(621)

Reprinted from ADVANCES IN X-RAY ANALYSIS, VOL. 18 1975
Edited by W. L. Pickles, C. S. Barrett, J. B. Newkirk, and C. O. Ruud
Book available from Plenum Publishing Corporation
227 West 17th Street, New York, New York 10011

SEMI-QUANTITATIVE DETERMINATION OF ASBESTIFORM AMPHIBOLE MINERAL CONCENTRATIONS IN WESTERN LAKE SUPERIOR WATER SAMPLES

P. M. Cook

National Water Quality Laboratory, U. S. EPA

Duluth, Minnesota 55804

ABSTRACT

The amphibole mineral, cummingtonite-grunerite, has been used as a tracer for taconite tailings discharged into Western Lake Superior. The discovery of many asbestiform amphibole fibers in the tailings and Western Lake Superior water lead to concern over fiber concentrations in municipal water supplies using this water. This concern was based on the association between human asbestos exposure and increased rates of cancer of the gastrointestinal tract and peritoneum. An x-ray diffraction external standard technique has been developed for rapid, inexpensive, semi-quantitative determinations of amphibole mass concentration in water. The average amphibole mass concentrations for different Western Lake Superior water intakes compare very well with the average electron microscope fiber counts for the same samples. Daily amphibole analysis of the Duluth water supply indicates an average amphibole concentration of 0.19 milligrams per liter.

INTRODUCTION

For several years x-ray diffractometry has been the key analytical technique for National Water Quality Laboratory studies of the distribution and fate of taconite tailings which have been discharged into Western Lake Superior at Silver Bay, Minnesota since 1956. A major component of this 67,000 ton per day discharge, the amphibole mineral cummingtonite-grunerite, provides an ideal tracer for the tailings. The cummingtonite-grunerite (310) peak at 29.1° 2θ for copper K_α radiation (d = 3.07 Å) is not found in x-ray diffraction patterns for natural lake sediments or suspended

