QUANTITATIVE X-RAY DIFFRACTION ANALYSIS FOR AIRBORNE ASBESTOS DUST IN INDUSTRIAL ENVIRONMENT

PART 1. APPLICATION OF X-RAY ABSORPTION CORRECTION METHOD

Norihiko KOHYAMA

*National Institute of Industrial Health, 21-1 Nagao 6-chome,
Tama-ku, Kawasaki 213, Japan*

(Received February 15, 1980)

The quantitative analysis of standard asbestos (chrysotile) for airborne asbestos dust in industrial environments was performed by X-ray diffraction technique combined with a X-ray absorption correction method. Through this investigation, it was revealed that airborne asbestos (chrysotile) of 5 to 50 μg per cm^2 mounted on a silver membrane filter could be quantitatively measured with high accuracy when an airborne dust sample contained 1 to 10% of chrysotile (w/w) in any matrix by this correction method. When an airborne dust sample was composed of pure or nearly pure chrysotile, the quantitative analysis could be done up to 5 mg per cm^2 . On the basis of these results, it was concluded that the X-ray absorption correction method is quite useful for determination of airborne asbestos dust in industrial environment and without knowledge on the kind and the percentage of matrix existing in an airborne dust sample, the true weight of chrysotile could be obtained in the range of 5 to 50 μg per cm^2 .

By considering that quantitative range, sampling condition, especially sampling air volume, was evaluated. As the diffraction intensity of chrysotile is fairly sensitive to physical and chemical condition of preparation, a proposal for making a standard sample was also cited.

Asbestos which is well known as one of fibrous minerals has been widely used in many industries for about a hundred years because of the excellent heat- and acid-resistibility and indestructibility. On the other hand, asbestos is also well known as a hazardous mineral in industrial and environmental hygiene. Up to date it is widely believed that asbestos is not only a causal material of asbestosis but a carcinogen causing such as lung cancer and mesothelioma.

The development of analytical technique has been necessitated to evaluate and to control an airborne asbestos concentration in both industrial working and public environments. For the analysis the membrane filter method (fiber counting method by using optical microscopy) has been in use for over fifteen years in the United Kingdom and

in the United states. Only a few years ago, the method was enacted to use in Japan. Many investigators¹⁻⁶⁾ have tried to improve this method for a long time, but the fundamental disadvantages of this method can not be avoided. For example, it is fairly difficult to distinguish asbestos fiber from other fibrous material, furthermore much time is required to count asbestos fibers and the large variability found in result is due to personal factor of the analyst.

X-ray diffraction method has been considered to be excellent to conquer these disadvantages and has been applied to the quantitative measurement of asbestos fibers by a number of investigators⁷⁻¹⁴⁾. Most of them have studied the analysis of pure or nearly pure asbestos in the linear range of the calibration curve on weight versus X-ray diffraction intensity and have scarcely discussed the X-ray absorption effect of matrix material usually included in actual airborne asbestos samples. The commercial asbestos such as chrysotile, amosite, and crocidolite are usually not pure minerals and for industrial use combined with many other materials, such as cement, clays, calcite, talc, organic materials, and so on. Therefore, airborne asbestos sample collected from industrial environments usually contains of many kinds of impurities, and a pure airborne asbestos sample, i.e. non-surrounding matrix, is rather rare.

Fig. 1. Diffraction intensities (count/sec) for chrysotile as a function of weight ($\mu\text{g}/2\text{cm}^2$) on silver membrane filter.

Chrysotile ($7.3 \text{ \AA}$ peak): pure ($\circ$) and mixed with talc matrix in 10% ($\times$) and 1% ($\square$) level (w/w).

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Fig. 1 shows an importance of X-ray absorption effect. The X-ray diffraction intensities of pure chrysotile increase linearly with the increase of chrysotile weight from 0 to 500 μg per 2 cm^2 , but the intensities of 10 and 1% chrysotile in other surrounding matrix, e.g. talc, show saturation around 50 and 10 μg per 2 cm^2 of chrysotile, respectively, and deviate from the linear line of pure chrysotile. The amount of chrysotile surrounded by any matrix would be measured smaller than that of pure chrysotile even the airborne asbestos sample contains the same weight of chrysotile. It is obvious that the X-ray absorption effect can not be ignored on the quantitative analysis in such a case.

This study intends to determine the airborne asbestos independently of the asbestos percentage and the kind of matrix in the total airborne dust sample by X-ray diffraction analysis employing X-ray absorption correction method. From the result, the sampling condition, especially sampling air volume, is discussed.

EXPERIMENTAL

Apparatus: Conventional X-ray powder diffractometer (Geigerflex 2037; Rigakudenki Co., Tokyo) was used with a scintillation counter and graphite monochromator to reduce background at diffraction peaks. Both conditions and parameters of the measurement were listed in Table 1.

