days after mounting, the counts using this method had declined to 40 percent of their first day value, and continued at this level with no further decline until counting was terminated 76 days after mounting.

A group of samples mounted as described in the section Mounting Sample using high-viscosity mounting medium were counted at one-day intervals for 11 days. No loss of concentration was apparent over this short period and a second group was similarly mounted and counted for a period of 46 days. No loss of concentration was detectable during the first 30 days, but the count declined to 85 percent of its original value by the 46th day, when the series was terminated.

A 6-mm square of membrane filter with a vacuum-deposited film of carbon was mounted in the manner described to provide a macroscopic observation of the distortion of the filter areas. After a few days, the square began to disintegrate at the edges, but the major portion showed no discontinuity during the initial 30 day period. By the end of 62 days, most of the square had disintegrated and the fragments migrated over an area 16 mm x 17 mm.

Evaluation

The filter samples mounted in the manner previously described are evaluated in terms of grain and fiber concentration, and fiber size. Binocular research microscopes equipped with fixed mechanical stages have been used. Phase contrast optics fitted to these instruments include an Abbe condenser with rotating phase turret and a 4-mm "high-dry" achromatic objective used for all membrane filter determinations. In all cases 10X Huygens eyepieces, one of which contained a Porton reticle at the level of the field-limiting diaphragm, were used. The left half of the Porton reticle field served to define the counting area of field.

A ribbon filament illuminator was critically adjusted to provide Kohler illumination through a clear blue filter.

Twenty fields located at random on the sample were counted and total grains, total fibers, fibers greater than 5 μ, and fibers greater than 10 μ were recorded. Any particle having an aspect ratio of three or greater was considered a fiber.

ANALYTICAL METHODS

Modern analytical methods and instrumentation used in the identification and characterization of asbestos minerals include x-ray diffraction, atomic absorption spectrophotometry, emission spectroscopy, electron microscopy, electron microprobe, thermoanalysis plus the necessary sample preparation procedures.[28]

Internal Standard Technique for Chrysotile

Chrysotile may be determined by the x-ray diffraction and internal standard technique.[29]

Sample Preparation. The substances to be analyzed may be classified as settled dust samples or as bulk samples of process materials. Settled dust samples analyzed for nonfibrous minerals by x-ray diffraction are usually passed through a 325-mesh sieve in the preparatory procedure. Fibrous structures, such as asbestos, do not have the aerodynamic properties associated with approximately spherical airborne particles; hence the preparation of asbestos-containing settled dusts consists only in a preliminary screening of gross particles followed by grinding to less than 3.5 microns. This is accomplished by dry grinding in a mixer mill for ten minutes.

Bulk samples may be obtained from the materials used in an industrial process. An alumina-ceramic vial and mixer mill are used in preparing this type of sample for analysis. A representative portion of the bulk sample is pulverized in the mixer mill, as described for settled dusts.

Procedure. The ground dust or bulk sample is first scanned with the diffractometer to establish a qualitative diffraction pattern. This preliminary analysis will verify the presence or absence of chrysotile and will demonstrate the presence of possible interfering substances, which are discussed in a subsequent section. Chrysotile is confirmed as present by comparison of the sample's qualitative pattern with that of the pure mineral. If the pattern is found, a rough estimation of the percentage of chrysotile is then made.

A mixture of the dried sample and the aquamarine, each weighed separately, is prepared. The combined weights should be approximately 1 g. The percentage of aquamarine in the mixture should be approximately the estimated percentage of chrysotile in the sample. The mixture is then wetted with isopropanol and ground in a mechanically driven boron carbide mortar for 15 minutes. After this final grinding the mixture is dried at 110°C and packed in the sample holder of the diffractometer for analysis.

The ratio of the area under the aquamarine 3.28-A peak to the area under the chrysotile 3.63-A peak is computed from the digital print-out record. Background corrections are applied to determine the net area of a given peak. The average background count, calculated from the values provided over a fixed interval extending on each side of the diffraction peak, is used to calculate the total integrated background correction under the diffraction peak.

With the standard curve taken as a reference, the ratio of the weight of aquamarine to the weight of chrysotile is determined. The percentage of chrysotile is computed from the ratio of aquamarine to chrysotile, the weight of the dust sample, and the weight of the added aquamarine as follows:

$$(A \times 100)/(S \times R) = \% \text{ Chrysotile}$$

Where:

A = weight of aquamarine
S = weight of sample
R = ratio of aquamarine to chrysotile (by weight) as read from the calibration curve

Standardization. A Brazilian aquamarine is used as the internal standard. The clearest portion of this mineral is selected for milling, and the ground material which passes through a 325-mesh sieve serves as the source of the internal standard. The sieved fraction of the aquamarine was sized by electron microscopy; 99% of its particles measured 3.0 microns or less. The ground chrysotile used in the preparation of the standard samples was also sized by electron microscopy; 99% of its fiber lengths measured 2.5 microns or less.

