By Bruce W. Harvey, Robert L. Perkins, John G. Nickerson, A. Jane Newland and Michael E. Beard

Formulating Bulk Asbestos Standards

With the NESHAP point-counting provisions, this new research performed for the EPA by Research Triangle Institute is of utmost concern to the industry.

Research Triangle Institute (RTI) has long been involved in the administration of proficiency testing programs for laboratories using polarized light microscopy (PLM) to analyze for asbestos in bulk building materials. Among these were the Environmental Protection Agency (EPA) Asbestos Bulk Sample Analysis Quality Assurance/Interim Accreditation Program, and currently the National Institute of Standards and Technology's National Voluntary Laboratory Accreditation Program, the Navy Asbestos Identification Proficiency Testing Program and the American Industrial Hygiene Association Bulk Asbestos Proficiency Testing Program.

A review of laboratory analyses from three of these programs (the Navy program does not require quantitation) indicates a pervasive tendency for laboratories to visually overestimate the amount of asbestos in test materials. This overestimation averages two to four times the estimates derived from gravimetric weight percent analyses. Overestimation is greater in samples containing less than 5 percent asbestos by weight, often being up to 10 times the gravimetric weight percent values, and decreases rapidly in samples containing greater than 10 percent asbestos by weight.

In reviewing these data, it was realized that the availability of bulk calibration standards might have a positive impact on the problem, and research to determine the feasibility of formulating a series of such standards was begun. Goals of the study included developing procedures for formulating standard materials, conducting extensive in-house analysis of all materials, distribution of material samples to independent laboratories for round-robin analysis, and evaluation of those analysis results.

FORMULATION PROCEDURE

Chrysotile, amosite and crocidolite were chosen for use because of frequency of laboratory encounter and degree of previous characterization, and hopefully to provide insight into the effect of fiber morphology on the formulation process and quantitation results, and in the case of crocidolite, the effect, if any, of fiber color contrast on quantitation results. Cellulose, mineral wool, calcium carbonate, perlite and vermiculite were selected for use in order to provide a variety of common, fibrous and nonfibrous matrix materials. The calcium carbonate was reagent-grade; the others were commercial materials purchased over the counter.

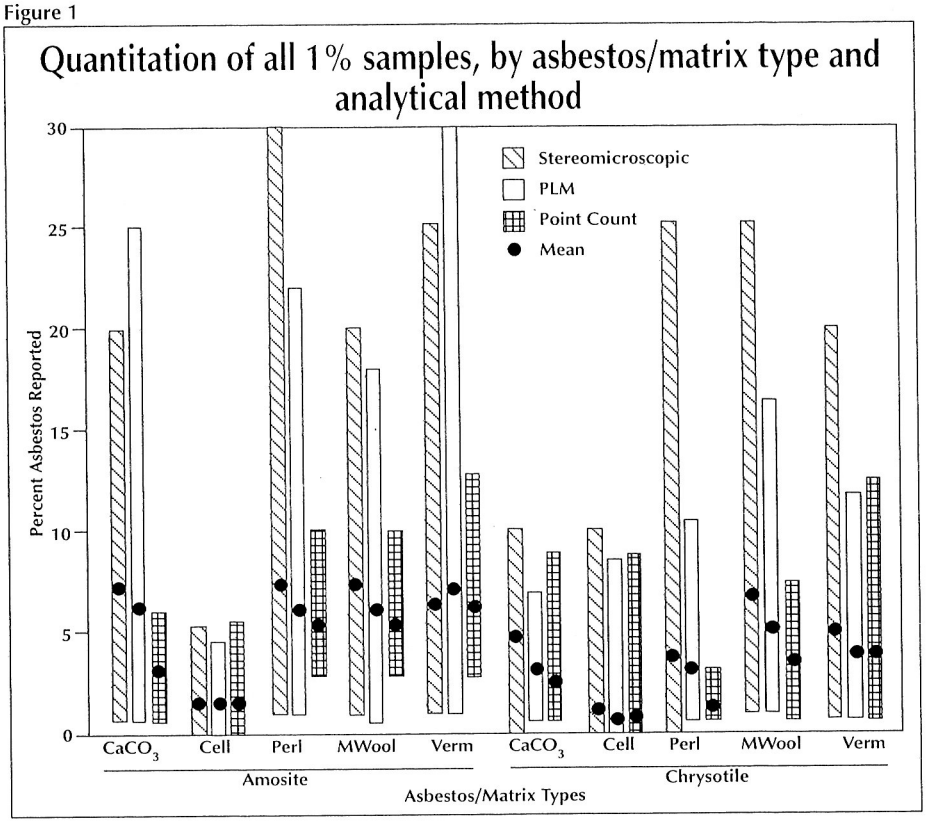
Amosite and chrysotile each were combined individually with the five matrix components, with asbestos comprising one, five and 10 percent of the samples by weight. This yielded 30 material combinations. A sample consisting of three percent crocidolite in calcium carbonate also was formulated. An initial blend of five percent amosite in calcium carbonate, formulated prior to a modification in the blending procedure, helped to determine the effect of extended blending time on homogeneity and fiber size reduction, and brought to 32 the total number of samples prepared.