Asbestos standard sample: Chrysotile, a most common asbestos mineral used in industry, was used to make the calibration curve and to establish the present method. Two pure chrysotile samples (*Cassier AA* from Cassier Mine, Canada and #3778, from Coalinga, California, U.S.A.) were cut by ultra-centrifugal mill (Retsch WG, W. Germany) three times with 20,000 rpm. Then these fibers were crushed by micro-rapid mill using agate balls for a few minutes. Through this process, most of these chrysotile fibers were

Table 1. Analytical conditions and measurement parameters.

Analytical conditions			
Voltage :	35 kV	Scan. speed :	1°/2 min.
Current :	20 mA	Detector :	scintillator
Target :	Copper	Monochrometer :	graphite
Slit system :	1°-1°-0.3 mm	Goniometer :	185 mm
Time const.:	1 sec.		
Measurement parameters			
Component	Analytical peak (2 θ)*	Scan range (2 θ)	Gonio. speed (2 θ /min)
Chrysotile	12.0°	15°-10°	0.5°
Silver	38.1°	39°-37°	0.5°

* : CuK α radiation (1.5418Å).

fined into below a few tens micrometers in length.

Reagents used for surrounding matrix: Talc powder was prepared by grinding in agate mortar from the pure massive rock produced in Korea. No impurity in this talc was recognized by X-ray diffraction analysis. Powders of LiF, CaCO_3 (calcite), and Fe_2O_3 (hematite) were commercial reagents produced by Wako Chemical Co., Japan. These powders were made up in size under 300 mesh sieve.

Preparation of thin sample layers on silver membrane filter: A weighed amount of chrysotile (10.0 mg of *Cassier AA*) was fairly ultrasonicated by an ultrasonic cell disruptor in a 100 ml isopropyl alcohol for a few minutes, then transferred into a mess-bottle of 1000 ml with isopropyl alcohol to make the suspension of $10\mu\text{g}$ per ml. Some other agents (10.0 mg) for matrix material were also subjected to make into suspensions of isopropyl alcohol in mess-bottles of 1000 ml and 100 ml, which provided the $10\mu\text{g}$ per ml and $100\mu\text{g}$ per ml, respectively. Each graded amount of suspension was pipeted after shaking vigorously by hand, and combined as binary mixture in such manners as chrysotile and talc, or chrysotile and Fe_2O_3 (hematite), and so on, making a constant percentage of chrysotile such as 10 and 1% in 100 ml glass-stoppered bottles in which the obtained suspensions were well mixed. Then, the suspensions combined were filtered using a silver membrane filter (FLOTRONICS, U.S.A.) and the Millipore miniature vacuum filtering funnel giving an effective deposition area of 2.0 cm^2 which is employed as an unit area for expressing X-ray diffraction intensity of chrysotile. Absolute weights of pure and impure (with matrix) chrysotile samples were graded from 10 to $500\mu\text{g}$ per 2 cm^2 on the silver membrane filter. These filters were attached on a slide glass using both-sides gluing tape and analyzed by X-ray diffractometer to make standard calibration curves.

Principle of X-ray absorption correction method: X-ray absorption is arisen from both the analyte (asbestos) and any surrounding matrix. The measured intensity ($\mathbf{I}_m$) for asbestos must be multiplied by a correction factor ($\mathbf{F}$) to give the corrected intensity ($\mathbf{I}_c$); $\mathbf{I}_c = \mathbf{F} \cdot \mathbf{I}_m$. Williams¹⁵⁾ developed a method that the absorption coefficient of a powder could be determined simultaneously in measurement of analytical intensity by making a thin layer of the powder on the surface of a metal plate. Leroux, *et al*¹⁶⁾ and Atree-Williams¹⁷⁾ applied this method successfully to determine milligram quartz sample using silver membrane filter instead of a metal plate. Recently Lange and Haarts¹⁸⁾ studied the quantitative X-ray diffraction analysis of microgram chrysotile sample using this X-ray absorption correction method.

The concept of Williams¹⁵⁾ is schematically illustrated in Fig. 2. As shown in Fig. 2(1), the diffraction intensity of an original Ag-filter ($\mathbf{I}_{\text{Ag}}^0$) is measured and then, as shown in Fig. 2(2), the both diffraction intensities from the analyte (chrysotile) and the silver-filter being attenuated by passing through the analyte layer is measured. As shown in Fig. 2(3), it is easily understood that the intensity of chrysotile surrounded by matrix is weaker than that of pure chrysotile by the effect of X-ray absorption even the same

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Fig. 2. Diffraction from a silver membrane filter and a thin layer of sample.

