R & D REPORT

DOW CHEMICAL U.S.A.

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1 5924

LABORATORY REPORT CODE: TC-505

DATE ISSUED: October 1, 1974

DEPARTMENT: Central Laboratory - Texas Division

LAB. NO. | PROBLEM NO.

CRI NUMBER

TITLE: A Critical Evaluation of Current Analytical Methods for the Determination of Chrysotile Asbestos

14 PAGES IN FULL REPORT

AUTHOR(S): S. I. Foster

AUTHOR(S) SIGNATURE(S): S. I. Foster

PLAINTIFF'S EXHIBIT

DOW-714

REVIEWER'S SIGNATURE: W. F. Snell

This report is: [X] INTERIM [ ] FINAL and mainly: [ ] [X] REVIEW

DESCRIPTIVE SUMMARY WITH CONCLUSIONS: (Include in this space references to data books, and to earlier relevant reports, patents and publications.)

This report outlines known analytical procedures for chrysotile (serpentine) asbestos fibers in various aqueous waste streams. Some of the topics covered are: Electron and Optical microscopy, chemical methods, infrared, ESCA, DTA, X-ray diffraction, etc. A bibliography of papers relating to currently used analytical procedures is included.

The conclusions drawn from this review indicate that TEM (Transmission Electron Microscopy) is the one technique which fulfills all present analytical needs (i. e. identification, counting, and sizing). However, due to the complexity of the method and the cost of instrumentation, a rapid survey analysis which could give an order of magnitude of asbestos concentration and could be implemented into a production facility is needed. The techniques discussed here, specifically, atomic absorption, I. R., light-scattering, ESCA, adsorption of dyes and tracers, and other chemical methods are being further evaluated as rapid scanning procedures and recommendations will be forthcoming.

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The Problem

We are principally concerned with aqueous samples, some with high concentrations of NaCl and/or NaOH. These samples, in general, will contain 10^8 to 10^{10} asbestos fibers/liter (typical concentrations by weight encountered to date are 0.1 - 200 μg/l, the fibers being approximately 2 to 9 microns long and 200 to 400 Å in cross section (i.e., 100 to 300 aspect ratio). Although this is the typical case, any particle with an aspect ratio 3 to 1 or larger will constitute a fiber. Representative samples may also be expected to contain additional suspended particulate matter such as: clay minerals (montmorillonite or kaolinite), diatoms, quartz, graphite, hydroxides, and minerals indigenous to the particular sample area. Important chemical and physical characteristics particular to chrysotile are summarized below:

TABLE 1

Physical:

1. Large aspect ratios (100/1 typical).
2. Specific gravity 2.5; density 2.56 g/cc.
3. Loss of crystalline water at 695°C (14 % by wt.).
4. Irreversible change of crystal structure at 840°C.
5. Characteristic I.R. spectrum.
6. Isoelectric point - 10.3.

Chemical:

1. Mg to Si ratio:
   Empirical composition: $3MgO \cdot 2SiO_2 \cdot 2H_2O$ or $Mg_6(OH)_6Si_4O_{11} \cdot H_2O$, i.e., 43.5 % MgO; 43.5% SiO_2; 13% H_2O.
   Typical impurities are:[1] Fe, 0-1% ; Al, Ca, Cr (light; Cu, Na (trace); nickel (medium).
2. pH-- 9 to 10.
3. Soluble in strong acids to 56 % by wt.

[1]Sample analyzed by emission spectroscopy on asbestos from Chlor-Alkali department.

The analytical problems associated with asbestos fibers are fourfold: concentration and separation, identification, sizing, and counting. These areas will be dealt with separately with the objective of describing available techniques and evaluating their usefulness.

CONCENTRATION AND SEPARATION

Filtration:

Of the concentration methods, filtration seems to be the most universal. Typically, a millipore©-type membrane made of cellulose esters and having a pore-size between 0.2 - 0.8 μm is employed either in a pressure of vacuum filtration

assembly.[3, 9, 27, 39 57-60, 67, 68]. These membranes can then be ashed at relatively low temperatures (350°C)[59, 67], dissolved, or extracted in order to free the insoluble fraction. The currently used technique employs a EFFA© condensation washer wherein the filter is bathed in acetone vapors and condensate until it dissolves. This procedure takes approximately one hour if a 2 mm (dia.) filter is used. An added benefit is that it is possible to wash from the filter soluble material which may interfere with successive analysis. An average filtering time for 1 liter of solution is approximately 10 min/in² of filter. This time will depend on how much clogging is experienced.

