THE MICROSCOPE Vol 57:1 pp 19-22 (2009)

Analysis of Amphibole Asbestos in Chrysotile-Containing Ores and a Manufactured Asbestos Product

J.R. Millette, A. Harmon, P. Few, W.L. Turner Jr., and W.R. Boltin
MVA Scientific Consultants*

KEYWORDS

Asbestos, amphibole, chrysotile, ore, tremolite, minerals, polarized light microscopy (PLM), transmission electron microscopy (TEM), Addison and Davies acid/base digestion

ABSTRACT

Using a heating/acid/base digestion of chrysotile bulk materials and a chrysotile-containing product, provided a very sensitive (<0.0001%) analysis for amphibole asbestos fibers. The analysis showed the presence of amphibole fibers at concentrations below 1% in a sheet gasket and some bulk chrysotile from Black Lake, Quebec, Canada. No amphibole fibers were found in a sample of bulk Union Carbide Calidria chrysotile.

INTRODUCTION

During an analysis using standard polarized light microscopy (PLM) techniques, a sheet gasket sample was found to contain a small amount of tremolite (less than 1%) in addition to the principal component of approximately 90% chrysotile asbestos. Based on general industry knowledge, the tremolite was thought to be associated with the chrysotile component. The association of amphibole fibers with some chrysotile ores has been noted in the scientific literature (1,2). Addison and Davies (3) reported finding 28 of 81 samples of chrysotile positive for tremolite and Ilgren and Chatfield (4) stated that chrysotile from the Jeffrey Mine in Quebec, Canada contained amphiboles but the chrysotile from the deposit in Coalinga, California did not. Williams-Jones et al. (5) reported that the bulk of the amphibole in the Jeffery Mine in Quebec, Canada is in the form of tremolite and actinolite, and is found mainly in sepentinite adjacent to or included within felsic dikes.

The analysis for low levels of amphibole fibers in chrysotile-containing samples requires that samples be prepared in a way that concentrates the amphibole fibers so they may be detected among the more voluminous chrysotile fibers. For example, a sample in which tremolite is present at the 0.01% level in the overall sample where chrysotile is nearly 100%, there will be over 10,000 chrysotile fibers for every tremolite fiber. Eliminating the chrysotile fibers will result in the concentration and detection of very small amounts of tremolite. In the Addison and Davies paper (3), heating combined with an acid/base digestion procedure was used to eliminate the chrysotile in ores and to prepare samples for subsequent analysis by light microscopy, x-ray diffraction, infrared spectrophotometry and scanning electron microscopy.

In the study presented here, a sample of a Garlock 900 gasket and two samples of different chrysotile ore (a Canadian chrysotile and a California chrysotile) were prepared using the Addison and Davies acid/base digestion procedure and then analyzed for amphibole fibers using standard transmission electron microscopy procedures.

* 3300 Breckinridge Boulevard, Suite 400, Duluth, GA 30096

MATERIALS AND METHODS

Materials

The gasket sample was a gray ring of sheet packing (gasket material) with "900 Garlock" printed repeatedly on one side. Analysis by PLM showed that it contained approximately 90% chrysotile by volume. A trace amount of tremolite (less than 1%) along with calcium carbonate, limestone, iron oxide and pigment comprised the remaining material. Magnetite, a common accessory mineral with chrysotile, was also present.

The Canadian chrysotile asbestos sample was collected from a bag of asbestos labeled "5R-4 Asbestos, Black Lake, Quebec, Canada."

The California chrysotile asbestos sample was received from Dr. Eric Chatfield of Chatfield Technical Consultants, Limited, Mississauga, Ontario. It was labeled "RG-144" and described as a sample of Union Carbide Calidria chrysotile.

Digestion Methods

In order to concentrate possible amphibole material, the Addison and Davies acid/base digestion procedure was used to eliminate the chrysotile. For each sample, 0.1 to 0.5 g of test material (chrysotile, product, etc.) was weighed accurately into a porcelain crucible, heated overnight at 600°C in a muffle furnace, allowed to cool, and reweighed. The material was transferred to a 100 ml round-bottom flask fitted with a reflux condenser and containing 80 mL of 2N H_2SO_4.

The suspension was boiled for 1 hour using a magnetic stirrer to prevent the flask from overheating and fracturing. The suspension was transferred to 15 mL centrifuge tubes and centrifuged at 2800 rpm for 30 minutes. The reflux procedure was then repeated using 4N NaOH. The final residue was collected by centrifugation. Residue was washed by resuspension in deionized water and then centrifuged.

Two distilled water centrifugation washes were performed. The residue was suspended in water and a small amount of dilute HCl was added to prevent the precipitation of Mg salts that might interfere with the analysis. Water was added to bring the suspension to 100 mL total volume.