The formulation procedure involved first weighing quantities of asbestos and matrix

material to give the desired asbestos weight percent. The matrix was placed into the pitcher of a standard over-the-counter blender, the pitcher being previously filled to one-fourth capacity with distilled water. Blending was performed at the lowest speed setting for 10 seconds in order to disaggregate the matrix. The asbestos was added, and additional blending of 30 seconds, again at lowest speed setting, was performed.

Ingredients of the pitcher then were filtered, with thorough rinsing of the pitcher to ensure complete material removal. The filtering apparatus consisted of a 6 x 6 x 6-inch stainless steel box with perforated bottom panel, lined with cheesecloth for support, on which the filter paper rested. Each material was drained thoroughly and transferred from filter paper to a foil dish, which was in turn placed on a hot plate. The material was covered and allowed to dry completely over low heat. A variation from this procedure involved the calcium carbonate mixtures, which were not filtered. Instead, the ingredients in the pitcher were rinsed into a series of shallow glass dishes, which were covered and placed on a hot plate until contents were thoroughly dried. The final step involved placing each formulated material into a plastic bag, then hand-mixing it to provide additional blending and to reduce clumps produced by desiccation. Each formulated material then was given a preliminary stereomicroscopic assessment.

Figure 1



The procedure contains a revision implemented after formulation of the five 5 percent chrysotile materials and the 5 percent amosite in calcium carbonate material.

For those, the asbestos was blended before the matrix was added, and each blending step involved blending times of at least two minutes. The resulting generation of very fine fibers in the amosite material was readily apparent during the stereomicroscopic assessment. It was decided that the material be used nonetheless, since the analysis data might be of interest. The effect of long blending time on the five units comprised of five percent chrysotile was not readily apparent, so they were not redone using the revised procedure. All other materials were formulated using the procedure described initially.

IN-HOUSE MATERIAL ANALYSIS

All formulations then were thoroughly examined, with semiquantitative analysis by stereomicroscopy and PLM, point-counting and, where applicable, gravimetric sample reduction.

Stereomicroscopic estimates for asbestos volume percentages were derived from examination of a large quantity of each material at 10X magnification. PLM estimates of asbestos area percentages were obtained by examining pinch mounts of each material in 1.550 or 1.680 HD refractive index (RI) oils at 100X magnification. Certain patterns were noted in the results of the stereomicroscopic and PLM analyses, which might suggest the sample types expected to present difficulties to others. These patterns included the following: a) overestimation was greatest in one percent samples, and appeared to be independent of asbestos or matrix material type; b) overestimation was very pronounced in amosite/vermiculite and amosite/perlite samples; and d) underestimation was common in cellulose-containing materials, and very pronounced in chrysotile/cellulose combinations.

Each sample was point-counted. Representative pinches of material were mounted with epoxy on glass slides. Epoxy was chosen as the mounting medium because of its extended shelf life and ability to minimize lateral migration of particles during placement of the cover slip. From 400 to 800 points were counted, with the aide of a cross-line reticle and mechanical point-count stage. It was determined during preliminary analysis that a majority of fibers were not being resolved at 100X magnification, so the magnification was increased to 500X for all slides. Most counts were much higher than the theoretical asbestos volume percentage calculated for each material, but not as high, in many cases, as the stereomicroscopic or PLM estimates.

Thickness differences between asbestos and matrix were determined where possible, for calculation of theoretical asbestos area percentages. It was noted that cellulose samples produced poor material distribution, and that chrysotile was difficult to detect in a cellulose matrix. The Red I plate seemed to improve the ability to differentiate between the two. Several slides prepared in 1.550 HD RI oil and examined using the central stop dispersion staining objective yielded similar counts to those in epoxy mounts.

