

Quantitative Analysis of Airborne Asbestos by X-Ray Diffraction

Final Report on Feasibility Study

L. S. BIRKS, M. FATEMI, J. V. GILFRICH, AND E. T. JOHNSON

*X-Ray Optics Branch
Material Sciences Division*

February 28, 1975



NAVAL RESEARCH LABORATORY
Washington, D.C.

Approved for public release; distribution unlimited. DDC-A

CONTENTS

INTRODUCTION	1
SPECIAL X-RAY DIFFRACTION GEOMETRY	2
SPECIMEN PREPARATION	5
RESULTS	8
DISCUSSION	9
REFERENCES	10
APPENDIX	11

FIGURES

1. (a) X-ray diffraction pattern from randomly oriented asbestos fibers	2
(b) Diffraction pattern from a bundle with preferred orientation	2
2. Morphology of chrysotile asbestos	3
3. Standard diffractometer geometry	3
4. Special x-ray optics for quantitative measurement of aligned asbestos fibers	4
5. Backlighted macrograph of asbestos sample	5
6. Experimental arrangement of the ultrasonic "cell disrupter"	6
7. Special multielectrode grid used in the alignment of asbestos fibers	7
8. Photomicrograph of aligned asbestos sample	7

Quantitative Analysis of Airborne Asbestos

by X-Ray Diffraction:

Final Report on Feasibility Study

INTRODUCTION

The purpose of this report is to introduce a novel x-ray diffraction technique for the measurement of airborne asbestos. It has been recognized for some time that the determination of pollutant levels of asbestos by conventional x-ray diffraction is impractical for two primary reasons: 1.) The x-ray diffraction pattern of chrysotile (which comprises nearly 90% of all asbestos used worldwide) is almost identical to a number of clay minerals of similar chemical composition; 2.) at the concentration levels of interest the x-ray diffraction lines of asbestos are relatively weak and they occur in the presence of a very large background.

As is the case for all fibrous materials, the intensity of a specific diffraction peak of chrysotile or amphibole asbestos is enhanced if the fibers are aligned parallel to each other. Further, if the aligned fibers can be mounted on a suitably thin (low mass) substrate, the background (due to scattering of the incident x-ray beam) can be minimized. In order to investigate the applicability of the x-ray diffraction principle to the asbestos problem, a feasibility study was conducted which addressed the following questions:

- 1.) Can a scheme be devised for aligning small quantities of standard chrysotile fibers and mounting them on a low-mass substrate?
- 2.) Can a special x-ray diffraction geometry be developed which would be optimized for measuring these aligned fibers quantitatively?

Both parts of the task have been accomplished successfully for laboratory samples of chrysotile. The 3σ limit of detection for chrysotile standards is $0.2 \mu\text{g}$ for ten-minute measurements. Thus, the method appears feasible and ready for further development into a practical tool for quantitative analysis of source or ambient air samples.

SPECIAL X-RAY DIFFRACTION GEOMETRY

Chrysotile asbestos, like all crystals, has a characteristic x-ray diffraction pattern. However, platy serpentine has almost exactly the same x-ray pattern as chrysotile and many other clay minerals have very similar patterns. Therefore, preferred orientation of the chrysotile fibers offers the only hope of distinguishing chrysotile uniquely. Figures 1a and 1b show x-ray patterns from random orientation and preferred orientation, respectively. In a mixed sample of platy serpentine and chrysotile, the serpentine rings would be superposed on the chrysotile arcs. The net intensity due to chrysotile is obtained by measuring the intensity at the arc position (A in Figure 1), and subtracting the intensity of the ring at 90° to the arc, position B. This simple principle forms the basis for the method developed at the Naval Research Laboratory. But several factors make the problem difficult as will be described in the following paragraphs.