Presented 23rd Annual Conference on X-Ray Analysis
August 7-9, 1974

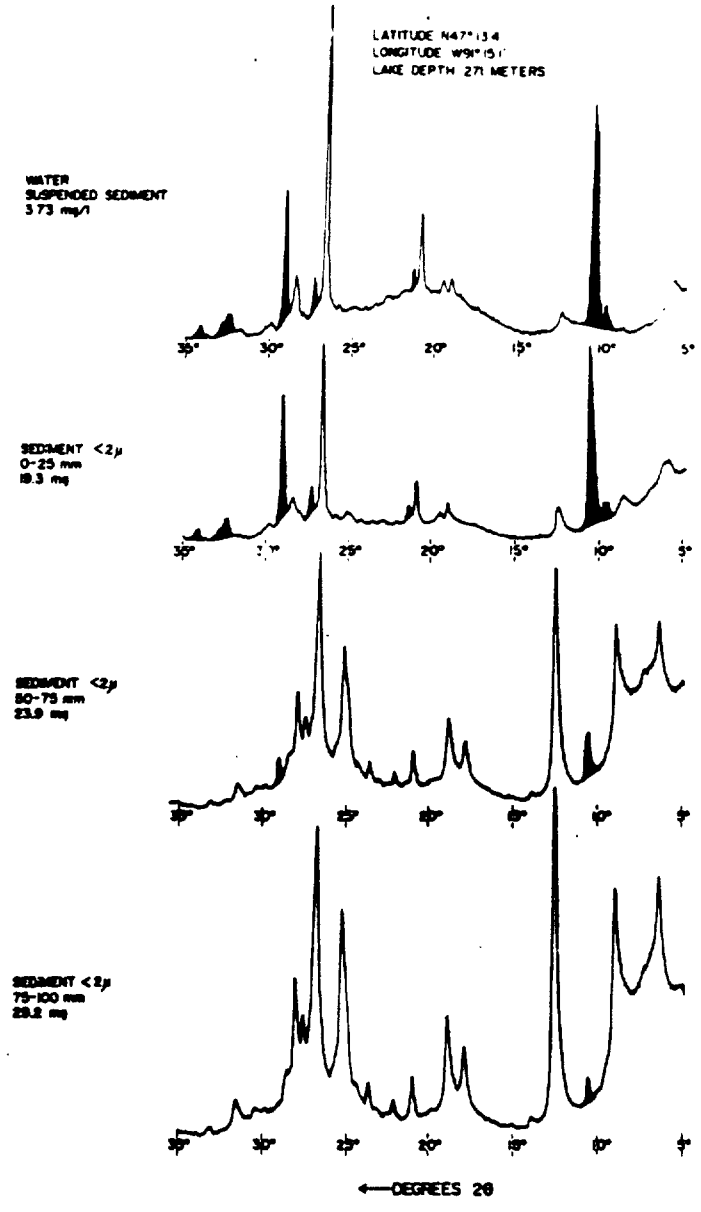

FIGURE 1---X-RAY DIFFRACTION PATTERNS (COPPER RADIATION) FROM SEDIMENT SAMPLES TAKEN AT SUCCESSIVE 25 MM INTERVALS IN AN AREA OF TACONITE TAILINGS DEPOSITION. CUMMINGTONITE-GRUNERITE, $(Mg,Fe)_7Si_8O_{22}(OH)_2$, PEAKS ARE SHADED. THE (110) PEAK AT APPROXIMATELY 10.6° 2θ IS COMMON TO MOST AMPHIBOLES

solids. X-ray diffraction patterns (Figure 1) of lake water suspended solids which contain taconite tailings and sediment from successive 25 mm sections of the lake bottom in an area of tailings deposition show a clear gradation from large amounts of cummingtonite-grunerite (shaded peaks) in very recent surficial sediments to no cummingtonite-grunerite and little amphibole in the older, underlying sediments (75-100 mm). X-ray diffraction study of hundreds of river suspended sediment samples also indicates no detectable cummingtonite-grunerite (<1%) and only 1-2% amphibole in the natural sediments entering Western Lake Superior. Much or all of the trace amphibole is the common, non-asbestiform mineral hornblende.

Further indication of the recent addition of cummingtonite-grunerite to Western Lake Superior water is provided by x-ray diffraction patterns of many suspended sediment samples saved from the years 1940, 1950, and 1964 (Figure 2). All samples from 1940 and 1950 did not contain detectable amounts of cummingtonite-grunerite and little if any other amphibole minerals as indicated by a (110) peak at 10.6° 2θ (d = 8.34 A). All of the 1964 samples, however, contained large concentrations of cummingtonite-grunerite as shown by the appearance of large (110) and (310) peaks. The (110)/(310) peak ratios for these samples are typical of those found for taconite tailings samples.

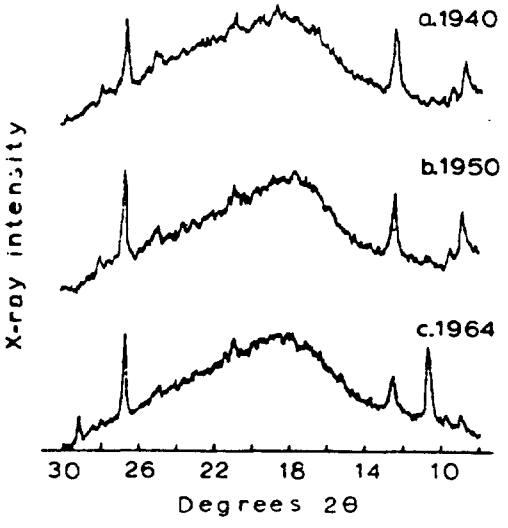

FIGURE 2---X-RAY DIFFRACTION PATTERNS FOR SUSPENDED SOLID SAMPLES OBTAINED FROM THE DULUTH MUNICIPAL WATER SUPPLY INTAKE: A HISTORICAL RECORD OF AMPHIBOLE CONCENTRATIONS IN DULUTH'S DRINKING WATER

In 1973, study of the morphology of amphibole particles in fine taconite tailings by transmission electron microscopy revealed the presence of many asbestiform fibers (Figure 3). The realization that many of these cummingtonite-grunerite fibers are indistinguishable from amosite asbestos fibers lead to concern over the use of Western Lake Superior water for municipal drinking water supplies. This concern was based on the association between human asbestos exposure and increased rates of cancer of the gastrointestinal tract and peritoneum (1) and daily x-ray diffraction analyses of Duluth, Minnesota drinking water samples which indicated the constant presence of high concentrations of taconite tailings. Transmission electron microscope analysis of Duluth water samples confirmed the presence of many amphibole fibers.