A known aliquot was extracted and filtered through a 0.2 μm pore size polycarbonate filter. The filter was dried and TEM grids prepared following standard direct preparation procedures (6). Laboratory blanks were also prepared using the entire procedure. Examples of the equipment necessary for sample preparation are shown in Figures 1 and 2.

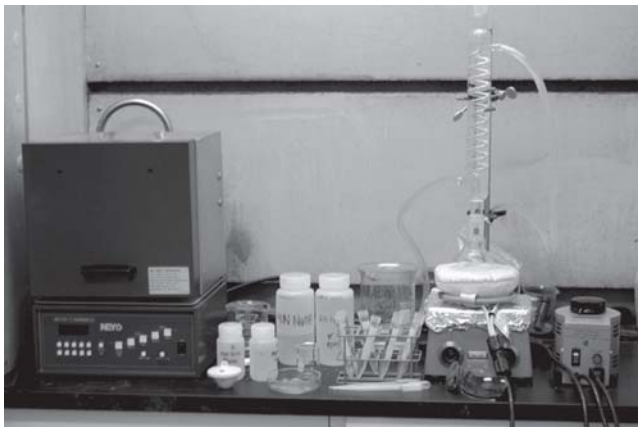

Figure 1. Digestion processing equipment, including furnace, crucible, chemicals, glassware, stirrer, heating mantle, and transformer shown here in a chemical exhaust hood.

Figure 2. Centrifuge used in acid/base digestion process.

Analysis Methods

Sample grids were analyzed by transmission electron microscopy (TEM). Amphibole particles were considered asbestos fibers if they were more than 0.5 mm in length, had at least a 5:1 aspect ratio and had substantially parallel sides. The mass of tremolite fibers was determined by summing the masses of individual fibers found. The mass of an individual fiber was calculated using the formula: length x width^2 x density. A value of 3.00 g/cm^3 was used as the amphibole density (7). (Note: the measured particle width is squared in the formula because particle thickness is assumed to be equivalent to its width).

Reported weight percent amphibole asbestos in each sample was calculated using **Equation 1:**

$$\frac{(M) \times (V_o) \times (EFA) \times 100\%}{(GO) \times (GOA) \times (V) \times (W)}$$

M = total mass of amphibole fibers counted (g)
$\mathbf{V_o}$ = original volume of suspension (mL)
EFA = effective filtration area of the final sampling filter (mm^2)
GO = number of TEM grid openings counted
GOA = average TEM grid opening area (mm^2)
V = actual volume taken from the original suspension and prepared for TEM analysis (mL)
W = original sample weight (g)

RESULTS

Using digestion-enhanced TEM analysis, tremolite was found in the Garlock 900 gasket at a weight percent level of 0.2%. It was noted during the analysis that some apparent amphibole fibers were embedded in matrix material and could not be counted. The single fiber analytical sensitivity of the analysis was 0.0000003%. No amphibole fibers were found in the laboratory blanks. Individual fiber size data are shown in Table 1. Tremolite was found in the Canadian chrysotile from Black Lake, Quebec at a weight percent level of 0.0094%. The single fiber analytical sensitivity was 0.0000003%. No amphibole fibers were found in the laboratory blank. Individual fiber size data are shown in Table 2.

No amphibole fibers were found in the sample of Union Carbide RG-144. The single fiber analytical sensitivity was 0.000000007%. It was noted during the analysis that antigorite fibers were present. In a second analysis of another portion of the same RG-144 material, no amphibole fibers were found. The analytical sensitivity of the analysis was 0.00000002%. Again, it was noted that antigorite fibers were present.

Table 1. Tremolite Fiber Sizes in Garlock 900 Gasket*

Fiber No.	Length (µm)	Width (µm)	Aspect Ratio
1	3	0.25	12
2	3.5	0.6	5.8
3	6.75	0.5	13.5
4	1.5	0.15	10
5	3	0.25	12
6	2.9	0.25	11.6
7	2	0.35	5.7
8	4.2	0.4	10.5
9	2	0.35	5.7
10	2.5	0.35	7.1
11	3.5	0.6	5.8
12	3.6	0.5	7.2
13	3	0.3	10
14	3.2	0.25	12.8
15	2.6	0.25	10.4
16	4	0.2	20
17	3.2	0.5	6.4
18	2.3	0.25	9.2
19	2.5	0.24	10.4
20	1.4	0.25	5.6
21	3.8	0.3	12.7
22	6.1	0.3	20.3
23	6.6	0.3	22
24	3.2	0.3	10.7
25	3.8	0.5	7.6
26	2.3	0.25	9.2
27	4.2	0.2	21
28	8.3	0.6	13.8

*Sample prepared by acid/base digestion.