Centrifugation:

Centrifugation offers an attractive alternative to filtration in that it is relatively fast and does not involve additional steps to free the filtering agent. It is routinely used as a technique to "spin-down" fibers onto an electron microscope grid[57] and also as a prefiltering aid to reduce clogging by large particles[59, 60].

The use of an ultracentrifuge and density gradient may prove helpful in separating unwanted suspended material from the asbestos fibers. On the other hand, a continuous centrifuge (e.g., Sharpless ©) might aid in concentration of the particulate matter from a large sample.

Agglomeration and Extraction:

It is well known that hydroxyl groups on the asbestos fibers are subject to attack by chloro- and alkoxy silanes to produce organic derivatives[15, 42, 47, 53-54, 62]. It has also been found that agglomeration or graft-polymerization will occur if the silane contains more than one reactive site. If the silane contains bulky organic substituents it may make the asbestos more soluble in organic solvents and thus extraction may be feasible[34].

Evaporation:

The disadvantage of this approach is that both soluble and insoluble material will be simultaneously concentrated. If, however, the soluble species can be extracted or perhaps dialyzed, evaporation may still provide a useful concentration method.

Electrokinetic Effect:

Asbestos fibers have been shown to carry a large surface charge (isoelectric point 10.3)[2, 38] and thus, electrophoresis may be applied in separation and concentration[38]. Whether or not the majority of fibers can be collected by this technique or if the fibers will be lost when the electrode is withdrawn is not presently known.

IDENTIFICATION METHODS

Methods of low-specificity

Chemical Methods:

Chemical techniques rely on the analysis of both Mg and Si in the bulk sample of suspended matter. The typical procedure is to analyze for both Mg and Si using whichever value is found to be lowest to calculate an upper limit of asbestos present. The particulate matter is solubilized with HF and $HClO_4$ or by Na_2CO_3 fusion and the Mg and Si are then analyzed by any of a number of wet chemical or instrumental methods. This approach is presently being carried out with atomic absorption spectroscopy at B-2406 of the Texas Central Laboratory (E. H. Holt, private communications).

X-Ray Spectroscopy:

X-ray fluorescence, whether X-ray or electron induced, exhibits a rather low sensitivity for either Mg or Si. It would therefore be doubtful if this technique would be applied successfully.

Atomic Emission Spectroscopy:

Emission spectroscopy does not lend itself easily to quantitative analysis. However, it has been estimated that a lower limit of 20 μg of asbestos can be determined if the sample is fused with Na_2CO_3. Again, it must be recognized that any foreign silicate or magnesium containing compound will interfere.

Radioactive or Chemical Tagging:

It is known that coupling reagents modified to contain a radioactive or fluorescent tag can be affixed to the asbestos fibers. Some of the more likely candidates are the chloro- and alkoxy silanes which contain a grouping which might chelate an easily monitored metal ion. It has been reported that some dyes[43, 34] can be adsorbed in aqueous solution and also that titrated chrysotile has been synthesized[23]. Tagging represents an important concept in the identification of chrysotile. If metal ions, dyes, or other surface active agents can be found to bond specifically to chrysotile this could give a major increment in analytical sensitivity and possibly specificity. Some reports indicate that a degree of specificity has already been observed[10, 16, 22, 34, 35, 40, 43].

Infrared:

It has been estimated that chrysotile in the range 20 to 700 μg[46] can be determined by using the 2.72 μm hydroxyl adsorption. However, this method is non-specific since other hydroxyl containing compounds may interfere. The specificity may

be improved by monitoring the 9-10 μm silicate adsorption.

Even with its drawbacks, I. R. represents a simple, cheap, and relatively fast method by which an upper limit could be obtained and thus may constitute a quick survey technique. A sensitivity of 0. 5 μg is readily attained in the absence of interferences.