I_{Ag}^0 : Diffraction intensity from Ag-membrane filter.

I_{Ag} : Diffraction intensity from Ag-membrane filter with sample layer.

I_m : Measured intensity of analyte (chrysotile).

amount of chrysotile is mounted on the filter surface. Following Williams¹⁵⁾ and Lange, *et al*¹⁶⁾, this correction factor (**F**) is expressed as follows:

$$\mathbf{F} = \mathbf{R} \ln \mathbf{T} / (\mathbf{T}^{\mathbf{R}} - 1)$$

where $\mathbf{R} = \sin \theta_{Ag} / \sin \theta_{ch}$, and θ_{Ag} and θ_{ch} represent the angles θ of the silver and chrysotile peaks, and $\mathbf{T} = I_{Ag} / I_{Ag}^0$. **F** value can be calculated when **T** and **R** are given. **R** is fixed by each analyte because the diffraction angles of silver and chrysotile are constant to every X-ray wave length. **T** is obtained as a ratio of the diffraction intensity of silver peak of each filter with and without sample layer. **F** values are calculated against various **R** and **T** for chrysotile on silver filter and shown in Table 4a~4d in appendix for the sake of routine work.

RESULTS

a) *Chrysotile peak intensity*: Two pure chrysotiles (>99%) collected from different localities were prepared by the same method, and measured the diffraction intensities. The X-ray diffraction intensities were measured by the two ways of peak height and integrated peak area as shown in Fig. 3 and Fig. 4, respectively. The figures show that the same weight of chrysotile sometimes produces different diffraction intensities due to the difference of locality, and there is no large difference in each sample between two different measurements of peak height intensity and integrated peak area one.

Diffraction intensity is usually affected by physical and chemical conditions in sample preparation, such as crushing, grinding, ultrasonic dispersion, chemical reaction with solution, and so on. Fig. 5 shows the decrease of diffraction intensity on (00 *l*) accompanying with lengthening the crushing period. In this case, a half of the chrysotile was changed into amorphous state by one hour crushing, and most of it by 18 hours.

b) *Mass absorption coefficient (μ^*)*: X-ray absorption effect depends upon the mass absorption coefficients of the matrix materials in airborne dust samples. Alexandar and Klug¹⁹⁾ proposed the theoretical equation for X-ray absorption effect considering the

Fig. 3. Comparison of diffraction intensity for pure chrysotiles from different localities. Intensity: measured by the peak height.

Fig. 4. Comparison of diffraction intensity for pure chrysotiles from different localities. Intensity: measured by the integrated peak area.

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Fig. 5. X-ray diffraction pattern of chrysotile (#3778) and the change due to crushing effect.

- 1: Raw fibers (cut in three times by ultra-centrifugal mill and crushed for a few minutes).
- 2: Crushed for one hour.
- 3: Crushed for 18 hours.

mass absorption coefficient. Mass absorption coefficient (μ^*) for asbestos minerals and some other materials were calculated and shown in Table 2. To determine the coincidence between theory and experiment for the equation given by Alexander and Klug¹⁹⁾, X-ray diffraction and absorption measurements were made on powder samples of binary mixtures of chrysotile and materials selected to cover a wide range of mass absorption coefficients, such as Lithium flouride (12.2), talc (31.4), calcite (70.9) and hematite (219.1). Weighed binary mixtures were well grounded in an agate mortar. The homogenized mixtures were mounted in aluminum sample holders and analyzed the X-ray diffraction

Table 2. Mass absorption coefficient (μ/ρ): μ^* for asbestos minerals and some inorganic compounds.

Compound	Chemical formula	μ^*	Compound	Chemical formula	μ^*
Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	28.9	ZrO_2		108.8
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	31.4	TiO_2		129.4
Amosite	$\text{Mg}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	113.5	Fe_2O_3		219.1
Crocidolite	$\text{Na}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	113.1	CrF_2		90.6
Brucite	$\text{Mg}(\text{OH})_2$	23.2	KCl		125.3
Quartz	SiO_2	34.6	Al_2O_3		31.2
CuO		41.0	LiF		12.2
ZnO_2		44.2	BeO		7.9
CaCO_3		70.9	Li_2O		6.5

Fig. 6. Comparison of calculated intensity-concentration curves (solid line) with experimental measurements (marked line with Δ , $\circ$, $\times$ and $\square$) for binary mixture of chrysotile and several materials.

intensity of chrysotile. Fig. 6 shows the observed values (dotted line) from materials of different mass absorption coefficients are in reasonable agreement with the calculated values (full line), although a slight difference exists which is probably due to experimental error.

c) *Chrysotile in talc (almost the same μ^*):* Chrysotile and talc have similar mass absorption coefficient as 28.9 and 31.4, respectively. Pure chrysotile and mixture of chrysotile in talc matrix in 10 and 1% (w/w) were used to determine the X-ray diffraction intensities as shown in Fig. 1. Even though the same weight of chrysotile exists in low

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Fig. 7. Normalized diffraction intensities from silver (101) of membrane filter with thin layers composed of various weights of chrysotile. Measured at the same time as Fig. 1.
Marks: same as Fig. 1.

