QUANTITATIVE DETERMINATION OF AIRBORNE ASBESTOS DUST IN OCCUPATIONAL ENVIRONMENT BY X-RAY DIFFRACTION USING CONVENTIONAL AND ROTATING ANODE X-RAY TUBE

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X-ray diffraction is used as an analytical tool for crystalline substances which are hazards in an occupational and natural environments. This paper describes a method for qualitative and quantitative determination of asbestos in airborne dust in the occupational environment. Airborne asbestos collected on glass fiber filter by means of high volume air sampler can be analyzed without removal of the dust from the filter and also without addition of internal standard material. For determination of amounts of total dust, the filter is weighed before and after the collection of the sample. For estimation of mass per unit volume of air, the total volume of air that passed through the filter is recorded. In order to obtain asbestos content in airborne particulates, two types of X-ray generators are used in this study. One is equipped with conventional sealed anode X-ray tube. It is applicable to determine quantitatively 1 to 5 mg of asbestos with this method. The other is equipped with rotating anode X-ray tube in order to generate high power X-ray. This procedure can be carried out routinely in a laboratory and in occupational environment when the total amount of sample is of the order of 0.01 mg of glass fiber filter of 3.8 cm² in area.

The results of field survey indicate very high concentration of both asbestos and total dust in working area of asbestos industry, especially of sprayed mineral fiber containing asbestos.

This investigation was initiated with particular reference to the asbestos industry, where is a need to evaluate an airborne asbestos concentration. The problem was to combine the most efficient sampling techniques with an accurate and rapid method of determining the asbestos content of the sample collected. In Great Britain and U.S.A. a technique for counting and sizing asbestos dust which has been collected upon a membrane filter is popular. The membrane filter method enables asbestos fiber which is 5–10 μ m long and with length to breadth rates of at least 3:1 to be counted. If samples are collected in an area containing some other material of fibrous nature, it is necessary to reject those fibers that obviously are not asbestos.

Whether this is a good method or not is a matter for argument. First, it is

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very difficult to distinguish asbestos from other fibrous materials by means of light microscopy. Secondly, this method needs too much time in counting and sizing asbestos fibers. Thirdly, this method can not collect a lot of airborne particulates during a short time in a clean working sites, because the airborne particulates are collected on a membrane filters by means of personal sampler or low volume air sampler.

In 1971, Ministry of Labour surveyed concentrations of some toxic materials, such as chromium, cadmium, beryllium, asbestos and others, in occupational environments, and decided to collect particulated on a glass fiber filter using high volume air sampler. Prior to this survey, an analytical method of asbestos content in dust on a glass fiber filter has been developed in the author's laboratory. In a method used hitherto, the dusts are collected on a glass fiber filter by means of a high volume air sampler, and the filters are then subjected to X-ray diffraction instruments. This procedure gives exact and rapid method for the measurement of crystalline substances which are hazards in an occupational environment.

METHOD

In sampling an atmosphere for the measurement of contaminants, it is necessary that the air containing the contaminants be captured and analyzed simultaneously, or that the contaminants be removed from the air and retained for subsequent analysis. The results of such determinations are usually expressed in terms of weight, number of particles, or parts per unit volume of the atmosphere sampled. Therefore the sample volume is equally important as in the quantitative determination.

Samples were taken using a high volume air sampler equipped with a glass fiber filter (Toyo GB 100) with a filter diameter of 11 cm both in the laboratory and various working sites of asbestos factory. Each high volume air sampler was checked before the field survey and/or periodically to determine their operating condition, because the accuracy of all sampling instruments depends on the precision of measurement of the air volume involved.

The contaminants adhered to a circular part with a diameter of 8.8 cm on the filter. A circle with a diameter of 2.2 cm was cut off from the filter and stuck on depression in sample holder which was specially prepared by the author's laboratory, and then it was analyzed by X-rays.

The X-ray analysis instruments used in this experiment were the following two kinds X-ray diffraction spectrometer systems.