Gravimetric analysis was performed on samples having a calcium carbonate or cellulose matrix. For each calcium carbonate sample, three 1-1.5 gram subsamples, chosen randomly from the total formulated bulk, were dissolved for 15 minutes in 20mL of concentrated hydrochloric acid, filtered through a vacuum filter apparatus, allowed to dry and reach equilibrium with ambient conditions before residue weights were calculated. Chrysotile residues averaged 1.1 times the expected weight percents, the amosite residues varied from 0.9 to 1.1 times the expected values, and the crocidolite residue was 0.8 of the expected value. Though a certain lack of homogeneity may be suggested by these data, the variation in results for each sample was less than the variability in quantitation estimates from in-house microscopic analyses, and far less than the variability in estimates from eventual round robin analysis of the samples.

Three subsamples each of the cellulose-containing samples were ashed by placing

them in covered crucibles, and those in turn into a muffle furnace for 12 to 14 hours at 470 degrees C. Samples were allowed to cool and stabilize before residue weights were determined. Initial residue weights were higher than expected. By ashing several samples of pure cellulose, it was determined that approximately 5.6 percent of the material was a nonashable component; this equated to 5.6 percent, 5.4 percent and 5.1 percent overages in samples containing 99 percent, 95 percent and 90 percent cellulose by weight, respectively. The residue weights were corrected for this component, and averaged 0.8 to 1.0 times the theoretical values. In that regard, the ashing results were similar to the results of acid dissolution of the calcium carbonate samples. The variation in results for each sample was less than the variability in quantitation estimates from in-house microscopic analyses, and far less than the variability in estimates from eventual round-robin analysis of the samples.

INDEPENDENT LABORATORY STUDIES

Samples were distributed to 23 independent laboratories for round-robin analysis. All laboratories received the three percent crocidolite and five percent amosite-in-calcium carbonate samples. The remaining 30 materials were divided into two groups, with each group containing as close to equal numbers of amosite samples, one percent samples, perlite matrix samples, and so forth, as possible. Laboratories were sent 17 samples, brief instructions and results reporting forms. They were asked to provide stereomicroscopic volume and PLM area estimates of asbestos present, and point-count area estimates if possible. Laboratories were encouraged to employ additional methods of analysis at their discretion, but to refrain from such until all stereomicroscopic and PLM analyses had been completed.

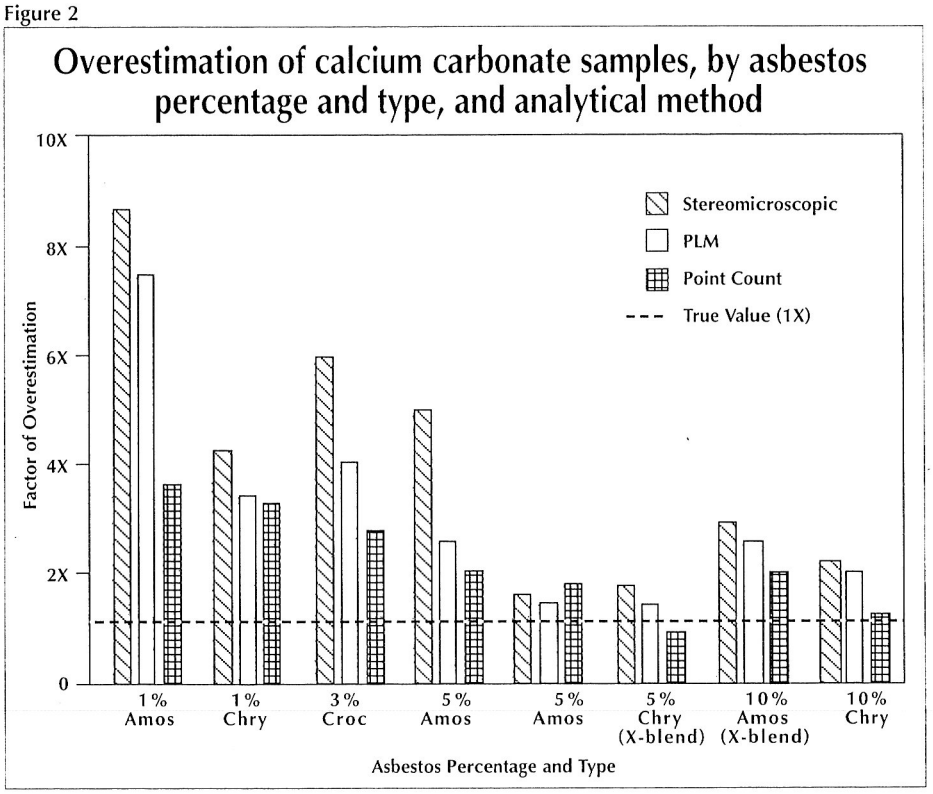
Results of analysis were received from 20 laboratories. All submitted stereomicroscopic and PLM quantitation estimates, while slightly more than half submitted point-count data. Results from one laboratory were discarded because stereomicroscopic and PLM data were combined into single estimates. Two laboratories included gravimetric analyses; one submitted scanning electron microscopy/energy dispersive X-ray (SEM/EDX) data.