Fig. 8. Diffraction intensities for chrysotile as a function of weight after X-ray absorption correction.
Chrysotile ($7.3 \text{ \AA}$ peak): pure (○) and mixture with talc matrix in 10% (×) and 1% (□) level (w/w).

weights, the diffraction intensities disagreed with each other among pure chrysotile and mixture of 10 and 1% chrysotile. T values (I_{Ag}/I^0_{Ag}) obtained at the same time are plotted in Fig. 7. Using these T values and R ($=3.100$ when $Ag=38.1^\circ$ and chrysotile $=12.1^\circ$ in 2θ), Fig. 1 is corrected as shown in Fig. 8. All these values are well coincided with each other between 10 to $100\mu\text{g}$ per 2cm^2 by this correction. The standard curve for pure chrysotile has a diffinitely wide range of linearity compared to that of 10 or 1% chrysotile, but by this X-ray absorption correction, the quantitative analysis can be done between 10 and $100\mu\text{g}$ per 2cm^2 without the knowledge of how much the matrix talc being contained with.

d) Chrysotile in various kinds of matrix: One percent of chrysotile by weight was mixed in various kinds of matrix selected for covering wide range of mass absorption coefficients. Fig. 9 shows that the X-ray diffraction intensities are rapidly saturated from large to small number in order of mass absorption coefficient of the matrix, i.e. the intensities of 1% chrysotile already showing the difference each other at $20\mu\text{g}$ per 2cm^2 and being all smaller than that of pure chrysotile. It is obvious that the sample being composed of large number of mass absorption coefficient of matrix produces comparatively large decrease in diffraction intensity. T values (I_{Ag}/I^0_{Ag}) which is obtained at the same time as the intensity measurement (Fig. 9) are shown in Fig. 10, which

Fig. 9. Diffraction intensities for 1% chrysotile in various matrixes (w/w) as a function of weight before X-ray absorption correction. Chrysotile ($7.3\text{ \AA}$ peak): Pure ($\circ$) and mixed with LiF ($\times$), talc ($\triangle$), CaCO_3 ($\square$) and $\alpha\text{-Fe}_2\text{O}_3$ ($\bullet$) matrix. Inset: enlarged the range of small weight.

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Fig. 10. Normalized diffraction intensities from silver (101) of membrane filter with a thin layer of 1% chrysotile in various matrixes (w/w). Marks of matrix: same as Fig. 9.

Fig. 11. Diffraction intensities for 1% chrysotile in various matrixes (w/w) as a function of weight after X-ray absorption correction. Marks of matrix: same as Fig. 9.

shows that Ag (101) diffraction intensities are also in order of the mass absorption coefficient of the matrix. Using these T values for the correction, the X-ray diffraction intensities in Fig. 9 are corrected as shown in Fig. 11. The large disagreement shown in Fig. 9 became smaller and well coincided with the intensities of pure chrysotile between 0 to $100\mu\text{g}$ per 2cm^2 of chrysotile weight. In other words in this range the quantitative analysis for chrysotile can be well done without knowledge of the amount and the kind of matrix in airborne dust samples.

e) *Linearity of pure chrysotile:* X-ray absorption correction was applied to pure chrysotile sample to determine the linearity of X-ray diffraction intensity against the weight. The X-ray diffraction intensity from pure chrysotile showed linearity up to $800\mu\text{g}$ per 2cm^2 before correction, and then gradually saturated as shown in Fig. 12 (as illustrated open circle). X-ray absorption correction was performed on this data using the observed T values shown in Fig. 13, and the X-ray diffraction intensities changed to show the linearity up to 10mg per 2cm^2 of chrysotile weight (black circle in Fig. 12). This means that if the airborne dust sample is composed of pure chrysotile, the quantitative analysis can be done for the chrysotile concentration of up to 10mg per 2cm^2 .

f) *On silver membrane filter:* The silver membrane filter used in this study is made of well-crystallized silver, hence which produces extremely low background on the diffraction pattern for copper X-ray target. The comparison of the background for some

Fig. 12. Diffraction intensities for pure chrysotile as a function of weight ($\text{mg}/2\text{cm}^2$) before ($\circ$) and after ($\bullet$) X-ray absorption correction.