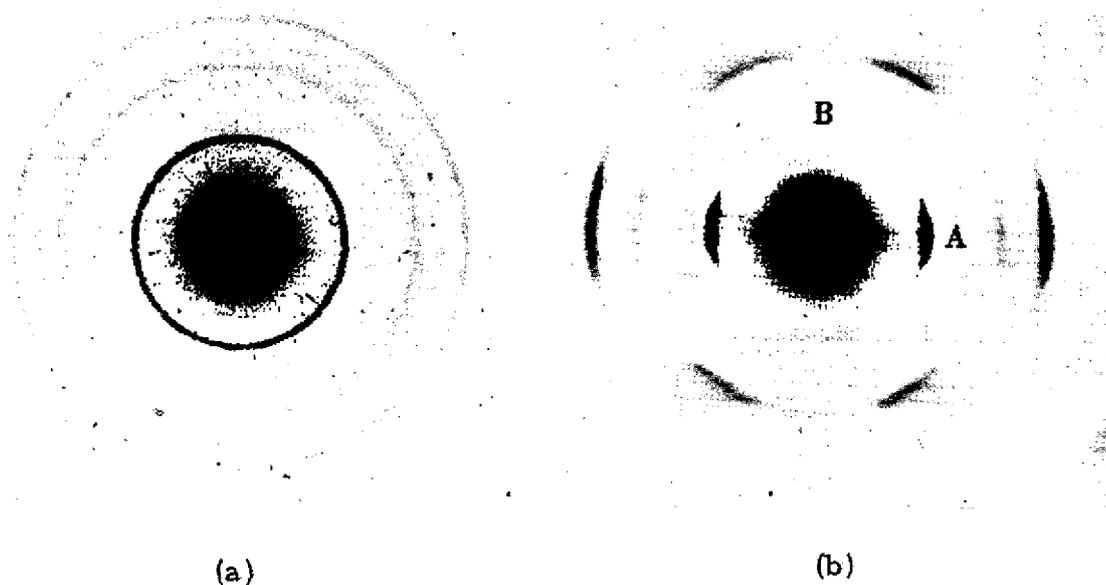


Figure 1. X-ray diffraction patterns (a) from randomly oriented asbestos fibers and (b) from a bundle with preferred orientation.

The first factor which makes measurement of asbestos difficult is that the quantity which can be collected from a reasonable amount of air is far too small to measure with x-ray film cameras. Therefore, diffractometers with electronic detectors are required, but this introduces a second difficulty because of the peculiar morphology of chrysotile. This morphology, which is that of a "rolled up" sheet of crystalline matter, is shown schematically in Figure 2. The a-axis of the monoclinic structure is parallel to the fiber axis; the c-axis is nearly perpendicular to the tube wall. Thus the axes b and c take

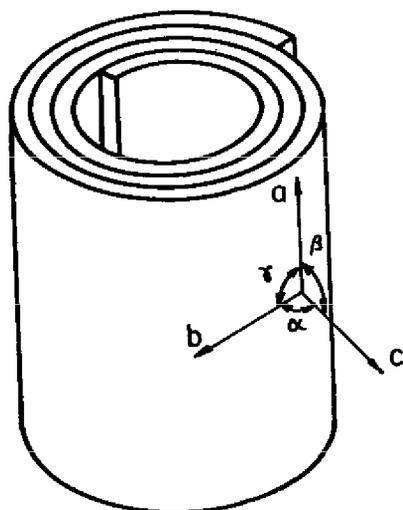


Figure 2. Morphology of chrysotile asbestos.

$$\alpha = \gamma = 90^\circ, \quad \beta = 93^\circ 16'.$$

different orientations depending on where on the fiber they are set up. This means that standard diffractometer geometry cannot be used even with an oriented sample because the major crystal plane, (002), diffracts equally well for either orientation; see Figure 3. Therefore a special geometry was developed specifically for asbestos.