For each sample, means and ranges of reported values were determined for stereomicroscopic, PLM and point-count estimates of asbestos present. Five individual reported values were deemed to be outliers and were not included in calculation of means. The means then were compared to theoretical volume percentages. Theoretical area percentages, to which PLM and point-count data should be compared, were not used. The assumption was that laboratories in general do not make the corrections for particle thickness and/or specific gravity differences necessary to calculate theoretical area percentage values, and that comparisons to volume percentages would more closely approximate laboratory practices. Similar patterns appeared to exist among the means and ranges of reported values on the one, five and 10 percent samples. These patterns, illustrated in Figure 1 for the quantitation data from the 10 one percent samples, include the following: a) mean values typically exceeded theoretical volume percentages; b) means were lowest, and ranges narrowest, for point-count estimates; c) means were highest, and ranges broadest, for stereomicroscopic estimates; d) amosite-containing samples yielded higher means and broader ranges (probably due to the effect of greater fiber disaggregation during blending), than equivalent weight percent chrysotile samples; and e) means were lower and ranges narrower on samples containing cellulose (probably due to lack of detection than on those containing the other four matrix materials). Similar conclusions regarding the greater accuracy and precision of quantitation by point-counting than by stereomicroscopic or PLM techniques have been drawn by Brantley et al. in round-robin testing of 22 laboratories as part of the development of the EPA Interim Method, and by Webber et al. in intralaboratory and interlaboratory comparisons of the quantitation of a series of formulated standards related to development of a stratified point-count method.[1,2,3]

Theoretical volume percentages, which ranged from 1.04 percent for chrysotile in calcium carbonate to approximately 0.10 percent for amosite in vermiculite, were omitted from Figure 1 to more clearly show those samples for which no asbestos was reported. Fifty-one "none detected" responses were received, for a false negative error rate of 3.6 percent. Table 1 shows the distribution of these responses. Failure to detect asbestos occurred most frequently during stereomicroscopic examination of samples containing chrysotile and cellulose. A similar problem was described by Jankovic et al. in analysis of cellulose ceiling tiles spiked with chrysotile.[4] For a greater number of false negatives to occur on the five percent rather than one percent samples further suggests the detrimental effect of sample overblending on quantitation accuracy.

Special interest was taken in results of analysis of samples containing the calcium carbonate matrix. These samples were among the easiest to formulate, their homogeneity was easily assessed by acid dissolution to be very good, and they resembled to some degree certain "real-world" samples. It also was the only matrix material with which crocidolite was blended. The examination made possible a determination of the effect, if any, of the type (morphology) and amount of asbestos, and length of blending time, on quantitation accuracy. It provided an opportunity to substantiate the patterns, illustrated in Figure 1, resulting from the examination of all