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kind of filter was done around the scan range of chrysotile (002) peak (12° in 2θ) under the same instrumental conditions and shown in Fig. 14. It is well known that the background of the silver membrane filter is the lowest (1/2 of glass, 1/15 of cellulose ester filter) and is very suitable for determination of small amount of subject such as air-

Fig. 13. Normalized diffraction intensities from silver (101) of the membrane filter with a thin layer of pure chrysotile.

Fig. 14. Comparison of background on several kinds of filter at the angle of the first peak of chrysotile (about 12° in 2θ). Full scale: 2000 count/sec.

borne asbestos in industrial environment. The background of the silver membrane filter at the second peak of chrysotile (about 24° in 2θ) is still lower than the area of the first peak, so the quantitative analysis using the second peak of chrysotile would also be very effective.

DISCUSSION

X-ray absorption correction method¹⁵⁾ was successfully applied to a standard asbestos sample prepared on a silver membrane filter in this study. Through this experiment using X-ray absorption correction method, it was revealed that pure chrysotile didn't need any absorption correction up to $800\mu\text{g}$ per 2cm^2 , and if the X-ray absorption correction was employed, the quantitative range was improved and extended to $10\sim 10,000\mu\text{g}$ per 2cm^2 . In the case of 10 or 1% chrysotile level, they didn't show any accurate X-ray diffraction intensities even the sample weight is small enough as $10\mu\text{g}$ per 2cm^2 when the X-ray absorption effect was not corrected. For example, $50\mu\text{g}$ chrysotile of 1% level in talc matrix would give an apparent weight of $25\mu\text{g}$ before absorption correction and $52\mu\text{g}$ after correction, in other words 1% chrysotile is measured smaller than pure one if the correction was not performed even they are present in a sample for low weights. Table 3 is the summary of this quantitative range. Basically this effective result is in good agreement with earlier data¹⁸⁾. On the basis of the results, the sampling conditions, such as sampling air volume (m^3) and running period of sampler, are estimated and plotted against chrysotile percentage in airborne dust sample in Fig. 15. In Fig. 15, the lines of 1, 2, and 3 mean the lower quantitative limit for total dust concentration of 0.1, 0.5 and 1mg per m^3 , respectively. The line of $\bar{1}$, $\bar{2}$, and $\bar{3}$ show their limits of higher side. A and B mean upper limit of possible sampling air volume in a day (8 hours) when sampling is proceeded by 20 liter per minute and 10 liter per minute of air flow volume, respectively. For example, if an industrial environment has total dust of 0.5mg per m^3 , sampling air volume should be

Table 3. Range of quantitative analysis.

	Lower limit		Upper limit	
Before correction				
100% chrysotile	10 ($\mu\text{g}/2\text{ cm}^2$)	—	800 ($\mu\text{g}/2\text{ cm}^2$)	
10% ^a chrysotile	10 ($\mu\text{g}/2\text{ cm}^2$)	—	50 ($\mu\text{g}/2\text{ cm}^2$)	
1% ^b chrysotile	—	—	—	
After correction				
100% chrysotile	10 ($\mu\text{g}/2\text{ cm}^2$)	—	10 ($\text{mg}/2\text{ cm}^2$)	
10% ^a chrysotile	10 ($\mu\text{g}/2\text{ cm}^2$)	—	100 ($\mu\text{g}/2\text{ cm}^2$)	
1% ^b chrysotile	10 ($\mu\text{g}/2\text{ cm}^2$)	—	100 ($\mu\text{g}/2\text{ cm}^2$)	

^a : in Talc matrix.

^b : in various matrixs; LiF, Talc, CaCO_3 , and Fe_2O_3 .

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Fig. 15. Sampling conditions for this quantitative X-ray diffraction analysis.

Sampling air volume (m^3) and sampler's running period are plotted against chrysotile percentage in airborne dust sample.

Notations are indicated in text.

done in the area of 2 and $\bar{2}$ for any chrysotile percentage. And if the total dust ($0.5 \text{ mg per } m^3$) can be supposed to include 10% chrysotile, the sampling air volume is fixed between 0.2 and $2 m^3$. The vertical scale of right hand side indicates sampling period (minutes) when sampling is performed by 20 or 10 liter per minute. The air volume of 0.2 and $2 m^3$ can be obtained for 10 and 100 minutes, respectively, when the sampling is proceeded by 20 liter per minute. Actually, the both total dust concentration and percentage of chrysotile included in airborne dust sample can not be known until the measurement is completed, but if these values are roughly assumed, a certain range of sampling air volume or sampling period can be estimated using this figure. The actual airborne asbestos dust in an industry is collected by using cellulose ester membrane filter and then transfered on silver membrane filter in laboratory. A transfer procedure of an airborne asbestos dust from cellulose ester membrane filter to silver membrane filter is cited in appendix. This transfered asbestos sample is supposed to be equivalent to the actual airborne asbestos dust collected by air sampler from an industrial environment.