ESCA:

ESCA can provide a quick semi-quantitative Mg and Si analysis. Its advantage may lie in its ability to look only at the first 50 Å or so of the surface. Thus, if the asbestos can be distributed on the top of a filtering agent, ESCA may be able to do the analysis without removing the filter.

Methods of Moderate to High Selectivity

TGA and DTA:

Chrysotile gives a characteristic endotherm at 695°C associated with its loss of H_2O (13% wt). It also exotherms at temperatures above 800°C which is indicative of a change in crystal structure[37, 44].

It has been reported that chrysotile in talc can be detected in the 1. 0% range on samples as low as 10 milligrams. Consequently, sample handling would constitute its main liability since the asbestos concentration is expected to be in the microgram/liter range.

THA:

Thermohygrometric analysis[28] relies on the detection of evolved water at 695°C using a sensitive hygrometer. If we assume 10 μg of chrysotile is contained in a 10 cc volume of dry gas, the water evolved would be in the parts/1000 range. This could be easily monitored by existing hygrometers. However, it is not known if other compounds will also evolve water at this temperature and thus the specificity of this technique remains in question.

Silicate Extraction:

Silicate minerals can act as sources of trimethylsilyl silicates when reacted with chlorotrimethyl silanes[62]. The particular silicate evolved can be characteristic of the mineral reacted. The trimethylsilyl silicate can be determined by G. C. in some cases. Sensitivity may be a problem, but this technique should be further researched.

Optical Microscopy:

Optical microscopy is considered useful for particles larger than 1 μm in smallest dimension. Since most individual asbestos fibers have been found to have a cross section of less than 0. 5 μm, this technique will not be applicable except for looking

at large bundles of fibers. Optical microscopy is widely used for analysis of asbestos in air samples[9,40,55].

Transmission Electron Microscopy:

TEM combined with selected area electron diffraction (SAED) and energy dispersive X-ray analysis (EDX) can identify, count, and size individual asbestos fibers. Its liability lies in involved sample preparation, small field of view, tediousness, and considerable capital investment. The usual technique is to filter the fibers onto a filtering membrane. The membrane is then ashed or dissolved and the residue dispersed onto a microscope grid (see filtering techniques). This technique is presently the standard method for chrysotile analysis. It can be successfully used to detect chrysotile in the ng range[3,27,33,51,57-61,

Scanning Electron Microscopy:

As far as sample preparation, SEM offers an advantage over TEM in that the filter does not have to be removed. Aside from this advantage, the inherently lower resolution and lesser degree of contrast should make SEM inferior to TEM as a method for asbestos analysis and fiber counting.

However, recent literature from the Kevex® Corp. indicates that X-ray spectroscopy, in conjunction with scanning electron microscopy (SEM), can be used to analyze individual asbestos fibers.

X-Ray Diffraction:

X-ray analysis is probably the most specific technique. It is not easily quantified except by elaborate standardization, and under normal circumstances is not very sensitive. Sensitivity is in the range 10 to 100 mg[21], but claims have been made of analysis in the 50 to 100 μg range[24]. The standard lines used for this analysis are the 7.36 Å and 3.66 Å lines.

COUNTING AND SIZING

The only direct method of counting fibers seems to be electron microscopy. However, if the asbestos fibers are found to fall within a certain size range, then bulk measurements of asbestos in a sample can be extrapolated to fibers present. Indirect measurements of the number of particles may be realized by applying one of the following concepts:

1. Light scattering: This technique offers a possible avenue for counting and sizing. The major problems arise from interference by other suspended particles, absorption of light by colored solutions, and in not knowing how these fibers will scatter. It is also unknown at present if light scattering can detect asbestos in the ppm or ppb concentration range.

2. Centrifugation: The Joyce-Loebl® disc centrifuge will allow for sedimentation and separation of particles based mainly on specific gravity differences. Its use of light scattering as a detection technique will also depend on whether or not these fibers will scatter in the visible light region.

Summary

At present, TEM stands as the one technique which fulfills all analytical needs (i. e., identification, counting, and sizing). However, a complimentary, rapid survey analysis which can give an order of magnitude asbestos concentration and could be implemented into a production facility is needed. The techniques discussed here, especially atomic absorption, I. R., light-scattering, adsorption of dyes and tracers, and other chemical methods are being further evaluated as rapid analytical procedures and recommendations will be forthcoming.

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