- 1) "Geigerflex" X-ray diffractometer consists of an X-ray generator with a horizontal goniometer and a conventional sealed cobalt tube, with an iron filter, operated at 35 Kv and 5 mA. A specimen rotating attachment which is attached to goniometer, is used to rotate the specimen to eliminate the effects caused by orientation and grain size of minerals.

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2) "Rotaflex" is composed of a high power X-ray generator with a rotating anode tube and horizontal goniometer. A rotating cobalt anode was turned 2500 r.p.m. and was operated at 40 Kv and 200 mA.

QUALITATIVE ANALYSIS

A qualitative X-ray analysis of particulates which adhered to glass fiber filter paper was undertaken to determine the types of asbestos and other constituents of the particulates. As shown in Figs. 1 and 2, chrysotile, amosite and crocidolite are dominant minerals in the dusts of asbestos textile industry with talc, ilmenite and magnetite as accessory constituents, while the airborne particulate in asbestos cement or insulation industries are composed of chrysotile, amosite crocidolite, quartz, talc, brucite, calcium carbonate and calcium silicates.

The X-ray diffraction techniques can easily distinguish the different types of asbestos from other constituents. However X-ray diffraction technique for determination of asbestos in dusts requires relatively large amounts of samples. In order to detect a small amount of airborne asbestos particulate, or to estimate asbestos in a small amount of airborne contaminants, a rotating anode X-ray diffraction technique has been the only instrumental method available with an ability

Fig. 1. X-ray diffraction patterns of airborne asbestos dusts in asbestos textile industry.

Note; 1: twisting, 2: carding, 3: weaving, 4-6: opening. Ch: chrysotile, A: amosite, T: talc, B: brucite, Q: quartz.

Fig. 2. X-ray diffraction patterns of airborne asbestos dusts in asbestos industry.

Note; 1-3: mixing of asbestos with other materials,

4-6: processing of asbestos products.

Ch: chrysotile, A: amosite, Cr: crocidolite,

B: brucite, Q : quartz.

Fig. 3. Comparison of X-ray diffraction pattern of airborne asbestos obtained by ordinary X-ray unit (bottom) with that obtained by rotating anode X-ray diffraction unit (top).

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to identify and quantify rapidly crystalline inorganic compounds and minerals. This unit exhibits effective results in X-ray diffractometry where detection of low intensity of diffracted peak of high speed scanning is required as well as in the photographic method where short exposure time is important.

The intensities of X-ray diffraction patterns obtained by the rotating anode X-ray diffraction unit is more than 10 times greater than that obtained by the ordinary unit. A comparison of X-ray diffraction patterns of both the instrument is presented in Fig. 3.

QUANTITATIVE ANALYSIS

The U.I.C.C. standard reference samples were not used in this study, because they contain some impurities estimating from mineralogical point of view.

The asbestos samples used as standard materials are listed below.

Chrysotile (Cassier AA) from Cassier mine, Canada.

Amosite (S-22) from Penge mine, South Africa.

Crocidolite (M) from Kuruman mine, South Africa.

These specimens were confirmed to be pure minerals by X-ray, differential thermal, infrared, and chemical analyses and observation of electron microscopy.

The standard samples for X-ray diffraction were prepared as follows.

- 1) The method used in this study was to pump dust from dust generator. The asbestos was collected on glass fiber filter by a high volume air sampler equipped with a horizontal elutriator which was 2 meters long. The desired amount of each asbestos standard sample is able to be collected by adjusting periods. These materials were described as HV. The intensity of representative diffraction peak of each asbestos standard sample was obtained using a diffractometer, as a peak height on the chart.
- 2) After the X-ray analysis was carried out, a small amount of distilled water was dropped on each sample, which was collected by a high volume air sampler. The major diffraction peak was counted by a method similar to the one mentioned above when the sample got dry. These were designated as HV & W.
- 3) For the preparation of the suspensions of the pulverized asbestos, aliquots containing 1 to 10 mg of a given asbestos standard were removed and transferred to individual glass fiber filter. These were designated as D.

The ordinary X-ray unit

The major diffraction peak was counted to determine peak height. The plotting of peak intensities after correcting for background and weight of asbestos provides the calibration curve. Calibration curves, based on the application of the procedure to pure asbestos minerals and the use of the pertinent primary diffraction peaks obtained by ordinary X-ray unit, are given for chrysotile, amosite and crocidolite in Figs. 4, 5 and 6.

