

Asbestos in Talc Test Methods: Applicability of reference materials and development of qualified standards

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In any analysis it is critical to first define the sample. It is rare that an entire material can be interrogated regarding its composition; it is nearly always that only a small sample is available, and the major question to be asked about any sample is whether it is sufficient to characterize the whole. In the world of asbestos analysis, the sample can be an air filter (or more often a portion of filter), soil, lung tissue, building material, bulk mineral, or a consumer product. The representativeness of the sample to the whole is a matter of considerable concern and has not always been addressed properly. A second question relating to any analysis is the nature of the analytical technique. Many are available, and their range of application is not always overlapping. In the case of asbestos-containing materials it is necessary to consider the magnification at which an examination proceeds, for example: eyeball to hand-lens; low-power stereo-microscope; polarized light and phase-contrast microscopes; scanning electron or transmission electron microscope. Examination at each level is for different purposes, and—quality assurance also varies by level. The final question relating to the analysis is the nature of the variation encountered between different tests in the same, or different, laboratories, and whether these variances might lead to different decisions. Analytical calibration, along with reference materials and proficiency testing schemes are all aids to resolving these differences.

In most analytical schemes there is at least a pure and homogeneous reference material to which the analysis can be benchmarked, but this is not the case with asbestos. Since asbestos has no consensus scientific definition, and the term is applied to commercial materials with a range of compositions and structures, we are left with comparison to “type” materials, rather like classifying paintings by “schools” or music by “genre”. Even chrysotile is not identical between mines; amphibole asbestos has greater variation, with tremolite-actinolite, anthophyllite, Amosite and crocidolite all appearing generally different because of different chemistries and different modes of crystallization, as well as exhibiting differences between similar compositions according to provenance. This is the case even for materials mined and sold as asbestos. As an example, consider the tremolite asbestos reference material from the National Institute for Standards and Technology (NIST) with that from the UK Health and Safety Laboratory (HSL). Both are tremolite and both were mined and sold as asbestos, but they are morphologically quite different. Within the field of a single mineral, compositional variation between locations is common, with, for example some tremolite asbestos containing iron all the way to the actinolite boundary, while in other locations iron in tremolite asbestos is difficult to detect at all. In some locations a range of individual particle compositions can cover several mineral classification fields. The minerals which are found as minor components of other products can be even more diverse. Thus, it is necessary to cast a wide net for “type” specimens. Even more importantly, it is essential not to become too bogged down in definition. A “true” definition of asbestos eludes scientists, and without a definition of asbestos “asbestiform” makes no sense. Commerce has had a definition of asbestos all along and now so does the legal arena. What should concern us, though, is the material(s) with potential to cause harm and it should not be so important how they are named. There are many commercial

deposits of asbestos which contain particles whose identity as asbestos can be argued over (e.g. Brown and Gunter, 2003), and there are many occurrences never commercially exploited where particles could be labelled as asbestos. Nature does as it pleases, and while man can often shoehorn its messy products into neat boxes, exceptions and indeterminacy abound and confound.

The NIOSH Current Intelligence Bulletin 62, Asbestos Fibers and Other Elongate Mineral Particles: State of the Science and Roadmap for Research, acknowledges the need for a “National Reference Repository for Minerals and Information” to support their recommended research activities. NIOSH noted that currently, no national repository exists to retain, document, and distribute samples of asbestiform and nonasbestiform reference minerals for research and testing, and that these reference samples should be well-characterized research-grade materials. The details of “well-characterized” need to be agreed (see below). The International Organization for Standardization (ISO) defines a reference material as “material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process”. A comprehensive approach to making reference materials available should consider this point carefully. As far as existing reference materials, the most popular have been the Union for International Cancer Control (UICC) materials. These were produced in large quantities from South African crocidolite and Amosite, Finnish anthophyllite asbestos, and Rhodesian (Zimbabwean) and Canadian chrysotile. The intent was to prepare a respirable product, and thus the materials were intensively processed, including the use of jet-milling. Jet-milling has imparted a rather unusual characteristic, at least to the amphiboles; some proportion of long fibers have shattered, and the short sections produced have become attached to other long fibers. This characteristic was not noted at the time because only light microscopy was used to characterize the product. Other materials, such as the tremolite asbestos used in studies by Davis and Addison (Davis et al., 1985) were not jet-milled and the materials consist of long fibers free of the shattered short sections. However, the appearance of the UICC materials can be recreated easily in tremolite asbestos by jet-milling. This salutary observation should remind us of the caution by Spurny et al. (2010) that “milling procedures not only change the size distribution, but also the particle shape and crystal structure of asbestos fibers.” He further reminds us that another common technique “Ultrasonic energy ... produces changes in fiber size and fiber concentration.” It has become popular in recent years to describe a “fibrosity index” to characterize fibrous minerals, but this can only be valuable when there is a standardized preparation procedure that allows “apples-to-apples” comparisons. The American Society for Testing and Materials (ASTM International) is an organization well placed to take the lead in developing a consensus standard.

The UICC Reference materials are now hard to obtain, as much of the remaining material has been landfilled, and the NIST Common/Uncommon Asbestos standards are no longer available with no plan to replace. NIOSH has small quantities of materials produced in the past by the Illinois Institute of Technology Research Institute (IITRI) and the UK HSL still has small quantities of their reference materials (Tylee et al., 1995) available to those who participate in their proficiency testing schemes. The author of this report worked under several projects at NIOSH to identify, collect and make available new reference materials. The first material to be made available is a tremolite asbestos (Harper et al., 2015), identical to the HSL reference material. This is available through Research Triangle Institute (RTI International), an organization which has elected to be a repository of materials in this field. New materials currently being processed by NIOSH include an anthophyllite asbestos from southern

California and an asbestos close to the compositional boundary of tremolite and actinolite from Arizona. Others may be forthcoming.