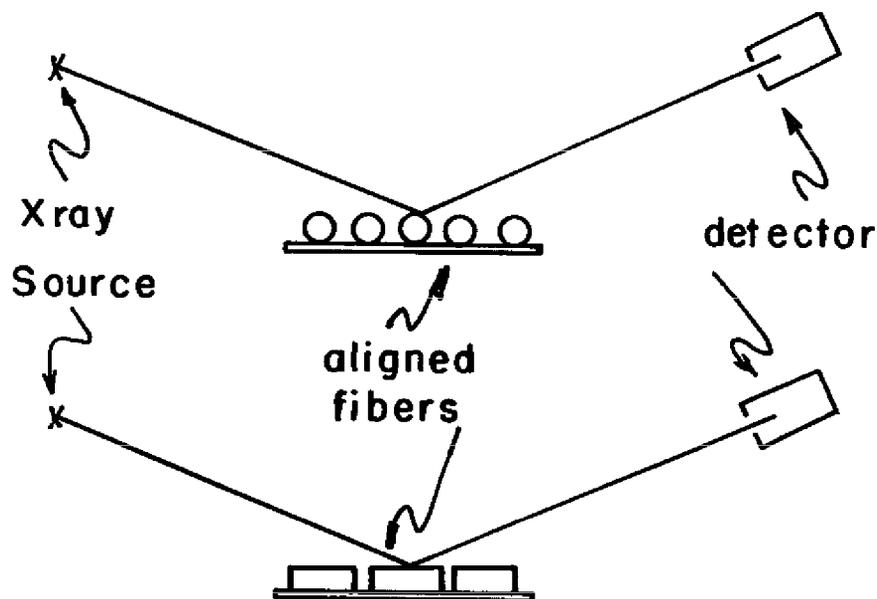


Figure 3. Standard diffractometer geometry. Diffraction from (002) planes is possible for all fiber rotations (where the axis of rotation is in the diffraction plane and perpendicular to fiber axis).

The geometry employed is shown schematically in Figure 4. Because of the manner in which the alignment is accomplished (described in the following section), the sample of asbestos is distributed over a circular area of about 1 cm diameter (as shown in Figure 5). In order to achieve diffraction from the entire sample, resulting in the highest signal, a large-cross-sectional-area x-ray beam is required;⁽¹⁾ in order to maintain good resolution, fine collimation is required. Figure 4 illustrates the use of a tubular-collimated broad x-ray beam from a spectrographic x-ray tube rather than a diffraction tube. The sample is mounted perpendicular to the x-ray beam to give an oriented pattern conceptually similar to Figure 1b. Using a chromium target x-ray tube the 2θ value for diffraction from (002) planes, $2d = 14.6 \text{ \AA}$, is 18° . By placing detectors at the two positions shown in Figure 4, the signal and background intensities are recorded simultaneously. During this feasibility study only one detector was available, so the signal and background were measured sequentially by rotating the sample 90° in its own plane between readings.

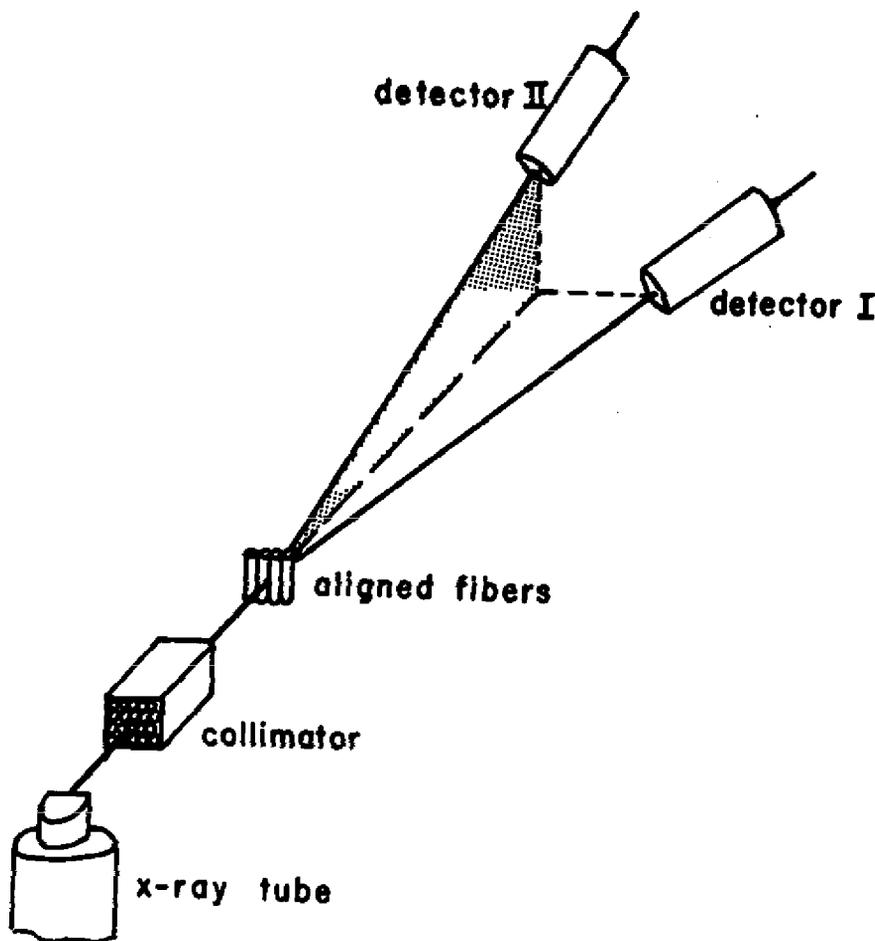


Figure 4. Special x-ray optics for quantitative measurement of aligned asbestos fibers.