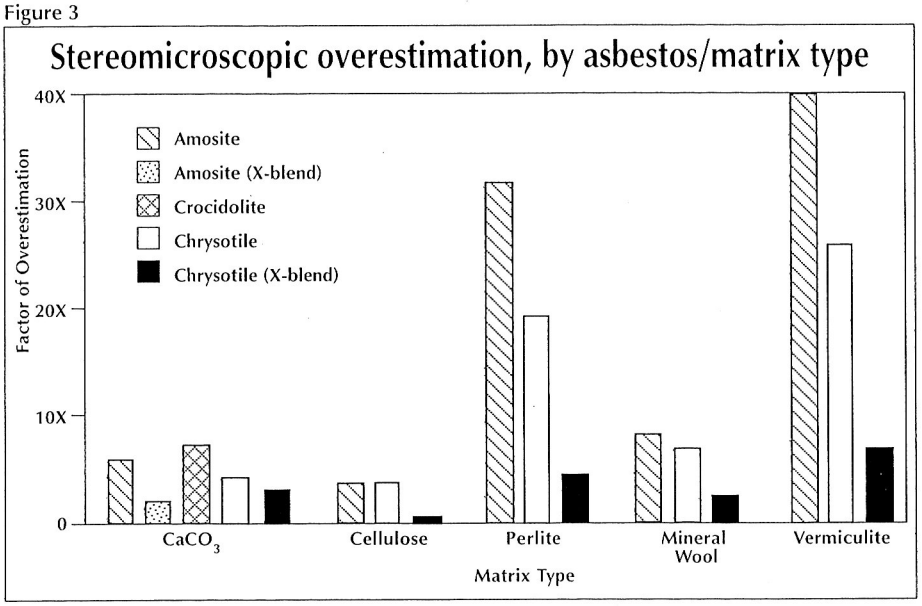
Figure 2



one percent samples. For each asbestos type and percentage combination, the means of reported stereomicroscopic, PLM and point-count estimates were calculated, then divided by the theoretical volume percentage for that sample, to determine a factor of overestimation.

As illustrated in Figure 2, these factors of overestimation then were plotted against asbestos type and percentage, and the following patterns were discerned: a) stereomicroscopic quantitation invariably was characterized by the greatest overestimation, while point-counts incurred the least overestimation; b) overestimation was greater in samples containing amosite or crocidolite than chrysotile, again probably reflecting a greater tendency for amphibole fiber bundles to disaggregate during blending, and a greater lack of detection of chrysotile in certain samples; c) for each asbestos type, overestimation increased as the percentage of asbestos decreased; d) the color contrast in the crocidolite/calcium carbonate sample did not appear to add to its degree of overestimation; and e) extreme overblending (and probable resulting lack of detection) was likely responsible for lower overestimation in the extra-blended five percent amosite and five percent chrysotile samples.

Figure 3



Because thickness relationships among amosite, chrysotile and calcium carbonate particles had been determined during in-house PLM analysis, each of the eight theoretical volume percentages was converted to its equivalent, theoretical area percentage. PLM and point-count means were divided by the appropriate theoretical area percentages, and corrected factors of overestimation were calculated. Since the amosite and crocidolite fibers were determined to be finer (thinner) than the calcium carbonate particles, PLM or point-count analysis of such material would tend to overestimate the asbestos percentage. Correction for this thickness difference would, in effect, lower the means of laboratories' reported values, and in the case of the amosite and crocidolite samples, reduce the PLM/point-count overestimations.

Conversely, chrysotile fibers were determined to be coarser (thicker) than the calcium carbonate particles. PLM or point-count analysis of such material would tend to underestimate the chrysotile. Correcting for this thickness difference would in effect raise the means of laboratories' reported values. Because the uncorrected means on the chrysotile samples already were greater than the theoretical volume percentages, factors of overestimation increased with correction of the data. As a result, point-counting results on the chrysotile samples were no longer the least overestimated of the three methods, at least for these round-robin laboratories. The blame is likely to be placed in the point-counting procedures used by the laboratories and not in the theory of converting volume percentages to area percentages (and vice versa).

The authors' point-counts on the chrysotile samples resulted in area percentage estimates consistently below theoretical volume percentages, and correction of those counts brought them in line with theoretical volume percentages. Perkins has used data from this study to more fully illustrate relationships between volume and area percentages.[5]

An appraisal also was made of the general relationship between matrix type and degree of overestimation of asbestos content, as determined by stereomicroscopic examination alone. Factors of overestimation for the one, five and 10 percent amosite samples, and the one and 10 percent chrysotile samples, were determined, averaged and plotted against matrix type in Figure 3. The values for the six extra-blended samples (five percent amosite in calcium carbonate and five percent chrysotile in each matrix type) were plotted separately. The following general tendencies were noted: a) by asbestos type, amosite (and crocidolite in the calcium carbonate) samples, regardless of matrix, incurred the highest overestimation; b) by matrix type, overestimation was highest among perlite and vermiculite samples and lowest among cellulose samples; and c) within each matrix type, the extra-blended samples were overestimated the least.