The standard curve is obtained by application of the procedure to a series of mixtures of aquamarine and chrysotile. This series includes weight ratios of aquamarine to chrysotile of 0.5:1, 1:1, 2:1, 3:1, 4:1, and 5:1. Each mixture, in approximately 1-g samples, is mixed in the mill and finally ground in a mortar, as described under Procedure. The ratios of

the intensities of the aquamarine 3.26-A peak to the chrysotile 3.63-A peak (both corrected for background) are plotted against the weight ratios to obtain the standard curve. Each plotted ratio is the average of three to five replicate packings and scannings of each mixture of sample and internal standard.

External Standard Technique for Chrysotile

Chrysotile may also be determined by an x-ray diffraction and external technique.[30]

Procedure. The substances to be analyzed may be classified as settled dust, bulk samples of process materials, or airborne dust samples. The preparation of asbestos-containing settled dusts consists of a preliminary screening of gross particles followed by grinding to fiber lengths of less than 3.5 microns. This is accomplished by dry-grinding in a mixer mill for ten minutes.

Bulk samples may be derived from the starting materials, intermediates or finished products encountered in industrial processes. A representative portion of a bulk sample is pulverized in the mixer mill as described for settled dusts.

The technique of mounting representative portions of dust samples on a molecular membrane filter has been described by Talvitie and Brewer.[31] For this purpose, a known weight of the finely comminuted sample is suspended in 250 ml of water in an MCA volumetric flask. Proper distribution of the material in water is insured by use of a wetting agent. Then the

sample, which may include agglomerations, is dispersed with the aid of a small ultrasonic bath. An aliquot of the thoroughly agitated suspension, containing a known amount of the sample, is filtered using a molecular membrane filter. This method provides a sample of known weight on the filter. This technique has proved to be applicable to dust samples containing asbestos fibers whose sizes are of the magnitude described in this paper.

In-plant samples of airborne asbestos collected on membrane filters are analyzed without size reduction. From fiber size measurements made at this facility, the range and the mean values have been determined to be of the same order of magnitude as those of the asbestos standards used to calibrate the method.

In-plant samples of airborne asbestos fibers collected on membrane filters may not be uniformly distributed on the filters. As a uniform distribution of the fibers is required for this procedure, an even distribution of the collected fibers is obtained by removing the sample from its original filter and redepositing it on a second filter. This is accomplished by placing the original filter sample in a test tube containing a few drops of a suitable wetting agent and sufficient water to cover the filter. The test tube is then immersed in an ultrasonic bath for five minutes to remove the dust deposit from the filter. The original filter is then removed from the test tube and the suspended dust is redeposited on a second filter using the technique described above. This is also a convenient point to aliquot heavy dust samples.

The membrane filter with the aliquot of dust adhering to its surface is mounted in the x-ray diffractometer. A qualitative scan, usually at 1°/min, is run on the sample to establish the presence or absence of asbestos minerals and of possible interferences.

The area under the major diffraction peak of each asbestos mineral present in the dust sample is determined in order to calculate the weight of that particular form of asbestos. If the major diffraction peak is affected by that of another mineral present in the dust, then the second most intense peak of the asbestos mineral is used for a quantitative determination. While determining the area of a peak, the diffractometer is operated at a low scanning speed (0.2°/min) and a slit combination of 1° beam slit, medium Soller slit, and 0.2° detector slit. The area under the peak is computed from the digital printout record. Background corrections are applied to determine the net area of a given peak. The average background count calculated from a fixed interval extending on each side of the diffraction peak is used to calculate the total integrated background correction under the diffraction peak.

The net area of a given peak, computed from the printout data, is referred to a standard curve relating peak area, expressed in counts, to the weight of the appropriate asbestos mineral, expressed in milligrams. The latter quantity is the amount of the mineral represented in the aliquot portion of the analyzed sample.

analyses performed for the standardization of the method involved two to three determinations per filter.

. These absolute deviations, represented as milligrams of a specific mineral, were uniform over most of the usable range of the method. The relative standard deviations were as follows: 1.8 to 5% for 1 to 10 mg of chrysotile, 2 to 5% for 1 to 8 mg of crocidolite, and 2 to 5.5% for 1 to 8 mg of amosite. On the basis of these data, the working ranges of the quantitative method are 1 to 10 mg of chrysotile and 1 to 8 mg of crocidolite or amosite if the deviations are to be held within the indicated limits.

Infrared Spectroscopy

Infrared spectroscopy involves mixing a dust sample with potassium bromide to make a pellet which is inserted into the IR spectrometer to obtain a spectrum of the sample components. From this spectrum one can identify the major dust components.