Accurate measurement of diffraction intensity is necessary to determine an airborne dust by X-ray diffractometry. X-ray diffraction intensity is largely affected by 1) stability of X-ray source, sort of target (wave length of characteristic X-ray), slit system,

scanning speed, time constant, etc., and 2) setting position of sample in goniometer, morphology of sample particle (platy, round, massive or fibrous), particle size, crystallinity, etc.. The group 1) is mostly due to instrumental conditions and skilled level of the operator. The group 2) is mainly due to the condition of sample itself. Here the factors in group 1) and the sample position in group 2) can be adjusted in good state by the operator. On the other hand, the particle size and the crystallinity of asbestos usually vary with the locality and the preparation. To determine an airborne asbestos by any method of X-ray diffractometry, a standard asbestos powder must be prepared. Comparing the diffraction intensity of airborne asbestos with that of standard asbestos, the amount of asbestos in an airborne dust sample can be obtained quantitatively. Therefore, the quantitative X-ray diffraction analysis necessitates the standard asbestos being similar to the asbestos in industrial airborne dust sample in physical (particle size, crystallinity, etc.) and chemical properties. Usually the size (length) of airborne asbestos fibers existing in industry would mostly be in the range between submicrometer and tens micrometers. The size of standard asbestos fibers should be in this range, but it is fairly hard to obtain such size of asbestos fibers from raw asbestos sample consisting of far large fibers by pulverizing it without any drastic physical change. As shown in Fig. 5, the diffraction intensity of chrysotile is largely influenced by crushing or grinding. As chrysotile is easily changed into amorphous by long crushing period, analyst should care for not to perform long crushing or grinding in the process of sample preparation.

On the other hand, the diffraction intensity of asbestos sometimes varies with every locality as shown in Fig. 3 and 4 even these chrysotiles are pure or nearly pure. If either of the chrysotile was used for a standard sample, the result would differ from either of them. At every industry and sort of work, the physical and chemical properties of asbestos would be altered by the processing and manufacturing in addition to its locality. Considering these various factors affecting on the diffraction intensity, we propose that the raw asbestos itself used in every subjected industry should be determined on the ratio of the diffraction intensity compared to a well-crystallized standard sample. The pure part in the raw asbestos is selected by hand picking and pulverized slightly into fine particles to determine the diffraction intensity ratio. This ratio would originate in difference of particle size and/or crystallinity between them. Doing this comparison, the better quantitative X-ray analysis would be achieved on the airborne asbestos samples in every industrial environment.

As the interference with the strongest peak of chrysotile (12° in 2θ), several minerals exist having the diffraction peak around it. They are, for example, kaolin minerals (kaolinite, halloysite, dickite and nacrite), non-fibrous serpentine minerals (lizardite and antigorite), chlorite minerals, and some inorganic compounds. The presence of these interferences can be recognized by X-ray diffraction analysis except for non-fibrous serpentine minerals. Consequently if interferences are present, another diffraction peak of chrysotile (e.g. (004) at 24.5° in 2θ) should be used for measurement. If a non-fibrous serpentine mineral is included in an airborne sample, the identification of

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chrysotile is very difficult. In this case, a comprehensive analysis, such as analysis by an analytical electron microscopy, thermal and infrared absorption analysis, should be employed for the identification.