In a range of a small amount, peak intensities are affected by amounts; they

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increase along with increasing amount of asbestos, which will be accumulated piling up on the filter. However on further increase in the amount of asbestos, peak intensities do not show a remarkable rise with increasing amount. The direct comparison method is available in a small amount range where there is a linear relationship between peak intensity and amount of asbestos. The direct comparison method in general requires less sample preparation, and is available in quantitative determination of minerals in the air of occupational and natural environments which contains a little of mineral dusts.

Fig. 4. Standard curves for X-ray diffraction determination of chrysotile.

Note; HV : dust was collected on glass fiber filter by high volume air sampler.

HV & W: after dust collection by means of high volume air sampler, small amount of distilled water was dropped on the specimen and then made dried.

D : specimen was made from the deposition of asbestos suspension.

Fig. 5. Standard curves for X-ray diffraction determination of amosite.

Note; same to explanation of Fig. 4.

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Fig. 6. Standard curves for X-ray diffraction determination of crocidolite.
Note; same to explanation of Fig. 4.

Degree of parallel orientation is a very important factor which gives an influence upon the intensity of X-ray diffraction peak. It is desirable to carry the experiment under a fixed degree of parallel orientation, for example, completely random and/or completely parallel. However such conditions are very difficult to be obtained. A given amount of distilled water was dropped on sample in order that degree of parallel orientation might make up a uniform condition. As far as this experiment concerned, the intensity of X-ray diffraction peaks obtained by this method (HV & W) become several times greater than that obtained by ordinary method (HV).

Using the standard samples in which a suspension of asbestos was deposited on a filter (method D), peak intensities of the major diffraction peak of asbestos exhibit intermediate values between the values obtained by the methods HV and HV & W, and/or show greater values than those obtained by the methods HV and HV & W. If we make of the calibration curve obtained by method D, the evaluation of asbestos content in dusts on filter should be greater than obtained from the calibration curve which was prepared by method HV. Hence the deposition on a glass fiber filter of a suspension of asbestos in a liquid was unacceptable. In this study, the airborne asbestos has been estimated by both the calibration curves which were prepared from the methods HV and HV & W.

Rotating anode X-ray diffraction unit

Several series of known samples were prepared to evaluate the detection limit of the determination for asbestos by high powered X-ray. The filters with deposits up to 15 mg of each asbestos were obtained, and were measured on the appropriate peak. Then the intensity corrected for background were plotted against the amount of asbestos on the filter. A linear relationship was obtained below 1 mg, but for higher loadings the graph tailed off. Fig. 7 illustrates calibration curves for chrysotile, amosite and crocidolite prepared in this manner. This

Fig. 7. Standard curves of asbestos by use of high power X-ray.

Note; Squares: amosite, Triangles: crocidolite,
Circles : chrysotile.

procedure is applicable to a quantitative determination in the 0.01 to 1 mg range for asbestos on the filter with a diameter of 2.2 cm and/or 3.8 cm² in area.

Table 1. Asbestos and total dust content of air in asbestos industry.

Operation		No.	Concentration of asbestos (mg/m ³)		Concentration of total dust (mg/m ³)	
			Range	Average	Range	Average
Opening	Asbestos cement	5	0.15—0.70	0.488	0.54—3.21	2.626
	Insulation	4	0.03—0.58	0.215	0.21—0.81	0.425
Twisting, Carding etc.	Asbestos textile	6	0.45—1.32	0.887	0.74—5.33	3.238
Mixing	Asbestos cement	2	0.15—0.22	0.184	4.04—4.52	4.280
	Insulation	6	0.01—0.27	0.156	1.72—17.46	8.348
Processing	Asbestos cement	1	0.03		1.23	
	Insulation	16	0.00 ₃ —2.24	0.211	0.66—9.26	2.539
Packing	Materials for spray	2	0.03—0.12	0.079	5.75—6.00	5.875
Crushing	Asbestos cement	1	0.04		9.33	
Spray		9	0.62—6.04	2.761	11.14—44.68	25.294

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FIELD SURVEY

Fifty-two samples which were collected from various working sites in asbestos industry, were analyzed by the above mentioned procedure. Table 1 shows the distribution of asbestos in different places in asbestos industry. This result shows that asbestos concentrations in the working environments where inorganic fiber containing asbestos is sprayed, are greater than in other operation sites of the asbestos industry. The second dirty place is working site in textile industry.

