Abstract: Ubiquitous biohazards complicated the employment of off-the-shelf asbestos in water or asbestos in soil methods by either PLM or TEM. Laboratory and personnel safety had to be considered before sample handling. The interferences also greatly diminished any reasonable targets for a working detection limit. Consequently the development of an analytical procedure that could remove the hazards and concentrate any suspect asbestos mineral was developed. Formulated reference materials used in the QA process were also studied.

Asbestos in Water?

How to Address Non-standard Samples of Industrial and Other Effluents

The now-famous ASTM D22.07 Johnson Conference has always yielded open (and sometimes heated) discussion of cutting-edge issues involving asbestos. In 1997, a special conference was held in Boulder, Colo., to discuss asbestos in settled dust and other ancillary issues. The talk of the conference was Mark Bailey and Meisheng Hu's presentation "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, I have seen countless examples of "non-standard" samples, including those with human tissue and biohazard-filled muck (use your imagination). Most memorably, a major building owner in a large city in the eastern United States once submitted a cockroach on the theory that it was responsible for transporting asbestos throughout the building.

The environmental health and safety and laboratory communities dealing primarily with asbestos hazards have a long history of developing and practicing the most effective protocols to ensure reliable analytical data, which are eventually used to promote worker safety and public health. Usually, these protocols address standard situations faced by professionals who design, engineer, remove, and test asbestos samples. This article will address non-standard samples, focusing primarily on asbestos in effluent.