Since the discovery of asbestiform amphibole fibers in the water supplies of Silver Bay, Beaver Bay, Two Harbors, Duluth, and Cloquet, Minnesota, extensive sampling programs by the Environmental Protection Agency and other groups have been undertaken for electron microscope fiber counts. These analyses while in agreement with the x-ray diffraction results, are very expensive, time-consuming, and imprecise. At this time fiber counts done by different laboratories are not comparable and intralaboratory replicate results usually vary by ± 50% of the mean. The amphibole fiber concentrations generally correlate with the amphibole mass concentrations determined by x-ray diffraction. Thus x-ray diffraction monitoring of water samples combined with occasional electron microscope fiber counts offers a faster, less expensive, and probably more accurate measure of amphibole fiber contamination. This technique has been particularly useful for evaluating various filtration media's abilities to remove amphibole fibers from drinking water.

AMPHIBOLE ANALYSIS OF WATER SAMPLES

Water samples from Western Lake Superior public water supplies, normally ten liters in volume, are pressure filtered through 0.45μ membrane fibers. When the turbidity of the sample is known, the volume filtered is adjusted to give a 4-8 mg sediment sample. The total suspended solids are determined by difference and a weighing correction applied to compensate for a small filter weight loss due to leaching (2). Distilled water blanks are run periodically to check for contamination. The dry membrane filter with sample is fastened to a glass slide with a thin film of lacquer, the filter edges trimmed, and the slide directly examined with a Norelco vertical diffractometer (copper K_α radiation) with a graphite crystal focusing monochromator.

The amphibole fibers and cleavage fragments assume a preferred orientation such that the c-axis, which corresponds to the long dimension of the fiber, is parallel to the filter surface. This

FIGURE 3—-ELECTRON MICROGRAPH OF <2μ TACONITE TAILINGS. a) LOW MAGNIFICATION (2,500X). b) HIGHER MAGNIFICATION (12,500X) VIEW OF AN AMPHIBOLE FIBER BUNDLE

causes the (110) reflection and, to a lesser extent, the (310) reflection intensities to be enhanced, permitting the detection of trace amounts of amphibole. As little as 0.05 mg of <2μ cummingtonite-grunerite produces measurable (110) and (310) peaks.

A semi-quantitative measurement of the amphibole concentration is made by an external standard technique. This technique has been

used to estimate trace amounts of chrysotile asbestos and amphibole asbestos in dust samples on membrane filters (3,4) and fulfills the need for rapid, standardized estimates of amphibole concentration in samples which are not amenable to the use of an internal standard. Three potentially large sources of systematic error had to be considered before accepting the external standard model: variability of particle size, sample mass absorption coefficient, and amphibole preferred orientation.

The external standard chosen for the preparation of standard curves of x-ray peak intensity versus mass of amphibole was the amphibole mixture found in the <2μ taconite tailings. This choice was made since the predominant amphibole in Western Lake Superior water is cummingtonite-grunerite from taconite tailings and natural amphibole concentrations in Lake Superior water are normally not detectable by x-ray diffraction. The <2μ taconite tailings were determined by the x-ray diffraction of cummingtonite-grunerite/quartz mixtures to contain approximately 80% amphibole and 20% quartz. Most of the amphibole is cummingtonite-grunerite with some actinolite-tremolite. Larger size fractions of the tailings contain less amphibole and more quartz with a small percentage of magnetite.

Reference samples were prepared by adding known amounts of the <2μ amphibole standard to ten liter samples of Lake Superior water having no detectable amphibole minerals. This water, obtained from Grand Marais, Minnesota, contained 0.4 mg/l suspended solids which consisted primarily of organic debris, diatoms, quartz, and clay minerals. These standard samples were then filtered and analyzed by x-ray diffraction in the same manner as unknown samples. The resulting x-ray diffraction patterns are identical in appearance to those for Duluth water samples.

The <2μ amphibole particle size (by gravity settling) for the external standard was shown to be appropriate by a centrifugation size-separation of Duluth water suspended solids from samples taken on fifteen different days. Ninety-five percent of the suspended solids were in the <2μ fraction with only a small amount of amphibole in the 5% which was >2μ. Thus variability in diffracted x-ray intensity due to mineral particle size >2μ is insignificant.