Method (Qualitative). A 0.3-mg dust sample (ground so that greater than 90% of the particles are less than 5 microns in diameter) is mulled for 5 minutes with 300 mg infrared quality potassium bromide until thoroughly mixed. This mixture is pressed in a 13-mm die for five minutes at 25 tons pressure after an initial five minutes of evacuation. A clear pellet about

0.79 to 0.83 mm will result. This pellet is then placed in the instrument and scanned from 6 to 30 microns. From the resulting spectrum one can identify the asbestos constituents.[32]

Method (Quantitative). Although this method has not been used for the quantitative determination of asbestos components, experiments have shown that 10 micrograms of quartz can be detected on $\simeq$ 3x scale expansion. In a 10 mg sample this is 0.1% sensitivity. Only under certain conditions could asbestos minerals be quantified.

Differential Thermal Analysis of Chrysotile

The implication of chrysotile as a causative agent in certain types of pneumoconiosis has resulted in the appearance of numerous methods of analysis (both quantitative and qualitative) for chrysotile. One of these methods is differential thermal analysis (DTA).

The relatively simple DTA experiment measures temperature difference between a sample and an inert reference material as both are heated or cooled at a uniform rate. By indicating the gain or loss of heat from a system, DTA signifies when a component undergoes a physical change such as fusion, sublimation, or vaporization. Since these physical changes generally occur at different temperatures, a unique thermogram can be obtained for most thermally active materials.

While the principle behind DTA has been known for a long time, it has only been recently that acceptable thermal analysis equipment has become commercially available.

Consequently, the DTA technique will undoubtedly improve with time. A large number of chrysotile samples from various locations throughout the world have already been characterized by DTA.[33-36]

The two principal reactions with chrysotile are a broad endotherm between 600 and 720°C and an exothermic peak about 810°C. These peak locations can be shifted by varying the particle size of the sample or the heating rate.

Differential thermal analysis has also been used to detect the presence of chrysotile in filled resins.[37]

Indirect Estimation of Chrysotile

An indirect estimation of chrysotile may be made by utilizing the determination of magnesium in chrysotile-bearing samples by atomic absorption spectrophotometry.

Chrysotile asbestos, a hydrated magnesium silicate, is readily broken down by mineral acids. On acid treatment the combined magnesium is dissolved out and can be determined by atom absorption.

If the general formula ($3MgO\ 2SiO_2\ 2H_2O$) is used for chrysotile, the theoretical magnesium content is about 26%. With this information and the

magnesium content of a given sample, it would be possible to calculate the approximate amount of chrysotile in the sample. The assumption would have to be made that the sample contained no other magnesium-bearing compounds other than chrysotile. Most of the samples analyzed to date have been airborne particulates collected on membrane filters.

Sample Treatment. To the membrane filter sample in an acid-cleaned Phillips beaker is added 10 ml of 6N HCl. The sample is then heated on a hotplate (130°C) for 20 to 30 minutes to totally break down the chrysotile. The resulting solution is transferred to suitable volumetric glassware and adjusted to a known volume.

Analysis. The magnesium content of the sample is determined by atomic absorption spectrophotometry. Both single element and multielement hollow cathode devices have been used to produce the Mg 2852A resonance line which is used for the analysis. The percent absorption at this line is used to calculate the magnesium content of the samples.

Aqueous standards are prepared from a stock solution made from a pure magnesium compound and a standardization curve is run. The range of the method as used is 0 to 2 μg of Mg per ml of solution. Each standard is 0.3N in HCl.

The absorption for unknown samples is referred to the standard curve. The magnesium content in μg per ml is determined, and a final value

for total magnesium in the samples is calculated by using the total volume figure for each sample.

This method has been used primarily for small samples (0.20 μg) obtained by using personal samplers. Large samples require such dilution that considerable error may be introduced by dilution factors alone.

Evaluation of Methods

There is no recommended procedure for the determination of chrysotile. Additional research is needed to develop analytical techniques which are capable of permitting a differentiation between the massive and fibrous forms. Also, there is a need for more sensitive procedures to identify single fibers which are encountered in biological samples.

CONCLUSION

The criteria, the interim standard, and the method for the collection and evaluation of dust exposures to asbestos recommended in this report are based on the best epidemiologic data and analytical methods that now exist.

On the basis of these data an interim standard is recommended to control workers' exposures to asbestos at no more than 12 fibers per milliliter as determined by the recommended method of counting only those fibers greater than 5 microns in length.

The criteria do not include desirable data apt to be developed; e.g., all of the facts that should be known about asbestosis, the relationship between exposure to the various forms of asbestos and the increased incidence of cancer associated with workers exposed to asbestos, the relationship between asbestos dust levels and minimal health effects. Nor is there a recommended analytical technique to differentiate massive forms of asbestos from the fibrous forms although several techniques are described in this report.

As the results of additional research in these and other areas become known, the criteria and interim standard for asbestos and the techniques utilized in control will be reviewed and modifications issued if necessary.

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