Recently Subcommittee for threshold limit of the dust recommended that threshold limit value for asbestos in air is 2 fibres per cubic centimeter (or 0.12 mg per cubic meter) of air based on a count of fibers greater than $5 \mu\text{m}$ in length, and

Fig. 8. Relationship between concentration of asbestos and that of total dust in asbestos industry.

Note; Open circles: opening of asbestos fibers,
 Solid circles: spinning of asbestos fibers,
 Open squares: mixing of asbestos fibers with other materials,
 Solid squares: processing of asbestos products,
 Open triangles: crushing of asbestos products,
 Solid triangles: packing of asbestos,
 Semi-Solid squares: spray of mineral fibers containing asbestos.

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the ceiling value for asbestos is 10 fibers, longer than 5 μm , per cubic centimeter of air¹⁾. Ministry of Labour decided on July, 1973 that suppression limit value of asbestos in air is 5 fibers per cubic centimeter (0.30 mg per meter)²⁾.

The results obtained, converted into concentration of asbestos and total dust, are illustrated in Fig. 8. It will be seen that more than a half of results fall within this suppression limit value and in remaining 41.18% (21 locations) where the concentrations of asbestos were in the range 0.3–6 mg per cubic meter. Six of these locations are working sites of textile industry, and 9 of these locations are working sites where spraying of inorganic fiber containing asbestos has been applied. Many men spraying minerals fiber containing asbestos used to wear no effective personal respiratory protective device. A special attention should be given to the personal protection of the workers in this operation.

On the other hand, the threshold limit value of the dust having less than 30% of free silica contents is 5 mg per cubic meter, and that of the dust having more than 30% of free silica content is 2 mg per cubic meter³⁾. Concentration of total dust of 19 locations are greater than the threshold limit value of 5 mg per cubic meter. The X-ray diffraction patterns of airborne asbestos collected from the asbestos industry revealed the presence of quartz frequently. So we should apply the threshold limit value of 2 mg per cubic meter. Concentration of total dust of 41 locations (59.61%) are greater than this threshold limit value. This study indicates that very high concentrations of both asbestos and total dust are found in the working environment of asbestos industry.

In the working environment of opening and spinning, such as carding, twisting and weaving, the concentration of asbestos is nearly proportional to that of total dust. This might be expected from the only use of commercial asbestos in these places. On the other hand, there is no relationship between concentration of asbestos and that of total dust in air of the mixing, processing and other operations. The contaminants in the air of these operations consist of asbestos, calcium carbonate, calcium silicates, quartz and other constituents. Therefore we should estimate concentration of asbestos and other toxic minerals simultaneously. This procedure mentioned above, can easily be performed for both qualitative and quantitative analyses of crystalline materials, such as asbestos, quartz and others, in the air.

DISCUSSION

The increasing knowledge of the health hazard caused by airborne asbestos has brought forward a problem that is a quantitative determination of asbestos in admixture with the many other constituents commonly found in contaminants.

Asbestos is the only natural inorganic fibrous material that has attained commercial importance. Although six species of asbestiform minerals are known, the three most commonly encountered types of asbestos in Japanese asbestos industry

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are chrysotile, amosite and crocidolite. These kinds of commercial asbestos are not pure mineral, and are used to contain a lot of impurities such as brucite, talc, magnetite etc.. Furthermore, asbestos manufacturing products are mixture of commercial asbestos and other materials such as calcium carbonate, diatomaceous earth and others. The percentage of asbestos in final products is quite variant and depends on the desired properties of the final products. Consequently the particulates which are generated from processing of manufacture and utilization of asbestos products, are not pure mineral, but the mixture of asbestos and other materials. Therefore we can not evaluate asbestos concentration by means of weighing the amounts of total dust on the scales and estimating the amounts of magnesium or silicon in total dust.

