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Asbestos in Water? How to Address 'non-standard' Samples of Industrial and other Effluents: An Overview

Abstract:

Biohazards and other interferences complicate the employment of off-the-shelf asbestos in water methods by traditional TEM techniques. Laboratories must implement creative strategies to prepare and analyze these samples to produce meaningful analytical data. Laboratory and personnel safety have to be considered before sample handling. The interferences also greatly diminished any reasonable targets for a working detection limit. Consequently the development of analytical procedures that remove hazards and concentrate any suspect asbestos mineral have been developed. Formulated reference materials used in the QA process were also studied.

ASTM D22.07's now famous Johnson Conference has always yielded open (and sometimes heated) discussion on cutting edge issues involving asbestos. In 1997 a special conference was held to discuss Asbestos in Settled Dust and other ancillary issues in Boulder Colorado. The proceedings of that event have been available through ASTM Special Technical Publication 1342. Imagine a symposium that featured the *usual* speakers and the *expected* topics ranging from Asbestos in Settled Dust, Airborne Issues, Development of Laboratory Methods, Asbestos in Drinking Water, Bulk Asbestos Analysis by all sorts of instrumental means, etc. The picture that I paint of the technical and regulatory community listening critically to its respected peers on rather 'safe' issues – was shaken (some laughed, some were shocked, yet most had a serious curiosity) when

Mark Bailey and Meisheng Hu, delivered their now famous, "Sludge, Crud, and Fish Guts: Creative Approaches to Non-Standard Water Samples for Asbestos."

As the Laboratory Director of a large asbestos environmental laboratory since 1992, like many of my colleagues, I have seen countless examples of 'non-standard' samples. Human tissue samples, biohazard-filled muck (use your imagination), and of course, who would forget the cockroach. Yes, a major building owner in a large East Coast city submitted a cockroach. Their theory… "this particular critter was responsible for transporting asbestos from place to place throughout the building." No kidding! We did analyze the cockroach by several means and found no evidence of asbestos mineral. We did however later learn that he was employed illegally and without the proper training and certification documents to perform any asbestos remediation. [I'm sure the *Synergist* editorial board will get some responses to this from my brothers and sisters involved in laboratories with even more bizarre stories.]

Figure 1: Typical 'non-standard' water samples for asbestos analysis

The environmental health and safety and laboratory communities dealing primarily with asbestos hazards, have a long history of developing and practicing the most effective field and laboratory protocols to assure reliable analytical data that eventually are used to promote worker safety and public health. Usually these are limited to the 'standard' situations that are faced by asbestos professionals doing the design, engineering, removal, and laboratory testing of what has become routine 'off-the-shelf' responses to asbestos issues. This particular overview will look once again at the 'non-standard' sample issue,

particularly as it deals with asbestos in effluent. Before that focus, however, a brief look at asbestos in water.

The Flow of Asbestos in Water Science

EPA released an official mandate on Asbestos in wastewater with the release of the initial Federal Water Pollution Control Act of 1972. This was the impetus for the Safe Water Drinking Act that followed. In 1994, asbestos was added to the list of hazards that were required to be tested in our nation's water system. Over the last thirty years there has been some significant research into asbestos in both potable and non-potable water.

The 1974 Lake Superior report by W. J. Nicholson, the Canadian Survey of Water Supplies by Chatfield and Dillon in 1979, and several studies published by Jim Millette have all noted the ubiquitous nature of asbestos in many water systems and the numerous sources from which it might originate. These include naturally occurring asbestos (a term this author would see changed to 'geologically free asbestos mineral') sources in reservoirs, rivers, and lakes. Many other sources exist including: deteriorating asbestos cement pipe (used extensively in public drinking and waste water systems), auto repair solvent reclamation and water run-off, mine waste and tailings, asbestos manufacturers dumping waste in or near water sources, asbestos building materials being illegally dumped in and near water sources, asbestos laden water from worker showers during removal activities, run-off of water after a catastrophic event such as the WTC 09/11/01 tragedy and other post-fire incidents. Other noted examples that warrant mentioning include the State of Illinois Waukegan Municipal Beach asbestos project, the BoRit Asbestos Site in Ambler, Pennsylvania, and PCB rich river sediment being dredged from the Hudson River as part of a current Superfund clean-up.