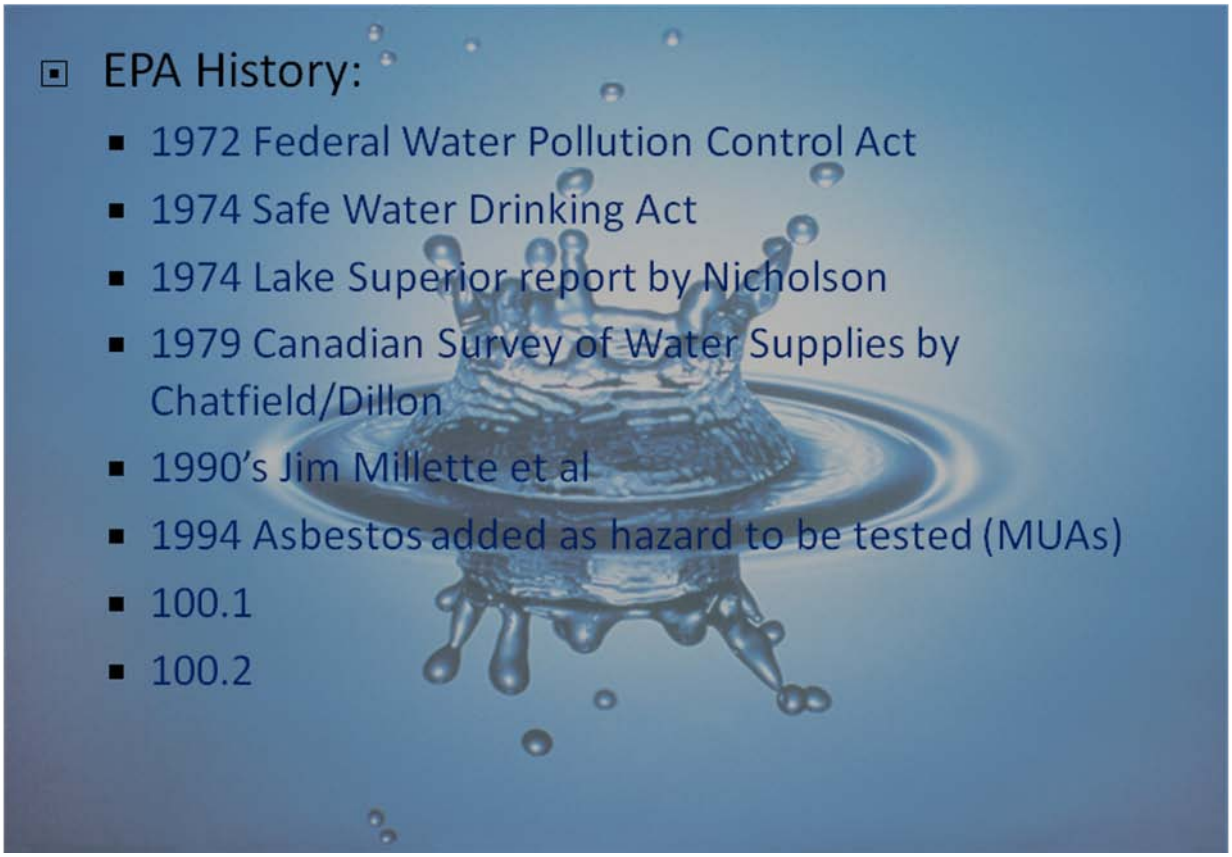
The Flow of Asbestos in Water Science

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.

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.



Creative Approaches

What do regulators have to say about improvisational, creative approaches to analytical investigations? AIHA's Affiliated Laboratory Programs has wrestled with laboratories' abilities to employ non-standard methods under their accreditation and approved field of testing. Yet laboratories perform a service by using good lab practices, due diligence, validation metrics, etc. when developing in-house methods to detect asbestos in irregular samples. Without official peer-reviewed and established methodologies, laboratories have little choice except to improvise.

The asbestos analytical community was fortunate that methods for asbestos in settled dust had been approved by ASTM prior to the World Trade Center catastrophe. Otherwise, consultants and laboratories would have employed a scattershot approach, resulting in suspect data. The efficacy of these asbestos dust analytical methods has now been recognized.

But no methods exist for addressing samples containing sludge, fish guts, muck, and bio-hazards. What techniques and methods can be employed for these samples? How much improvising is required?

Grab and Go

The industrial hygiene professional uses many tools to collect samples in the field. These tools vary from 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 circumstances, the experience of the practitioner, precedents in the industry, regulatory guidelines (requirements), and the ability to adapt all of these to challenging situations. The question confronting professionals concerns how to gather a sample for testing without adding false positives (contamination) or contributing 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, practitioners must know how to minimize potential liabilities through their sampling.

At this point, many professionals just "grab and go" without thought to the analytical or legal consequences. These issues are beyond the scope of this article, but a CIH must be aware of them when collecting their "fish guts and crud" samples.

An example of a challenging environment is a building known to have contained asbestos that has been demolished in a catastrophic incident. Professionals may be tasked with assessing the now stagnant pools of water that have gathered in and around spilled chemical waste drums. The field samples are usually collected in 1L nalgene containers, without preservation, and 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. Doing so gives the laboratory a chance to safely receive and pre-treat 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 or contaminants, the laboratory can select the best means of handling the sample to ensure optimum asbestos recovery.

Laboratories would like to have as little improvisation as possible, but basic science and laboratory principles may have to be creatively employed. Upon receiving such a submission, the laboratory sample management team usually confers with its technical staff and management in order to choose the best way to treat the sample. Unlike many other analytes, asbestos is affected only by the harshest of conditions, so damage to any asbestos mineral may be unlikely. In fact, laboratory separation techniques rely on these unique properties. 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 separate the asbestos from interferences. Laboratories must take care 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. 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--labs must select one that won't dissolve during the preparation process--are just some of the considerations for lab technicians.