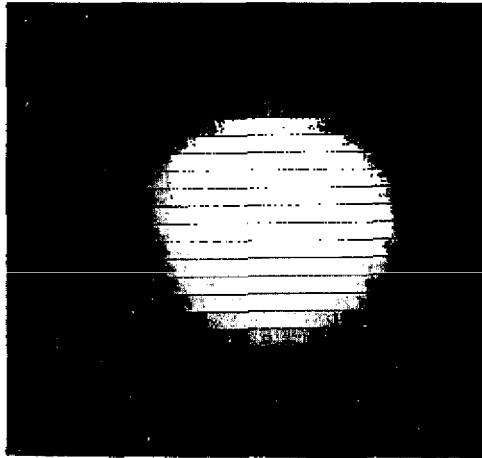


Figure 5. Backlighting macrograph of asbestos sample showing the distribution of aligned fibers on the multielectrode alignment grid; 3 X magnification.

SPECIMEN PREPARATION

Electrostatic alignment of asbestos fibers appeared to be the most obvious approach and had been suggested by an early patent. (2) This patent, however, concerned itself with bulk alignment of relatively large quantities of fibers in a liquid dielectric medium. For the small amounts of asbestos to be measured by the x-ray technique, the procedure described in reference 2 did not succeed in aligning the fibers completely enough to achieve optimum x-ray sensitivity nor was it possible to recover the specimen quantitatively from the alignment medium.

A significantly different alignment procedure (described below) was employed to produce a sample which was directly suitable for the x-ray measurements. Initial attempts did not accomplish adequate alignment, however, because of the "silky" nature of the chrysotile fibers. Breaking these "silky" fibers into straight fibrils was necessary if the full potential of the x-ray technique was to be realized. Ordinary ultrasonic cleaners were unsatisfactory, but the "cell disrupter" type, illustrated in Figure 6, succeeded in reducing the fiber size sufficiently.

Without going into detail on the numerous variations in sample preparation which were tried, the following procedure has been adopted and used successfully for orienting chrysotile standards:

Step 1. 3.0 mg of UICC standard Canadian chrysotile is placed in 1/2 ml of 1% aerosol OT solution in water. (The OT is necessary as a dispersing agent.) The suspension is sonicated for 45 minutes at 100 watts power using the cell disrupter as shown schematically in Figure 6.

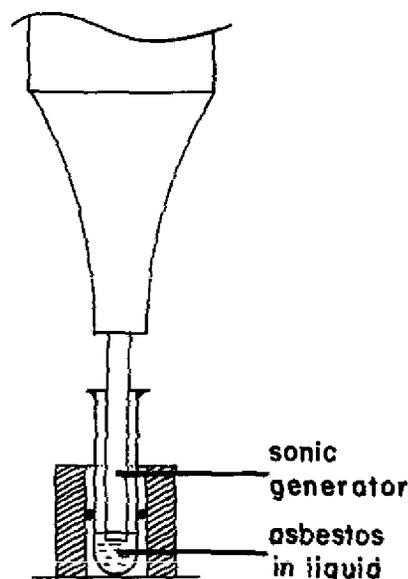


Figure 6. Experimental arrangement of the ultrasonic "cell disrupter" for reducing the size of the fibers.

Step 2. The sonicated suspension is diluted to 500 ml, making the asbestos concentration $6 \mu\text{g/ml}$.

Step 3. A 25 ml aliquot of the diluted suspension (containing $150 \mu\text{g}$ of asbestos) is vacuum filtered onto a 25-mm disk of millipore.

Step 4. The millipore disk is folded and placed in a test tube and ashed for 2-1/2 hours in a low-temperature radio-frequency asher.

Step 5. 30 drops of a 0.001% solution of parlodion in distilled amyl acetate is added to the ashed residue, and the suspension is sonicated for 8 minutes to insure homogeneous distribution of asbestos.

Step 6. One drop of the suspension containing $5 \mu\text{g}$ asbestos is placed on a special grid, Figure 7, and 240 volts AC is applied to the electrodes (preparation of the grid is described in Appendix 1). It takes about 5 minutes for the amyl acetate to evaporate (the voltage is kept on the electrodes until evaporation is complete). Figure 5 shows the appearance of the dried sample, and Figure 8, at higher magnification, shows the alignment of the chrysotile fibers.