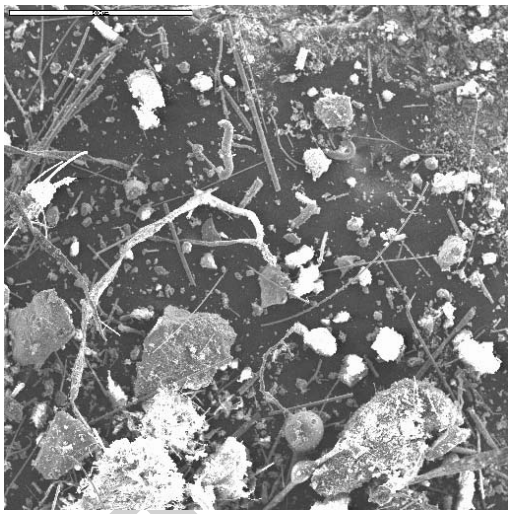

Figure 2: SEM image of Asbestos-laden WTC dust.

Piecing together several studies, EPA estimated that 33,000 pounds of asbestos fibers were released into the public's drinking water systems between 1987 and 1993. But what does this mean? The health and toxicity dose/response relationships and thresholds for bioactivity have not been clearly established by public health regulators. Philip Cooke's 1983 study looked at ingested asbestos and potential disease. In summary, no one really knows quantitatively what may create a health risk and subsequent illness resulting from the ingestion of asbestos-contaminated drinking water. Studies done in San Francisco by Kanarek and Conforti revealed a positive relationship between Chrysotile asbestos in drinking water and some esophageal, stomach, digestive organ and pancreatic cancers. Other investigations have demonstrated similar correlations. In Duluth, Minnesota, when levels of asbestos in the drinking water were high, mortality rates also were elevated for gastrointestinal and pancreatic cancer. In the Puget Sound area of Washington state, ratios for tumors of the small intestine were consistently elevated when levels of asbestos in the water supply also were high. Perhaps the most elegant study looked at asbestos from public water sources in Woodstock New York. The issue was as much related to asbestos 'in the water' as it was to measurable asbestos that became airborne (or had the potential for re-entrainment) when the water dried in showers and bathrooms.

Table 1

Distribution of Reported Asbestos Concentrations in Drinking Water
from 406 cities in 47 states, Puerto Rico, and the District of Columbia, USA.

Highest asbestos concentration, 10^6 fibers/liter	Number of Cities	Percentage Below detectable limits
	117	28.8
Not significant (|is less than~0.5)	103	25.4
is less than~ 1	113	27.8
1 - 10	33	8.1
is greater than~ 10	40	9.9
Total	**406**	**100**

From Millette - 1983

This brings us back to our 'non-standard' asbestos water sample. Mark Bailey was certainly correct when he employed 'creative' approaches to analytical investigations. This requires that laboratories develop their own 'creative approach'. What do regulators have to say about this type of improvisation? AIHA's LQAP has wrestled with 'modified' analytical methods and a laboratory's ability to employ these non-standard methods under their accreditation and approved field of testing. Yet, the laboratory is doing a service by employing good lab practices, using due diligence, utilizing validation metrics, etc. in developing various in-house methods to help solve client problems of detecting asbestos in these irregular samples. Again, without official peer reviewed and established methodology, laboratories have little choice except to improvise.

The asbestos analytical community was fortunate that asbestos in settled dust methods had been recently approved by ASTM prior to the World Trade Center catastrophe. Otherwise, a scattershot approach among consultants and laboratories would have been employed virtually assuring that any data's precision was suspect. The efficacy of these asbestos dust analytical methods has now been recognized. So again, what about the sludge, fish guts, muck, bio-hazard samples sent for asbestos analysis? There are no methods to address these varied matrices. What 'creative approach' techniques and methods can be employed for asbestos? How much improvising is required?

Grab and Go:

The Industrial Hygiene professional uses many tools to collect samples in the field. Literally, these tools are as varied as a soil auger to tweezers, from a five gallon pail to filters and hand collection devices of all shapes and sizes. Figuratively, the *tools* that must be employed are based upon the circumstance, the experience of the practitioner, past precedents in the industry, regulatory guidelines (requirements), and the ability to adapt all of these to challenging situations. The bottom line: how can I gather a sample for testing where my collection technique will neither add false positives (contamination), contribute to any false negatives (artifacts or interferences), while still using the most efficient means to have the 'best' sample that might represent the circumstance or field situation and yield the best detection limit in the laboratory? Furthermore, are there questions of potential liability that I can minimize through my sampling scheme?