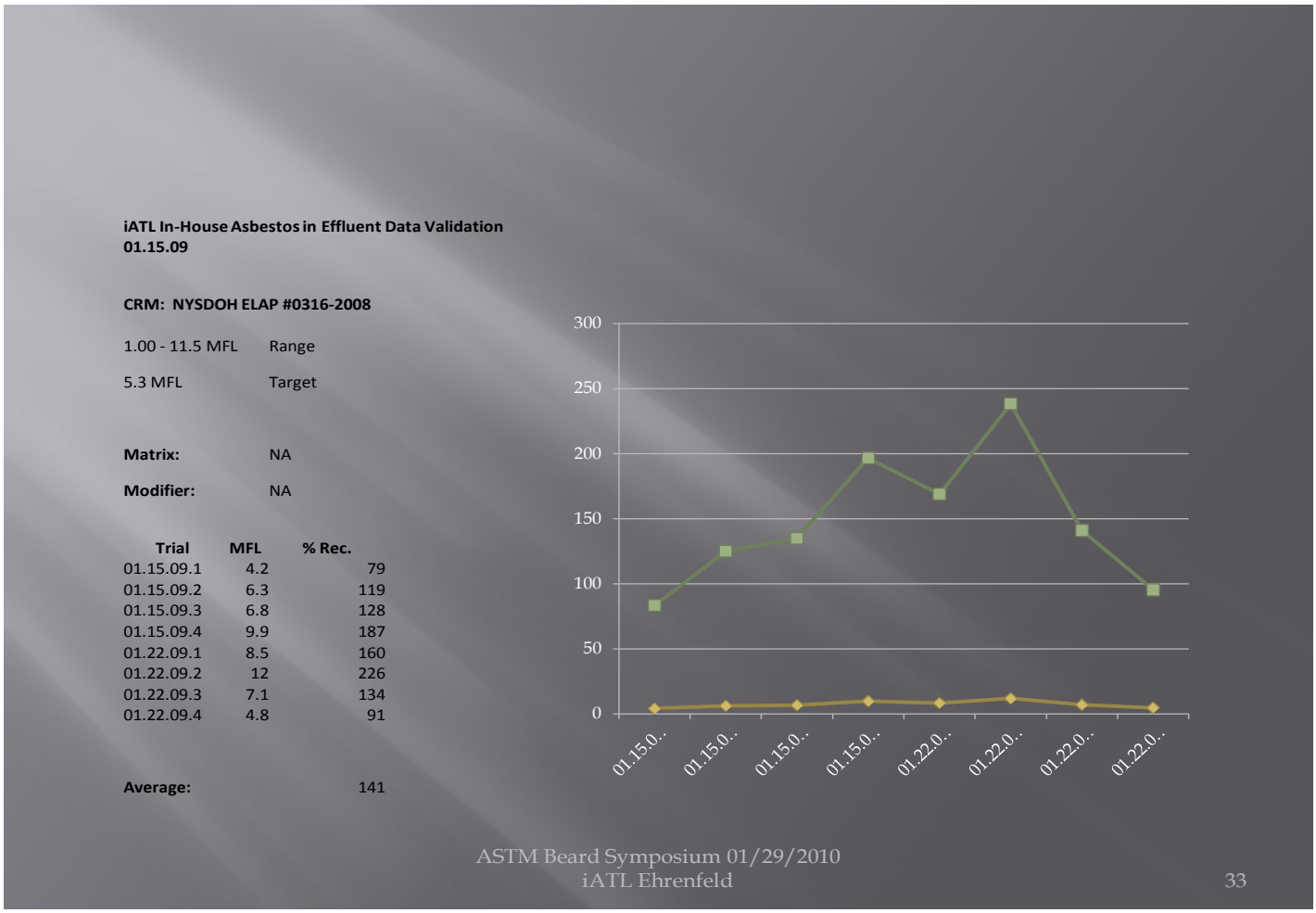
Routinely, samples of sludge with organic contaminants are "shocked" with a heavy dose of Clorox for 24 hours while UV/Ozone percolates through the sample. A like treatment of acid can then be used to achieve a pH close to 2. This technique usually destroys biological agents and achieves safer (yet not always completely safe) conditions. Laboratory safety procedures that call for proper ventilation and "trial" doses of these pre-treatment chemicals are warranted in case of potential reactions.

If the sample contains heavy levels of inorganic particulate, serial dilutions must be run. Sources of inorganic particulate include carbon combustion product from post-fire sites, diatomiteious interferences from ponds and wells, clay, dendritic or other residual precipitates. Often, the addition of traditional matrix modifiers (for example, $AgNO_3$) will aid in precipitating out unwanted metal particulate. A centrifuge can be used to concentrate select components of a sample, but this method may require diligent investigation techniques that warrant study of all resulting phases. Diminished analytical sensitivities are, of course, the drawback to having to run a series of dilutions. Many times, this cannot be avoided in order to produce a "readable" final filtration, which is then prepared for transmission electron microscopy (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 polarized light microscopy (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.