X-ray diffraction method is analytical tool for crystalline substances which are hazards in an occupational and natural environments. The preferred method of quantitative analysis by X-ray diffraction is the internal standard method. Quantitative X-ray diffraction technique, based on internal standard method, was applied to the evaluation of mineral dusts in the air of occupational environment by numerous investigators^{4~9}). They have estimated the minerals which have been implicated as causative agents in silicosis, pneumoconiosis and other related occupational lung diseases. However, it is difficult to apply this internal method to the samples collected for analysis in the field of air pollution and occupational health work, because we could neither collect a fixed amount of dusts on filter, nor prepare to grind or mix an internal standard material with the sample collected by air sampler, without reduction of its amount.

Direct comparison method which does not require the addition of an internal standard is also used for the quantitative analysis of finely divided crystalline powders. This method has been effectively applied to minerals of occupational health significance^{10~16}). Generally speaking, the direct comparison method requires less sample preparation. This procedure is applicable to quantitative determination in the range from 1 to 3 mg of asbestos on the glass filter of 3.8 cm² by means of the ordinary X-ray unit. An amount as small as 0.01 mg on the same filter is detectable by powered X-ray.

There are many merits in this procedure:

- 1) Airborne dust collected on a filter can be analyzed without removal of the dust from the filter. Small amount of samples can be effectively analyzed by X-ray diffraction without loss of sample.
- 2) Using high power X-ray, this procedure can determine asbestos content when sample is of the order of 0.01 mg.
- 3) The amounts of asbestos and other toxic minerals in airborne dust can be estimated simultaneously.
- 4) This method is rapid and non-destructive or non-consumptive. After X-ray diffraction analysis, the sample can be analyzed chemically by X-ray fluorescence.

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REFERENCES

- 1) Subcommittee for threshold limit of the dust (1973). *Jap. J. Ind. Health*, **15**, 289. (in Japanese)
- 2) Ministry of Labour (1973). Kihatsu No. 407 (On sampling and evaluation of airborne asbestos dusts), 1. (in Japanese)
- 3) Japan Association of Industrial Health (1973). *Jap. J. Ind. Health*, **15**, 281.
- 4) Talvitie, N. A. and Brewer, L. W. (1962). *Am. Ind. Hyg. J.*, **23**, 214.
- 5) Hayashi, H. (1963). *Ind. Health*, **1**, 37.
- 6) Hayashi, H. and Oinuma, K. (1964). *Ind. Health*, **2**, 172.
- 7) Crable, J. V. and Knott, M. J. (1966). *Am. Ind. Hyg. Assoc. J.*, **27**, 383.
- 8) Crable, J. V. and Knott, M. J. (1966). *Am. Ind. Hyg. Assoc. J.*, **27**, 449.
- 9) Goodhead, K. and Martindale, R. W. (1969). *Analyst*, **94**, 985.
- 10) Sakabe, H., Matsushita, H., Hayashi, H., Nozaki, K. and Suzuki, Y. (1965). *Ind. Health*, **3**, 126.
- 11) Kaslak, R. and Burnet, D. (1966). *Anal. Chem.*, **38**, 174.
- 12) Crable, J. V. (1966). *Am. Ind. Hyg. Assoc. J.*, **27**, 293.
- 13) Bradley, A. A. (1967). *J. Sci. Instrum.*, **44**, 287.
- 14) Hayashi, H. (1968). *J. Ind. Hyg. Jap.*, No. 9, 70. (in Japanese)
- 15) Hayashi, H. (1970). *Ind. Health*, **8**, 66.
- 16) Crosby, M. T. and Hamer P. S. (1971). *Ann. Occup. Hyg.*, **14**, 65.
- 17) Hayashi, H. (1972). Ekkususen Bunseki no Shinpo IV (Advances in X-ray Analysis), Ekkususen Kogyo Bunseki No. 8. (Edited by Japan Society for Analytical Chemistry), p. 186. Kagaku Gijyutsusha, Tokyo. (in Japanese)