It is at this point that many professionals just 'grab and go' without thought to the analytical or legal 'bottom line'. This overview is not intended to focus on these issues, but a CIH must be aware of these factors when collecting their 'fish guts and crud' samples.

Figure 3: Non-potable Water Collection

Arriving at a site where there had been known asbestos in a building that was demolished from a catastrophic incident and being tasked with assessing the now stagnant pools of water that have gathered in and around spilled chemical waste drums is one such challenge. The field samples are usually collected in 1L nalgene containers, without preservation, and many times shipped on ice. Chain of Custody and field Sample Logs may be vague – but the client wants to know… is there asbestos in this water and how much?

Night at the Improv:

It is imperative that the environmental client communicate with the laboratory professional about the nature of these 'non-standard' samples. If done in advance, the laboratory then has a chance to be proactive in its approach to safely receiving and pre-treating the samples. Laboratory technicians faced with a sample from an unknown source with possible biohazards might end up treating the sample in a way that should be avoided. Similarly, with advance knowledge about the sample source and possible interferences/contaminants the laboratory can select the best means of handling the sample to assure optimum asbestos recovery.

Laboratories would like to have as little improvisation as possible – but also realize that using basic science and laboratory principles may have to be creatively employed to obtain desired results. The laboratory sample management team upon receiving such a submission, usually selects to confer with its technical staff and management team in order to choose the best way to treat the sample. Unlike many other analytes, asbestos, by its nature, is only affected by the harshest of conditions, so damage to any asbestos mineral may be unlikely. In fact, laboratory separation techniques use these unique properties to the advantage of the 'bottom line'. Samples can be treated, under controlled conditions, with chemicals, exposed to high temperatures, and mechanically manipulated without affecting the integrity of the asbestos mineral. These practices are tools to separate the asbestos from interferences. Caution must be employed to prevent

leaching a sample in acid for too long, leaving it in a furnace over 500^{o}C, or milling it until it is unrecognizable so as to not alter the asbestos. It may seem like more art than science for these samples… experience and good practices play a key role in achieving the overall analytical objective.

Interferences must also be accounted for in the pre-treatment of a sample. Inorganic particulate, a variety of miscible and immiscible organic liquids, potential for flammability of organic wastes, and the effect of solvent laden samples that impact the choice of filters (select one that won't dissolve during the preparation process) are just some of the considerations for lab technicians.

Routinely samples of sludge with organic contaminants are 'shocked' with a heavy dose of Clorox for 24 hours while percolating UV/Ozone through the sample. This can be followed with a like treatment of acid to achieve a pH close to 2. This usually assures that biologicals are destroyed and that safer (yet, not always completely safe) conditions are achieved. Laboratory safety procedures that call for proper ventilation and 'trial' doses of these pre-treatment chemicals are warranted in case of potential reactions.

Figure 4: Multiple Vacuum Filtration Apparatus

If the sample contains heavy levels of inorganic particulate then serial dilutions must be run. Sources of inorganic particulate include carbon combustion product from post-fire sites, diatomiteious (spelling??) interferences from ponds and wells, clay, dendritic or other residual precipitates to name a few. Many times the addition of traditional matrix modifiers (ex. $AgNO_3$) will aid in precipitating out unwanted metal particulate. The use

of a centrifuge to concentrate select components of a sample can be employed, but may require diligent investigation techniques warranting study of all the resulting phases. Diminished analytical sensitivities are, of course, the drawback to having to run a series of dilutions. Many times, this can not be avoided in order for a 'readable' final filtration that is then prepared for TEM analysis.

Other creative approaches may warrant, using sieves of various sizes to separate solids and then capturing the liquid phase(s) for further preparation. The solid fractions can be studied and measured for moisture content, and through gravimetric reduction, possible mechanical, thermal, and chemical separation techniques – prepared and analyzed as sub-samples for asbestos content by both PLM and TEM. Off-the-shelf methods can then be employed for these fractions. ASTM D22.07 is currently working on asbestos in soil methods that may further standardize each field professional and each laboratory's approach to these unusual samples.