Laboratories often ultrasonicate liquid samples in order to "free" any asbestos mineral from binding particles. Careful documentation with in-house standards is necessary to ensure 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 expensive practice, but the value added to a client's final analytical data can lead to assurances of quality results.



In-house study of CRM recoveries using off the shelf method.

Validation

iATL In-House Asbestos in Effluent Data Validation
01.15.09

CRM: NYSDOH ELAP #0316-2008

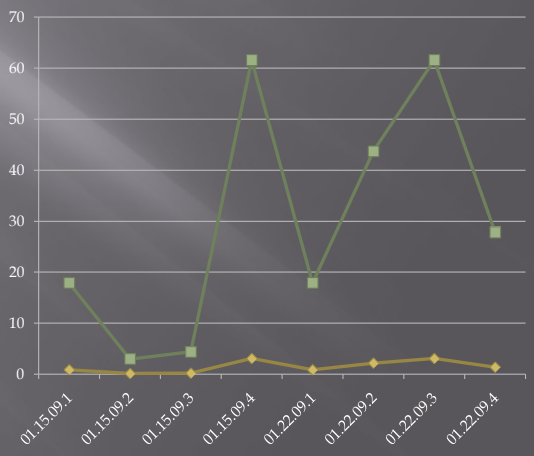
1.00 - 11.5 MFL Range

5.3 MFL Target

Matrix: 100mg PS1

Modifier: NA

Trial	MFL	% Rec.
01.15.09.1	0.9	17
01.15.09.2	0.15	3
01.15.09.3	0.22	4
01.15.09.4	3.1	58
01.22.09.1	0.9	17
01.22.09.2	2.2	42
01.22.09.3	3.1	58
01.22.09.4	1.4	26
Average:		28



In-house study using CRM and interfering soil/mixture. Note poor recoveries.

Validation

iATL In-House Asbestos in Effluent Data Validation
01.15.09

CRM: NYSDOH ELAP #0316-2008

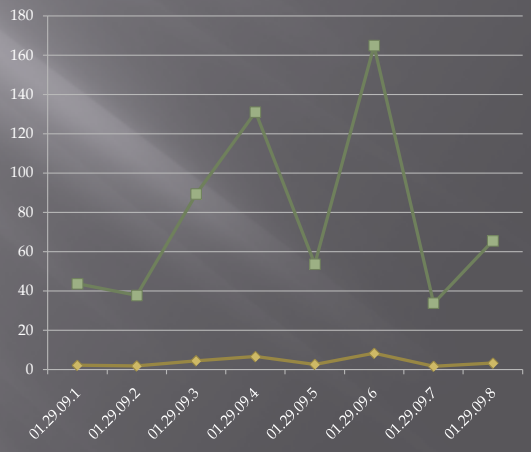
1.00 - 11.5 MFL Range

5.3 MFL Target

Matrix: 100mg PS1

Modifier: GAA/E 10%

Trial	MFL	% Rec.
01.29.09.1	2.2	42
01.29.09.2	1.9	36
01.29.09.3	4.5	85
01.29.09.4	6.6	125
01.29.09.5	2.7	51
01.29.09.6	8.3	157
01.29.09.7	1.7	32
01.29.09.8	3.3	62
Average:		74



Same as above, but with a matrix modifier to improve recoveries.

Analysis

Many labs, including our laboratory, avoid the seemingly easy final step of drop mount preparations, which lead to possible systematic error and potential loss of analyte, in favor of a final filter transfer to grid step. Final filter preparations are 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 industrial hygienist 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 percent 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 (that is, 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 sample was worker-decontamination shower water from a Superfund cleanup 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 reused, 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 health risk is created by not using filtration.

More Guidelines Needed

No matter your definition of a non-standard water sample, industrial hygienists and laboratory professionals must exercise caution when employing creative preparation steps to obtain meaningful analytical data. In all cases, the larger the sampling pool, the more likely the data will reflect the actual asbestos content of the site being investigated.

Finally, 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 and solid phases and in the drinking and waste water systems.

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