DISCUSSION

Although the Addison and Davies acid/base preparation procedure reports that the reason the chrysotile sample is heated to 600°C is to aid digestion by opening and dehydrating the chrysotile fibers, this step also eliminates organic material such as cellulose fibers from asbestos products such as the gasket material before the acid/base treatment.

The limited data provided here confirm that amphibole fibers can be found at levels less than 1% in both chrysotile asbestos-containing ores and a manufactured product. The data also indicate that the association between chrysotile and amphiboles in ore deposits is not ubiquitous. Determination of the presence or absence of low-level amphibole fiber concentrations using digestion-enhanced TEM is potentially useful for comparing chrysotile from manufactured products with suspected source ore materials.

Addison and Davies reported that the acid/base preparation procedure improved the sensitivity of the amphibole analysis using x-ray diffractometry by at least 10-fold, giving an amphibole detection limit

Table 2. Tremolite Fiber Sizes in Canadian Chrysotile Sample from Black Lake, Quebec*

Fiber No.	Length (μm)	Width (μm)	Aspect Ratio
1	3.3	0.14	23.6
2	2.4	0.19	12.6
3	2.1	0.14	15
4	2.6	0.38	6.8
5	6	0.24	25
6	2.9	0.19	15.3
7	2.9	0.33	8.8
8	3.1	0.14	22.1
9	10.5	0.29	36.2
10	4.8	0.24	20
11	2.1	0.14	15
12	4.5	0.48	9.4
13	2.6	0.29	9
14	3.3	0.38	8.7
15	2.4	0.29	8.3
16	3.3	0.29	11.4
17	2.4	0.19	12.6
18	5	0.62	8.1
19	2.6	0.1	26
20	5	0.57	8.8
21	3.8	0.14	27.1
22	2.1	0.24	8.8
23	4.3	0.19	22.6
24	2.4	0.12	20
25	2.9	0.19	15.3
26	2.9	0.38	7.6

*Sample prepared by acid/base digestion.

of 0.01-0.05% in chrysotile. The present study demonstrates considerable improvement in TEM analytical sensitivity for amphibole fibers when the acid/base digestion procedure is employed. The theoretical analytical sensitivity of the analysis used in this work is based on finding a tremolite fiber of minimal detection size (length = 0.5 μm, width = 0.025 μm, assumed thickness = 0.025 μm) at typical TEM analysis magnifications (15,000x to 20,000x). Using the minimal fiber size, the single fiber analytical sensitivity (as determined by Equation 1) can be on the order of 0.0000001% to 0.000000001%. While this value should not be considered as a practical detection limit, it does provide a useful way to compare analyses in which no amphibole asbestos is detected.

Using transmission electron microscopy following acid/base digestion can provide a very sensitive (<0.0001%) analysis for amphibole asbestos. Initial observations of the residues by polarized light microscopy do not suggest that the digestion procedures change the refractive indices of the amphiboles significantly. Additional study with multiple analyses will be necessary to determine the variability associated with the digestion-enhanced method in assessing low levels of amphibole in chrysotile-containing ores and manufactured products.

REFERENCES

1. Gibbs, G.W. and LaChance, M. "Dust Exposure in the Chrysotile Mines and Mills of Quebec." Archives of Environmental Health, **24**, pp 189-197, 1972.

2. Nayebzadeh, A., Dufresne, A., Case, B., Vali, H., Williams-Jones, A.E., Martin, R., Normand, C., Clark, J. "Lung Mineral Fibers of Former Miners and Millers from Thetford-Mines and Asbestos Regions: A Comparative Study of Fiber Concentration and Dimension." Archives of Environmental Health, **56 (1)**, pp 65-76, 2001.

3. Addison, J. and L.S.T. Davies. "Analysis of Amphibole Asbestos in Chrysotile and Other Minerals." Ann. Occupational Hygiene, **34 (2)**, pp 159-175, 1990.

4. IIgren, E. and Chatfield, E. "Coalinga Fibre—A Short, Amphibole-free Chrysotile." Indoor Built Environ, **7**, pp 18-31, 1998.

5. Williams-Jones, A. E., Normand, C., Clark, J.R., Vali, H., Martin, R. F., Dufresne, A., and Nayebzadeh, A. "Controls of Amphibole Formation in Chrysotile Deposits: Evidence from the Jeffery Mine, Asbestos, Quebec." The Health Effects of Chrysotile Asbestos: Contribution of Science to Risk-Management Decisions, Can. Mineral., Spec. Publ., **5**, pp 89-104, 2001.

6. ISO 10312. "Ambient Air—Determination of Asbestos Fibres—Direct-transfer Transmission Electron Microscopy Procedure." International Standards Organization, 1995.

7. ISO 13794. "Ambient Air—Determination of Asbestos Fibres - Indirect-transfer Transmission Electron Microscopy Procedure." International Standards Organization, 1999.