Reference amphiboles that are not asbestiform are another matter. An expected source might be dealers of minerals for colleges and schools (in general, specimens are not sufficiently spectacular to find their way onto the open shelves of museums or private collectors). However, care is warranted. Analysis is often cursory and in error, for example, enstatite labelled anthophyllite and inesite as tremolite. In addition, anthophyllite seems to always have a component of talc. The following minerals were used in an inter-laboratory study on asbestos fiber and cleavage fragment differentiation: actinolite from Wrightwood, CA, NIEHS tremolite from New York State, grunerite from Tras os Montes, Portugal, and riebeckite from Colorado Springs, CO. Preparing fiber-like cleavage fragments is not a simple matter, crushing produces less than 1% of particles meeting the World Health Organization countable fiber definition. Beneficiation procedures allowed the preparation of small quantities of the 50% fiber-like particles used for the study. The exact composition was unimportant to the study since the laboratories were compared with each other, but it allowed slides to be prepared with nominal mixtures of cleavage fragments and asbestos fibers. The results are published: width appeared to be a good tool to differentiate populations of particles, in line with other studies, but the more subjective descriptors of asbestos particles (visible bundling, curvature, split ends, etc.) produced very inconsistent results. While this study involved phase-contrast microscopy (PCM) and thus is not relevant to electron microscopy, the finding that morphology is not a good guide to identity is likely generalizable to polarized light microscopy at similar magnification. Finally, while width is a good predictor for populations, it may not be usable when the numbers are small. Of special importance when attempting to discriminate asbestos fibers from cleavage fragments is the toxicity of the latter. While the US Occupational Safety and Health Administration (OSHA) initially included cleavage fragments in fiber counts, it no longer does so (but the discrimination is based on decisions of its own microscopists in its own laboratory). NIOSH and EPA continue to include cleavage fragments as fibers to be counted, in part because they remain unconvinced they are safe, but also because of the lack of a good procedure for discrimination under PCM (although width could be helpful here, as in ASTM D7200). Further batches of fiber-like cleavage fragments (tremolite and riebeckite) have been prepared for use in ongoing toxicological studies, which results should help settle the matter.

The importance of the characterization of reference materials has been alluded to. If the desired function is simply qualitative or quantitative analytical standards, less needs to be done, but it is still important to characterize chemistry, mineralogy and purity as accurately as possible. X-ray diffraction can give mineral identities, but only down to a finite percentage admixture, and it says nothing about the fibrosity. The electron microscope can give more information, but not all have the same capabilities. It is very important to have quantitative calibration of energy-dispersive or wavelength dispersive spectrometers and an understanding of beam effects on chemistry. Many particles need to be "sampled" to give a clear picture of composition, and the interpretation should consider the limitations and variance of the analytical procedure and acknowledge any natural compositional variance of the material. The practice of publishing a chemical formula to three significant figures (and no uncertainty) based on an average of, for example, ten particles analyzed by an uncalibrated or poorly-calibrated instrument (with guesses as to how much iron is ferric and the coordination of aluminum) is a travesty of analytical chemistry that needs to be ended immediately. It is also well-known that electron diffraction patterns can mislead if not thoroughly researched. For materials to be used for toxicity

research even more must be known. For example, a paper characterizing a fibrous glaucophane has been submitted for publication, which includes bulk X-ray powder diffraction and high-resolution synchrotron powder diffraction for mineralogy; polarized light microscopy for optical properties; both scanning and transmission electron microscopy for fiber sizing, morphology, and electron diffraction patterns; electron microprobe for chemistry supplemented by ^{27}NMR spectroscopy (Al coordination), Mössbauer spectroscopy (ferrous/ferric iron); Fourier-transform infra-red spectroscopy and X-ray photoelectron spectroscopy for surface chemistry; inductively-coupled plasma optical emission spectroscopy for trace element chemistry; specific surface area; zeta-potential; and biodegradability. Subtle disagreements between techniques further point to the need for this full characterization.

Finally, the best assurance of analytical competence is proficiency with blind test samples, a typical requirement for third-party accreditation. Proficiency testing is generally carried out to determine the competence of laboratories to detect, define and quantify asbestos at characteristically high percentages (>1%) in building materials. This may not have much value when attempting to determine traces in other products. However, an occasionally valuable sample appears. The HSL Asbestos in Materials Scheme (AIMS) Round 62 included a sample with 0.1% chrysotile and Amosite, which were not detected by several laboratories, and a crushed marble with wollastonite where many saw asbestos: 23 labs by PLM-only, 6 with EM. The HSL also operates a Low Asbestos Content Scheme (LACS), where Round 2 was a sample of talc containing wollastonite (no asbestos) – 18% of labs incorrectly reported presence of asbestos. ASTM International has several related work items including ASTM WK30024 Test Method for Polarized Light Microscopy (PLM) Analysis of Cosmetic and Pharmaceutical Talc for Asbestos and ASTM WK30352 Test Method for XRD Analysis of Talc for Asbestos. Both work items involve round-robins. Full results will be presented or published by the study organizers.

The objective of the event for which this report has been written is to review the status and possible future steps to be taken to analyze for the presence of asbestos in talc and products derived from it. It is important to recognize that it is impossible scientifically to prove a negative; asbestos is only not there for as long as one continues not to see it. Absent a critical level to be used as a stopping point one could continue forever. Attempting to show the purity of UICC chrysotile B, Frank et al., 1998, essentially analyzed 20,000 particles without finding amphibole, and yet the presence of trace tremolite and Amosite has since been reported.