A step that laboratories often employ is to ultrasonicate liquid samples in order to 'free' any asbestos mineral from binding particles. Careful documentation with in-house formulated standards should be done so that the energy going in to the sample can be calibrated and controlled. An unintended false positive-rich environment might be 'created' when bundles or aggregates of asbestos mineral become disassociated and separated during aggressive sonication. Likewise, loss of analyte may 'create' the unintended consequence of false negative-rich samples due to poor practices of filtration, dilution, and sample transfer. Overall, laboratories must document their practices to achieve maximum sensitivity and recovery of analyte in standards. This can be a time consuming and therefore an expensive practice – but the value added to a client's final analytical data can lead to assurances of quality results.

Analysis:

Many labs, including our laboratory, avoid the seemingly easy final step of drop mount preparations, as leading to possible systematic error and potential loss of analyte, in favor of a final filter transfer to grid step. Final filter preparations are then prepared using standard techniques involving collapsing the filters chemically and etching them in a high temperature plasma, coating them in a high vacuum carbon evaporator, and transferring portions of the carbon replica to indexed grids on a solvent wick.

Analysis can proceed by TEM using USEPA 100.1 or 100.2 protocols. Additionally, modified or proprietary analytical regimens may prove more effective if all asbestos minerals are sized at high magnifications and mineral specific gravity/density ratios are utilized to calculate percent by weight for solids and numbers of structures per volume of liquid.

Now what?:

How would the IH professional interpret a final result for just one sample of Total asbestos at 10MFL (million fibers per liter), asbestos >10μm at 0.1MFL, and the solid fraction at 0.01% asbestos by weight?

If this were a drinking water sample, the EPA threshold of 7MFL for structures >10μm would not have been eclipsed – so the water could be disposed of through municipal treatment systems. But this fictitious sample does not closely resemble potable water. In fact, limits of quantitation as high (as poor) as 1-10MFL, might be common due to the effect of serial dilutions. Would this mean that the sample result is meaningless? Perhaps. Of course if the laboratory prepared additional parallel duplicate, replicate, and blank samples and there is acceptable correlation, then conclusive evidence of asbestos contaminate could be concluded.

Suppose this was worker decontamination shower water from a Superfund clean-up or from any asbestos abatement site? OSHA 1926.58 outlines the procedure required to minimize asbestos fibers leaving the worksite and contaminating those outside. Contaminated clothing, equipment and tools which may be re-used are cleaned in the "dirty room," while personal protective equipment such as respirators are wet-wiped and eventually washed in the shower area to remove residual fibers. Contractors *might* filter this waste water before disposal. However, it appears that there are no federal regulations specifically requiring the filtration of waste shower water generated within a decontamination facility. This practice probably results from interpreting broadly OSHA's 1926.58, Appendix F, Work Practices and Engineering Controls for Major Asbestos Removal, Renovation, and Demolition--Non-Mandatory, which simply provides guidelines for compliance with this regulation and indicates that further regulations may be required under the National Emission Standards for Hazardous Air Pollutants (NESHAPS) or EPA's Clean Water Act. Noted exceptions are New York State under their Industrial Code 56, and some additional requirements in Pennsylvania and Connecticut.

It seems unlikely that shower water from asbestos abatement projects would contribute to significantly higher concentrations of fibers in a public water supply, given the dilution factor in the volume of water. However, the possibility exists that part of the asbestos found in the drinking water may have been generated by these very projects. It would seem logical, therefore, to not only take preventive measures, but also to attempt to determine if there is a health risk created by not using filtration.

Conclusion:

No matter what your definition of a 'non-standard' water sample, the IH and laboratory professional must exercise caution when employing creative preparation steps to obtaining meaningful analytical data. In all cases, the larger the sampling pool, the better chance of this data reflecting the actual asbestos content of the site being investigated.

Finally, best practices and any creative approach aside, analytical results produced from small data pools may not stand up to legal scrutiny because there are no established and recognized methods for these crud, muck, and mire samples. The analytical community should continue to press for standards and guidelines and public health officials should have enough evidence that further biological studies are needed to assess asbestos in various liquid/solid phases and in the drinking and waste water systems.

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