The degree of overestimation is to a great extent related to the theoretical asbestos volume percentage, which in turn is very sensitive to the specific gravity value for each matrix material. Commercial perlite and vermiculite materials routinely undergo some degree of expansion during processing, resulting in wide ranges of possible specific gravities. It was determined that the specific gravities of perlite and vermiculite used in this study were no greater than 1.0, based on total flotation in water. Minimum specific gravities of 0.4 for perlite and 0.3 for vermiculite were determined by dividing specific gravities of each unexpanded material by the average commercial expansion for each. These values were used in determining the factors of overestimation shown in Figure 3.

Had specific gravities of 1.0 been used for each, overestimation would have been reduced by a factor of two for the perlite and three for the vermiculite, but still would have resulted in much greater overestimation on these two matrices than on the other three. The specific gravity values for these two matrices could increase from the minimum values quoted, depending on the amount of any additional blending. The increase would likely be more pronounced

Table 1

Distribution of 51 "none detected" responses

By Analytical Method	
Stereomicroscopic	34
PLM	10
Point Count	7
By Asbestos Type	
Amosite	11
Chrysotile	40
By Asbestos Percentage	
1%	21
5%	27
10%	3
By Matrix Type	
$CaCO_3$	4
Cellulose	38
Perlite	4
Mineral Wool	5

Table 2

Results of alternative methods of analysis

Sample Type	Acid Dissolution	Low-Temp Ashing	Density Separation	SEM/EDX
1% amos/$CaCO_3$	0.93			
/cell		6.55, 3.97		
/perl		2.00	5-10	
5% amos/$CaCO_3$	5.16, 4.58, 4.40			
/$CaCO_3$ (xb)	4.94, 4.79, 4.40			
/cell		8.63		
/m wool			4.44	10
/verm			21.54	5-10
10% amos/$CoCO_3$	11.02			
/cell		14.38, 14.44		
/perl			10.39	50
1% chry/$CoCO_3$	1.10, 0.97			1-5 chry, 1-2 amos
/cell		6.37		
/m wool				1-2
/verm				2-5 chry, 1 amos
5% chry/$CaCO_3$	5.32			
/cell		8.80, 2.90		5 chry, 1-2 amos
/perl				50
10% chry/$CaCO_3$	10.77, 9.30, 9.80			20-30
/cell		13.82		
/m wool				10
/verm				20
3% croc/$CaCO_3$	2.51, 3.10, 2.10			10

in perlite. In either case, this would in turn result in an additional decrease in the amount of overestimation. These numbers underscore the tremendous impact of low matrix specific gravity on determination of theoretical volume percentages and equivalent area percentages, and on the need to correct for significant differences in asbestos/matrix specific gravity differences. Relationships between weight and volume percentages in bulk samples have been described in detail by Stewart.[6]

In addition to the requested stereomicroscopic, PLM and point-count data, two laboratories submitted gravimetric (acid dissolution and/or ashing) analysis results, one submitted limited density separation data, and one submitted SEM/EDX data. These data, along with RTI in-house gravimetric data, are listed in Table 2.

Asbestos residue weight percentages in calcium carbonate matrix samples, as determined by acid dissolution, appeared to be very reasonable, suggesting that calcium carbonate, when used as the matrix, yielded a blend whose homogeneity was good and easily verified by the laboratory. All but one of the residue weight percentages derived from ashing were higher than expected, but did not take into account the nonashable component discovered to be present in the cellulose. Subtracting the effect of that component from these data left all results somewhat below the expected weight percentages for those samples. The density separation data was very limited, with the accuracy of two of four estimates considered reasonable.

A comparison was made between quantitation data derived from the three microscopic analysis methods and that determined by SEM/EDX (also shown in Table 2) to appraise the worth of the latter. Only samples containing calcium carbonate or mineral wool matrices for which SEM/EDX data were submitted (seven samples) were considered. It was only among these samples that reasonable matrix/asbestos particle thickness relationships had been determined with any surety. A theoretical asbestos area percentage was calculated for each sample, to which were compared the mean values of laboratories' PLM and point-count data, and the single set of SEM/EDX estimates. Means of the laboratories' stereomicroscopic estimates were compared to theoretical asbestos volume percentages. As shown in Table 3, the SEM/EDX quantitation data compared favorably to those of the other methods; however, they represented an extremely small data set in comparison to the others.