REFERENCES

- 1) Edwards, G.H. and Lynch, J.R. (1968). *Ann. Occup. Hyg.*, **11**, 1.
- 2) Harness, I. (1973). *Ann. Occup. Hyg.*, **16**, 397.
- 3) Beckett, S.T. and Attfield, M.D. (1974). *Ann. Occup. Hyg.*, **17**, 85.
- 4) Reist, P.C. (1975). *Amer. Ind. Hyg. Assoc. J.*, **36**, 379.
- 5) Rajhans, C.S. and Bragg, G.M. (1975). *Amer. Ind. Hyg. Assoc. J.*, **36**, 909.
- 6) Beckett, S.T., Hey, R.K., Hirst, R., Hunt, R.D., Jarvis, J.L. and Rickards, A.L. (1976). *Ann. Occup. Hyg.* **19**, 69.
- 7) Crable, J.V. (1966). *Amer. Ind. Hyg. Assoc. J.*, **27**, 293.
- 8) Crable, J.V. and Knott, M.J. (1966). *Amer. Ind. Hyg. Assoc. J.*, **27**, 383.
- 9) Crable, J.V. and Knott, M.J. (1966). *Amer. Ind. Hyg. Assoc. J.*, **27**, 449.
- 10) Goodhead, K. and Martindale, R.W. (1969). *Analyst*, **94**, 985.
- 11) Rickards, A.L. (1972). *Anal. Chem.*, **44**, 1872.
- 12) Hayashi, H. (1973). *Ind. Health* **11**, 225.
- 13) Rohl, A.N. and Langer, A.M. (1974). *Environ Health Prosp.*, **9**, 95.
- 14) Kohyama, N. (1974). *Environment Research in Japan*, **II**, 84-1, Environment Agency, Japan.
- 15) Williams, P.P. (1959). *Anal. Chem.*, **31**, 1842.
- 16) Leroux, J., Davey, A.B.C. and Paillard, A. (1973). *Amer. Ind. Hyg. Assoc. J.*, **34**, 409.
- 17) Atree-Williams, S. (1977). *Anal. Chem.*, **49**, 429.
- 18) Lange, B.A. and Haartz, J.C. (1978). *NIOSH Technical Information* (in press).
- 19) Alexandar, L. and Klug, H.P. (1948). *Anal. Chem.* **20**, 886.

APPENDIX

A procedure for sampling and sample preparation on actual airborne asbestos sample is cited as follows:

1. Airborne asbestos dust in industrial environment is collected by low volume air sampler with cellulose ester membrane filter of 47 mm in diameter and $0.8\mu\text{m}$ in pore size.
2. Sampling conditions such as air flow volume and sampling period for this X-ray diffraction analysis should be decided by making reference to this text (Fig. 15).
3. Filter which collects airborne asbestos dust, is cut into half and the both are attached on a slide-glass by a few droplets of acetone.
4. The slide-glass holding the filter is set in the sample chamber of the low temperature asher using forceps and should be ashed gently for a few hours by constant indication of watts and oxygen flow to prevent the asbestos dust from whirling up and being lost. Chrystal structure of chrysotile would not be affected by this treatment of

low-temperature ashing.

5. After ashed, the slide-glass with airborne dust is put in about 100 ml isopropyl alcohol in beaker and the airborne dust is dispersed by ultrasonic cell disruptor. Then the cleaned slide-glass is taken out of the beaker.

6. The suspension of the isopropyl alcohol in which the airborne dust contained is filtrated with silver membrane filter of 25 mm in diameter and of $0.2\mu\text{m}$ in pore size using the Millipore miniature vacuum filtering funnel. The effective area on the filter is just two square centimeter.

7. The silver membrane filter prepared as written above is analyzed by X-ray diffractometry, and the true asbestos amount is determined by the method written in this text.

8. For the sake of routine work, the calculated correction factors (F) commonly used are listed as follows (Table 4a~4d).

Table 4a. Commonly used correction factor (F) for chrysotile.
 $R=3.100$ (38.1° (Ag)/ 12.1° (chrysotile) in 2θ).

T	0.09	0.08	0.07	0.06	0.05	0.04	0.03	0.02	0.01	0.00
1.0										1.0000
0.9	1.0050	1.0316	1.0480	1.0646	1.0816	1.0990	1.1167	1.1348	1.1533	1.1722
0.8	1.1915	1.2112	1.2313	1.2519	1.2730	1.2945	1.3165	1.3389	1.3619	1.3854
0.7	1.4095	1.4341	1.4592	1.4850	1.5113	1.5383	1.5659	1.5941	1.6231	1.6527
0.6	1.6831	1.7141	1.7460	1.7786	1.8121	1.8464	1.8815	1.9176	1.9546	1.9925
0.5	2.0314	2.0714	2.1124	2.1545	2.1977	2.2421	2.2878	2.3347	2.3829	2.4325
0.4	2.4834	2.5359	2.5899	2.6455	2.7028	2.7618	2.8226	2.8853	2.9499	3.0167
0.3	3.0856	3.1568	3.2303	3.3064	3.3851	3.4666	3.5511	3.6386	3.7295	3.8238
0.2	3.9219	4.0240	4.1303	4.2411	4.3568	4.4777	4.6044	4.7371	4.8766	5.0235
0.1	5.1784	5.3421	5.5158	5.7004	5.8975	6.1087	6.3360	6.5820	6.8499	7.1437
0.0	7.4689	7.8329	8.2459	8.7230	9.2876	9.9790	10.8705	12.1273	14.2760	—

Table 4b. Commonly used correction factor (F) for chrysotile.
 $R=3.577$ (44.3° (Ag)/ 12.1° (chrysotile) in 2θ).

