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Asbestos in Water

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14.1 Background

Asbestos is a commercial/industrial term rather than a mineralogical term that refers to a group of hydrated silicate minerals that occur naturally in fibrous bundles [1]. This unique fibrous morphology imparts properties such as high tensile strength and heat resistance that have made these minerals commercially valuable, especially in the twentieth century [2]. Six minerals are generally recognized as asbestos. Chrysotile, the only serpentine asbestos, is actually formed when a silicate layer is scrolled inside an opposing brucite (MgOH) layer. This is the most widely exploited type of asbestos, accounting for more than 90% of historical worldwide production (Figure 14.1). The other five regulated asbestos types are amphiboles, with double-chain silicate layers sandwiching cations. Amosite, an iron-rich fibrous grunerite, was named for its mine source, Asbestos Mines of South Africa. Crocidolite, also predominantly from South Africa, is fibrous riebeckite. It is characterized by its iron and sodium content. Anthophyllite asbestos is anthophyllite’s (a Mg amphibole) fibrous form and was exploited most widely in Finland. Tremolite asbestos and actinolite asbestos are fibrous forms of tremolite and actinolite, which are the end members of a solid-solution series of calcic amphiboles.

A primary source of asbestos in water is naturally occurring asbestos in bedrock. Asbestos is generally associated with certain types of ultramafic rocks and as such, its presence can be predicted [3]. Another source of waterborne asbestos is asbestos–cement pipes that are deteriorating from aggressive water or severe fluctuations in hydraulic activity, or have been damaged by improper maintenance [4].

14.2 Health

The diseases caused by asbestos were recognized even before the beginning of the twentieth century. Asbestosis, some lung cancers, and mesothelioma are now clearly linked to inhalation of asbestos. The extremely narrow (<0.1 μm) diameter of airborne asbestos fibers allows them to bypass the upper respiratory gauntlet and reach the lungs’ alveoli. Macrophages are unable to remove the long fibers deposited in the alveoli and the fibers’ silicate durability ensures long residence. A variety of chemical and mechanical perturbations can eventually lead to the mutations that cause cancer [5].
A linkage between ingestion of asbestos and disease is less clear cut. Small asbestos fibers can pass through the intestinal submucosa and migrate throughout the body, but the fate of these fibers and their relationship to disorders are not well understood [6,7]. Only a modicum of research concerning health impacts of asbestos in water has been published since a review by Webber and Covey in 1991 [8]. One recent study documented a correlation between asbestos in drinking water and stomach cancer [9] while another did not [10]. An investigation of rats that ingested chrysotile-laden drinking water revealed significant \( p < 0.05 \) mesothelial proliferation and asbestos bodies in lungs [11]. The authors concluded that ingested asbestos traveled from the gastrointestinal system to the lungs, likely via a lymphohematological route. A noningestion route of hazard of asbestos in drinking water was suggested when increased concentrations of airborne asbestos were detected in Woodstock, NY, houses with asbestos-contaminated drinking water [12]. The investigators speculated that a portion of drinking water evaporated on household surfaces, leaving behind fibers that later became entrained into the air. A study of the Woodstock residents 20 years later did not see a likely link between exposure to asbestos in drinking water and cancer occurrences [13]. Because of nonmalignant gastrointestinal tumors associated with long-fibered asbestos in rat diets, the U.S. Environmental Protection Agency (EPA) in 1985 promulgated a maximum contaminant level (MCL) of 7 million fibers per liter (MFL) of asbestos fibers longer than 10 μm [14]. The World Health Organization, on the other hand, concluded that ingestion of asbestos from drinking water did not pose a risk of increased cancer [15].
14.3 Analysis

14.3.1 Analytical Instruments

Asbestos imposes a unique analytical challenge. Its constituent elements (Si, Mg, Fe, Ca, Na) are so ubiquitous that elemental fingerprints would not work. Furthermore, the crystalline structures of the various asbestos types are identical to their nonfibrous mineral analogs. Hence, for example, x-ray diffraction cannot differentiate crocidolite from riebeckite or amosite from grunerite.

This leaves the analyst with microscopy as the only suitable method for confirming the fibrous morphology of asbestos minerals. Phase-contrast microscopy, used for monitoring airborne fibers in occupational settings [16,17], is not suitable for water because it can neither detect fibers narrower than 0.2 μm nor differentiate asbestos fibers from nonasbestos fibers. Polarized-light microscopy is capable of identifying all six types of asbestos, but its resolution is limited to fibers wider than ~0.3 μm [18]. Only electron-beam microscopes provide the resolution needed for the thinnest (0.02 μm) asbestos fibers expected in water. State-of-the-art scanning electron microscopes (SEM) can resolve these thin fibers when properly aligned and energy-dispersive x-ray detectors (EDX) integrated into SEMs can yield elemental composition of these fibers [19]. However, SEM cannot determine the crystalline structure and thus cannot positively identify as asbestos those fibers with appropriate chemical compositions.