The filtration of ten liters of Duluth water normally results in 4-8 mg of suspended solids retained on the 0.45μ membrane filter. When the suspended solids exceed 0.8 mg/l, smaller volumes are filtered. A sample weight of 8 mg and an average density of 2 g/cm^3 results in a hypothetical sample thickness of 3μ on the filter. This thin sample thickness should preclude variability due to differences in sample absorption coefficients. Direct evidence for this is provided by the linearity of a plot of percent amphibole versus x-ray intensity for samples in this weight range; the uniform

intensity of filter background in the x-ray diffraction pattern with increasing sample weight to 10 mg; and the linearity of a plot of quartz peak (d = 3.33 Å) intensity versus weight of quartz, regardless of total sample weight in the range 0–12 mg.

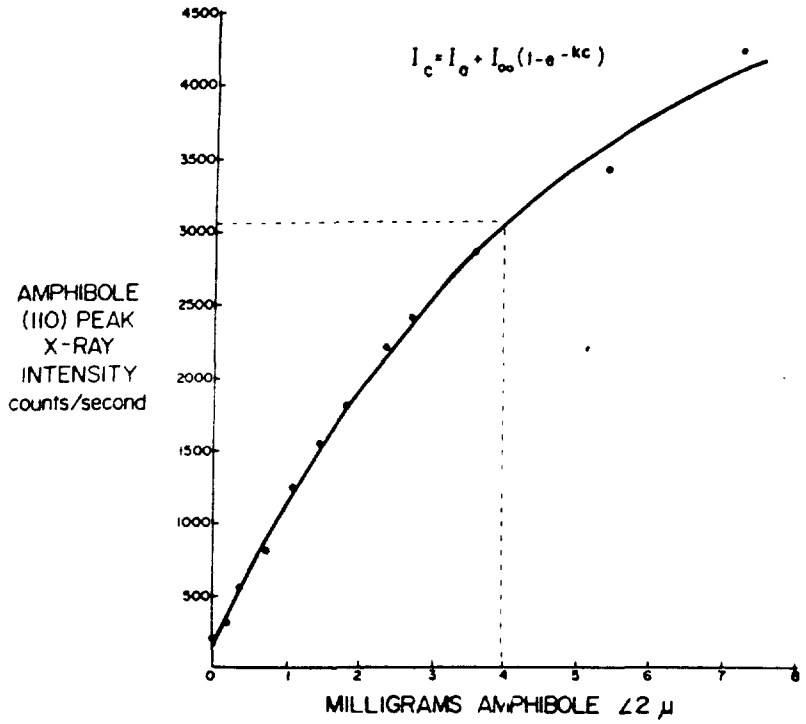

FIGURE 4---EXTERNAL STANDARD CURVE FOR AMPHIBOLE SEMI-QUANTITATIVE ANALYSIS

The non-linearity of the external standard curve (Figure 4) is due to a decreasing degree of preferred orientation as the amount of amphibole increases. This is indicated by decreasing amphibole (110)/(310) and amphibole (110)/quartz peak ratios with increasing weight of the standard amphibole-quartz mixture on the filter. The utility of the external standard curve depends on how well the curve models amphibole preferred orientation in environmental samples. Similar curves based on samples prepared with increased amounts of natural sediment agreed well with the standard curve used. With large amounts of natural sediment, the amphibole peak intensity is weakened which would cause an underestimation of amphibole concentrations. Other standard curves were employed to estimate the amphibole concentration in the few samples with a very high concentration of non-amphibole minerals.

External standard curves, such as Figure 4, were plotted from the non-linear least squares refinement of amphibole mass versus amphibole (110) peak intensity data points. The data fit an equation of the form: $I_C = I_o + I_\infty(1 - \exp{-kC})$, where I_C = intensity at concentration C (mg amphibole); I_o = intensity at C = 0; I_∞ = intensity at C = ∞; and k is a constant. This equation is consistent with a model in which the degree of preferred orientation decreases as more amphibole particles are placed on the membrane filter. Standard curves utilizing amphibole (110) peak height above background are identical to curves plotted from the (110) peak areas. Both measurements are used and give the same amphibole concentrations for environmental samples. Use of an amphibole (310) peak curve gives the same results but with less precision due to lower peak intensity.

Replicate (five) analyses of Duluth water samples indicate a standard deviation of ± 3% for determining amphibole concentrations in typical samples with 0.1-0.3 mg/l amphibole. For samples having lower amphibole concentrations (<0.1 mg/l) and high suspended solids (>1.0 mg/l), this precision is reduced to ± 25%. Overall suspended solids determinations have a standard deviation of ± 6% of the mean. Detection limits for determining amphibole concentration depend on the volume of water filtered and can be as low as 0.5 µg/l.