T	0.09	0.08	0.07	0.06	0.05	0.04	0.03	0.02	0.01	0.00
1.0										1.0000
0.9	1.0181	1.0366	1.0555	1.0748	1.0945	1.1147	1.1354	1.1565	1.1781	1.2002
0.8	1.2229	1.2460	1.2697	1.2939	1.3187	1.3440	1.3700	1.3966	1.4238	1.4516
0.7	1.4801	1.5093	1.5392	1.5699	1.6012	1.6334	1.6663	1.7000	1.7346	1.7700
0.6	1.8063	1.8435	1.8817	1.9208	1.9609	2.0020	2.0442	2.0875	2.1319	2.1775
0.5	2.2243	2.2723	2.3215	2.3721	2.4241	2.4775	2.5323	2.5887	2.6466	2.7061
0.4	2.7674	2.8304	2.8951	2.9618	3.0305	3.1011	3.1739	3.2490	3.3263	3.4060
0.3	3.4883	3.5732	3.6609	3.7515	3.8452	3.9420	4.0423	4.1462	4.2538	4.3655
0.2	4.4814	4.6019	4.7272	4.8577	4.9938	5.1360	5.2846	5.4402	5.6035	5.7752
0.1	5.9561	6.1472	6.3495	6.5645	6.7937	7.0390	7.3028	7.5880	7.8984	8.2385
0.0	8.6148	9.0356	9.5129	10.0640	10.7160	11.5140	12.5430	13.9933	16.4727	—

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Table 4c. Commonly used correction factor (F) for chrysotile.

R=1.551 (38.1° (Ag)/24.3° (chrysotile) in 2 θ).

T	0.09	0.08	0.07	0.06	0.05	0.04	0.03	0.02	0.01	0.00
1.0										1.0000
0.9	1.0078	1.0157	1.0238	1.0320	1.0403	1.0487	1.0573	1.0660	1.0749	1.0839
0.8	1.0931	1.1024	1.1119	1.1215	1.1313	1.1413	1.1514	1.1618	1.1723	1.1830
0.7	1.1939	1.2050	1.2163	1.2278	1.2396	1.2516	1.2638	1.2763	1.2890	1.3019
0.6	1.3152	1.3287	1.3425	1.3566	1.3709	1.3857	1.4007	1.4161	1.4318	1.4479
0.5	1.4643	1.4812	1.4984	1.5161	1.5342	1.5528	1.5718	1.5913	1.6114	1.6320
0.4	1.6531	1.6748	1.6972	1.7201	1.7438	1.7682	1.7933	1.8191	1.8458	1.8734
0.3	1.9018	1.9312	1.9616	1.9931	2.0257	2.0596	2.0947	2.1311	2.1690	2.2085
0.2	2.2496	2.2925	2.3373	2.3842	2.4334	2.4849	2.5391	2.5962	2.6564	2.7201
0.1	2.7877	2.8595	2.9360	3.0179	3.1059	3.2008	3.3036	3.4151	3.5384	3.6742
0.0	3.8256	3.9964	4.1918	4.4193	4.6908	5.0260	5.4617	6.0809	7.1474	—

Table 4d. Commonly used correction factor (F) for chrysotile.

R=1.791 (44.3° (Ag)/24.3° (chrysotile) in 2 θ).

T	0.09	0.08	0.07	0.06	0.05	0.04	0.03	0.02	0.01	0.00
1.0										1.0000
0.9	1.0090	1.0182	1.0275	1.0370	1.0466	1.0564	1.0664	1.0765	1.0869	1.0973
0.8	1.1080	1.1189	1.1299	1.1412	1.1526	1.1643	1.1762	1.1883	1.2006	1.2132
0.7	1.2260	1.2390	1.2523	1.2659	1.2797	1.2938	1.3082	1.3229	1.3379	1.3533
0.6	1.3689	1.3849	1.4012	1.4179	1.4350	1.4524	1.4703	1.4886	1.5072	1.5263
0.5	1.5460	1.5660	1.5866	1.6077	1.6293	1.6515	1.6742	1.6975	1.7215	1.7462
0.4	1.7715	1.7975	1.8243	1.8518	1.8802	1.9094	1.9395	1.9706	2.0027	2.0358
0.3	2.0700	2.1053	2.1419	2.1798	2.2190	2.2597	2.8020	2.3458	2.3915	2.4390
0.2	2.4885	2.5401	2.5940	2.6505	2.7095	2.7715	2.8367	2.9052	2.9776	3.0540
0.1	3.1351	3.2211	3.3128	3.4109	3.5160	3.6293	3.7519	3.8853	4.0314	4.1926
0.0	4.3721	4.5742	4.8048	5.0728	5.3917	5.7844	6.2934	7.0143	8.2519	—