The single analytical instrument that is appropriate for analysis of waterborne asbestos, then, is transmission electron microscopy (TEM). This high-resolution instrument clearly displays the narrowest asbestos fibers on its bright phosphor screen at magnifications of 10,000× to 20,000×. When the intermediate lens is focused on the back focal plane of the image, electron-diffraction (ED) patterns can be produced. Amphibole or chrysotile crystalline structures can be positively identified by measuring these patterns. Finally, specific species of amphiboles can be differentiated by EDX detectors inserted near the specimen holder [20].

14.3.2 Sample Preservation

Some waterborne microbes produce polysaccharides that can cause asbestos fibers to become stuck to the walls of collection vessels. Hence, water samples should be kept chilled (4°C) and filtered within 48 h of collection to minimize microbial growth and fiber loss. The use of mercuric chloride as a preservative is no longer allowed because of its hazardous properties. If samples cannot be kept cold and filtered within 48 h of collection, an ultraviolet (UV)-ozonation procedure must be used to destroy any microbes and their polysaccharides before filtration is done [21].

14.3.3 Sample Filtration and Grid Preparation

Asbestos fibers are separated from water by filtration onto membrane filters. The greater the water volume filtered, the better the analytical sensitivity. However, care must be taken not to allow too heavy an accumulation of particles on the filter surface. Particles can obscure asbestos fibers and can also tire the analyst as each of the myriad particles in a field of view requires decisions about probable asbestos identity. Chatfield recommends that surface loadings not exceed 20 μg/cm² [22].

While asbestos contamination of virgin filter surfaces is less commonplace than two decades ago [23], blank samples should always be prepared and analyzed with each set of water samples. An aliquot (at least 0.5 mL/mm² filter surface) of asbestos-free water should be filtered through a filter that accompanies the rest of the filters from the batch.

Mixed cellulose ester (MCE) filters with nominal pore sizes between 0.1 and 0.22 μm are commonly used. Larger pore sizes must be avoided as they allow shorter fibers to penetrate too deeply for recovery [24]. Once MCE filters are dry, they are collapsed to a smooth transparent plastic using acetone of dimethyl formamide (DMF). While 0.22 μm pore MCE filters tend to filter larger volumes more quickly than 0.1 μm MCE filters, ~5% etching in an oxygen plasma is generally required because some fibers can penetrate beyond retention by the applied carbon film. This thin (~20 nm) carbon coat is applied to the
collapsed MCE surface in a high-vacuum (<10⁻⁵ Torr) evaporator to trap the exposed fibers. Care must be taken to adjust the geometric configuration during carbon evaporation or fibers can be lost [24].

0.1 μm pore polycarbonate (PC) filters can be less troublesome because their flat surface does not require collapsing and etching. Rather, a thin carbon coat is directly evaporated onto the filter surface immediately after drying. Once filters are carbon-coated, sections are excised and placed on 200-mesh TEM relocator grids. These grids are placed in either jaffe-wick or condensation washers with appropriate solvent to dissolve the filter material. PC filters are dissolved using chloroform, n-methyl-2-pyrrol- idone, or ethylenediamine (1,2-diaminoethane), or a combination of these [25]. MCE filters are dissolved by acetone or DMF, or a combination or sequence of the two. This leaves fibers (and other particles) suspended on the grid in an electron-transparent carbon film.

The EPA has issued two methods for analysis of waterborne asbestos. Method 100.1 [20] is a research method developed in 1984 that measures and counts all asbestos fibers longer than 0.5 μm. Only 0.1 μm PC filters are allowed by this method. Method 100.2 [26] was published 10 years later to reduce counting to only fibers longer than 10 μm (in accordance with the EPA MCL) and to incorporate many of the analytical shortcuts of the widely used Asbestos Hazard Emergency Response Act (AHERA) TEM method for measuring airborne asbestos concentrations [27]. The use of MCE or PC filters is allowable and the minimum analytical magnification is 10,000× versus 15,000× for Method 100.1.

Both methods employ similar TEM strategies. The entire area of carbon film within a TEM-grid opening (typically 0.01 mm²) is scanned at the appropriate magnification and all fibers with aspect ratios exceeding 5 are measured to determine if they are longer than the appropriate minimum (0.5 μm for Method 100.1 or 10 μm for Method 100.2). Fibers sufficiently long are first evaluated by ED. Both chrysotile and amphibole asbestos have 0.53 nm layer-lines that can be verified by insertion of a calibrated objective aperture [28]. Additional measurement of the 002, 020, 004, 110, and 130 reflections of chrysotile will usually suffice for its definitive identification. Suspect amphibole fibers must be further characterized by EDX, whereby the electron beam is narrowed and focused on the fiber and a spectrum of emitted x-rays is collected between 0 and 10 keV. This spectrum is compared to the spectra collected from the five regulated amphibole asbestos types for positive identification.

Waterborne asbestos concentrations (MFL) are calculated by multiplying the number of fibers counted by the surface area of the filter and dividing this by the product of the number of grid openings analyzed, the area of a grid opening, and the volume of water filtered. The mandated analytical sensitivity for Method 100.2 is 0.2 MFL (fibers > 10 μm).

REFERENCES

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