Step 7. A solution of 2.5% parlodion in amyl acetate is sprayed gently onto the dried sample to embed the fibers in a thin plastic film which can easily be removed by dipping the grid plate into water. This film has a mass density of about $60 \mu\text{g/cm}^2$; the reason for wanting a thin film is to minimize the background intensity contributed by x-ray scattering from the film.

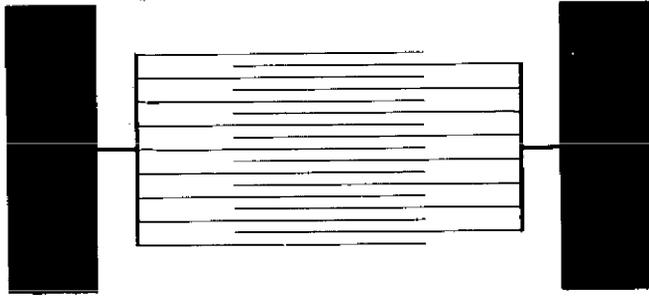


Figure 7. Special multielectrode grid used in the alignment of asbestos fibers. Interelectrode distance is approximately 0.8 mm.

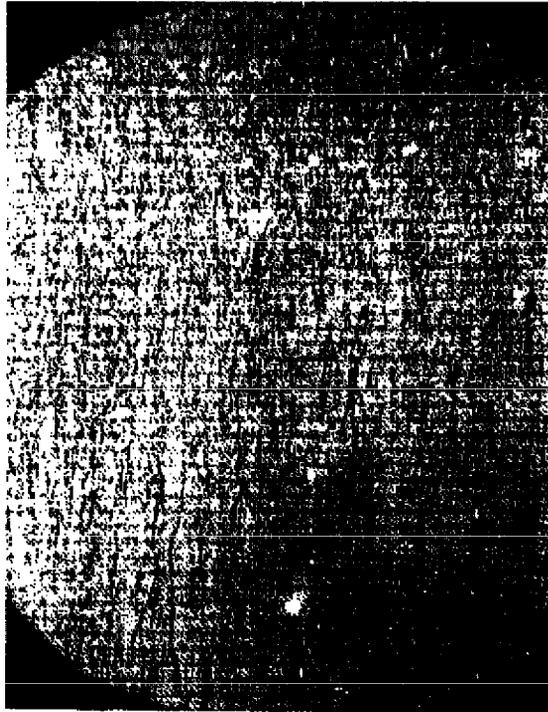


Figure 8. Photomicrograph of aligned asbestos sample; 500 X magnification.

RESULTS

Seven inexperienced test subjects were selected to try out the alignment procedure as described above. Their results are shown in Table I.

TABLE I. MEASUREMENTS OF ASBESTOS STANDARDS

Analyst	Quantity of Asbestos per sample (μg)	Signal Above Background (c/s)	Background (c/s)	Sensitivity S (c/s/ μg)	C_L^* (μg)
1	4.89	32.9	48.3	6.8	0.14
		27.9	63.0	5.7	0.18
		21.5	55.0	4.4	0.22
		30.3	55.5	6.2	0.16
2	4.38	23.3	44.5	5.3	0.17
		19.6	51.7	4.5	0.22
		30.7	36.9	7.0	0.12
3	4.75	32.9	54.5	6.9	0.14
		33.3	50.3	7.0	0.14
		21.4	39.5	4.5	0.19
		21.0	33.8	4.4	0.18
4	4.75	24.7	46.7	5.2	0.18
		25.9	54.4	5.4	0.18
		24.5	48.0	5.2	0.18
5	4.32	25.6	35.8	5.9	0.13
		28.4	33.4	6.6	0.12
		28.5	28.4	6.6	0.11
		27.9	35.2	6.5	0.12
6	4.75	32.9	35.4	6.9	0.11
		31.4	31.9	6.6	0.11
		31.2	36.4	6.6	0.12
7	4.75	23.1	45.0	7.0	0.13
		28.2	67.5	5.9	0.19
		24.4	59.1	5.1	0.20
	Average			5.9	0.16
	Relative Standard Deviation =			16%	

* Limit of Detection, C_L , from the Formula

$$C_L = 3\sqrt{N_B}/(S \times \text{Time}),$$

where N_B is the background over the counting interval, which conforms to the definition recommended by IUPAC.

In this table, C_L is calculated for a 500-second counting interval.