WATER SUPPLY AMPHIBOLE ANALYSIS

Daily analyses of Duluth water samples for amphibole and suspended solids concentrations began in March 1973 and continues to date. Results through January of 1974 are shown in Figure 5 with climatological data and intake water temperatures. X-ray diffraction analysis provides a picture of daily and seasonal fluctuations in amphibole and suspended solids concentrations. For example, periods of heavy rainfall are followed by abrupt increases in suspended solids due to river run-off and shore erosion. These increases in suspended solids do not coincide with increases in amphibole, indicating a different source for amphibole sediment.

Maximum amphibole concentrations (up to 0.8 mg/l) occur in the late fall and spring. Minimum amphibole concentrations (0.04 mg/l) occur during the late summer and early fall when a thermocline is present in Western Lake Superior. The average amphibole concentration measured was 0.19 milligrams per liter with 0.83 milligrams per liter total suspended solids.

During the period August 22-November 28, 1973, personnel from Region V of the Environmental Protection Agency obtained weekly water samples from municipal water supplies using Lake Superior water from Grand Marais, Minnesota to Marquette, Michigan. These

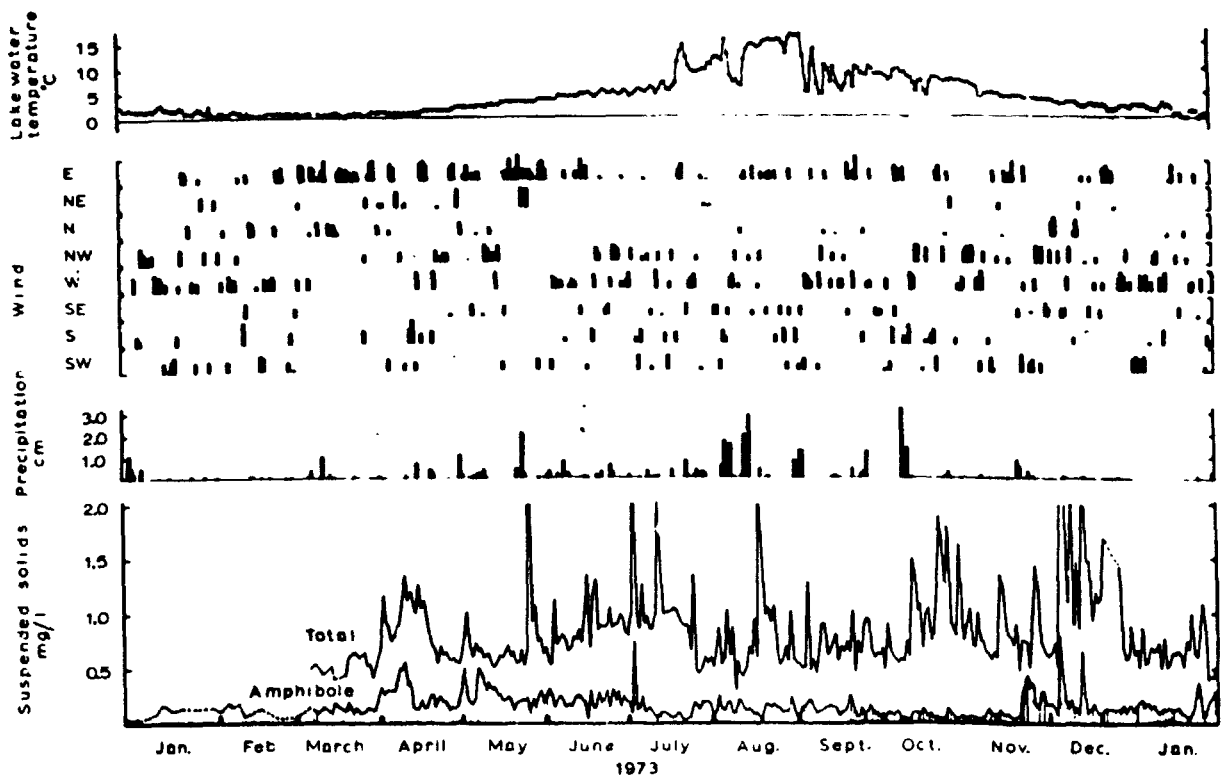

FIGURE 5---DAILY AMPHIBOLE AND SUSPENDED SOLIDS CONCENTRATIONS FOR DULUTH WATER WITH CLIMATOLOGICAL DATA AND WATER INTAKE TEMPERATURES

samples were analyzed for amphibole mass concentration at the National Water Quality Laboratory and amphibole fiber concentration by transmission electron microscopy at the Ontario Research Foundation in Sheridan Park, Ontario and McCrone Associates in Chicago, Illinois. Figure 6 depicts the average x-ray diffraction and electron microscope measurements for each station. The agreement between these two measurements is obviously very good. The pattern of maximum concentrations at Beaver Bay and decreasing concentrations in a counterclockwise direction around Western Lake Superior is consistent with large quantities of amphibole fiber discharged at a point between the Silver Bay and Beaver Bay, Minnesota water supply intakes and then transported towards Duluth (southwest) by the predominantly counterclockwise currents of Western Lake Superior (5).

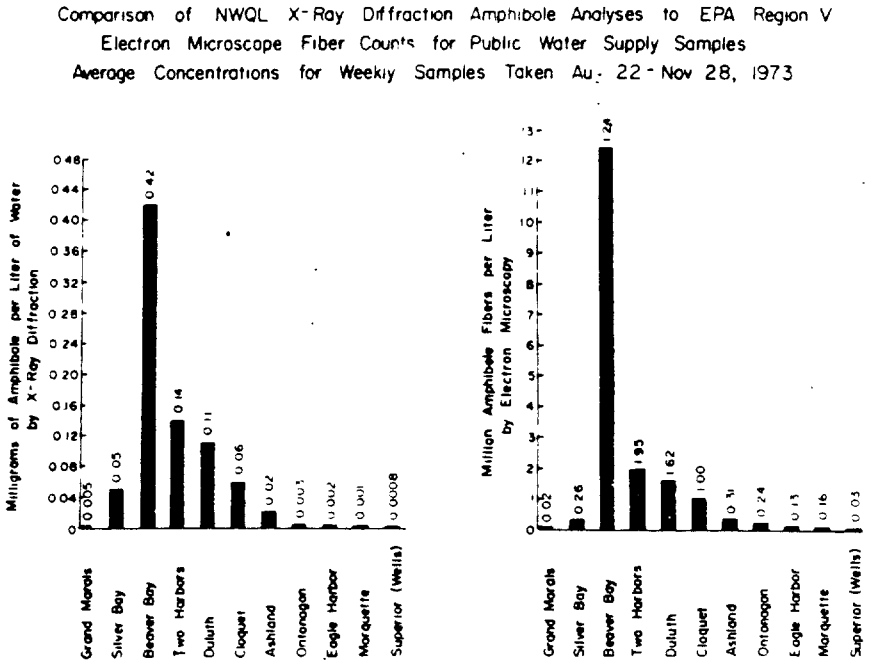

FIGURE 6---COMPARISON OF AMPHIBOLE MASS CONCENTRATION DETERMINED BY X-RAY DIFFRACTION TO TRANSMISSION ELECTRON MICROSCOPE AMPHIBOLE FIBER COUNTS FOR LAKE SUPERIOR WATER INTAKES

ACKNOWLEDGEMENTS

The author wishes to gratefully acknowledge the assistance of Mr. James Tucker of the National Water Quality Laboratory for electron microscope examinations of water and tailings samples; Mr. Robert Fulton and Mr. David Marklund for their excellent work in preparing many of the samples examined by x-ray diffraction; and Dr. Billy Fairless of the Environmental Protection Agency, Region V, Central Regional Laboratory, for providing water intake fiber counts.

REFERENCES

1. I. J. Selikoff, E. C. Hammond and J. Churg, "Carcinogenicity of Amosite Asbestos," Arch. Environ. Health 25, 183-186 (1972).

2. J. G. Eaton and G. E. Likens, "Use of Membrane Filters in Gravimetric Analyses of Particulate Matter in Natural Waters," Water Resources Res. 5, 1151-1156 (1969).

3. A. L. Rickards, "Estimation of Trace Amounts of Chrysotile Asbestos by X-Ray Diffraction," Anal. Chem. 44, 1872-1873 (1972).

4. J. V. Crable, "Quantitative Determination of Chrysotile, Amosite, and Crocidolite by X-Ray Diffraction," Am. Ind. Hyg. Assoc. J. 27, 293-298 (1966).

5. C. E. Adams, "Summer Circulation in Western Lake Superior," Proc. 13th Conf. on Great Lakes Res., 862-879 (1970).