SUMMARY AND CONCLUSIONS

The formulation procedure used for the preparation of materials was deemed to be very satisfactory. Material homogeneity varied slightly, based on in-house visual and gravimetric analyses, but did not appear to be responsible for the variability in laboratories' quantitation. Materials containing cellulose presented problems in blending and asbestos detection, and overblending was determined to affect quantitation accuracy significantly.

Laboratory results produced patterns in the accuracy of quantitation similar to those seen in quantitation data from the major proficiency testing programs. Overestimation was still the pervasive tendency. Based on comparisons to theoretical volume percentages only, the stereomicroscopic estimates showed the greatest degree of overestimation and the greatest variability of reported values, while point-counting showed the least. Overestimation from properly done point-counts, if adjusted for thickness and specific gravity differences between asbestos and matrix, would have been significantly lower.

Overestimation seemed higher in samples containing amosite or crocidolite than chrysotile, perhaps due to the greater tendency for amphibole bundles to disaggregate during blending, and to a greater tendency for chrysotile to escape detection in certain samples. Overestimation generally increased as the percentage of asbestos in the sample decreased. Overestimation was greater in samples whose asbestos and matrix mate-

Table 3

Overestimation of calcium carbonate and mineral wool samples, by analytical method

Sample Type	Stereomicroscopic[a]	PLM[b]	Point Count[b]	SEM/EDX[c]
5% amos/$CaCO_3$	5.1X	1.7X	1.1X	1.2X
/m wool	5.7X	1.0X	0.9X	0.6X
1% chry/$CaCO_3$	4.5X	9.8X	9.0X	1.0X
/m wool	7.7X	6.6X	4.5X	2.0X
10% chry/$CaCO_3$	2.3X	5.2X	3.1X	7.4X
/m wool	3.0X	3.6X	2.3X	1.3X
3% croc/$CaCO_3$	6.4X	2.2X	1.3X	2.0X
average	5.0X	4.3X	3.2X	2.2X

[a] compared to theoretical volume percent
[b] compared to theoretical area percent:
amos thickness = 0.5 $CaCO_3$ thickness
amos thickness = 0.2 m wool thickness
chry thickness = 3.3 $CaCO_3$ thickness
chry thickness = 1.3 m wool thickness
[c] very limited data; compared to theoretical area percent

rial (vermiculite and perlite) differed substantially in specific gravity and/or thickness. The influence of these factors on the accuracy of quantitation estimates is probably not fully appreciated by the laboratory community as a whole.

Alternative methods of analysis provided small populations of data and yielded varying results. Results of gravimetric analyses provided clear-cut indication of good homogeneity in the calcium carbonate samples, but gave less obvious indication of the same in the cellulose samples. Density separation results were very limited and inconclusive. SEM/EDX data, though also very limited, appeared to fall within the range of quantitation accuracy of the other microscopy methods.

The preparation and conscientious use of in-house standards would no doubt provide valuable and much-needed calibration of microscopists. The data from this study also suggested that laboratories may not be able to accurately determine whether a sample being analyzed actually is greater than one percent asbestos by weight (or area or volume) or not. To those ends, findings of this study relative to the general overestimation of asbestos in bulk materials, and specific recommendations and guidance relative to the formulation of calibration standards, interpretation of stereomicroscopy, PLM and point-count data, and relationships among weight, volume and projected area percentages, are being incorporated into the Test Method for the Determination of Asbestos in Bulk Building Materials, currently being prepared by RTI for the Quality Assurance Division of the Atmospheric Research and Exposure Assessment Laboratory, U.S. EPA. ❑

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REFERENCES

1. Brantley, E.P., Jr., K.W. Gold, L.E. Myers and D.E. Lentzen. 1982. U.S. Environmental Protection Agency. Bulk Sample Analysis for Asbestos Content: Evaluation of the Tentative Method. EPA-600/4-82-021. Environmental Systems Laboratory, Research Triangle Park, N.C.

2. U.S. Environmental Protection Agency. 1982. Interim Method for the Determination of Asbestos in Bulk Samples (EPA-600/M4-82-020). Department of the Interior, Washington, D.C.

3. Webber, J.S., R.J. Janulis, L.J. Carhart and M.B. Gillespie. 1990. Quantitating asbestos content in friable bulk samples: development of a stratified point-counting method. American Industrial Hygiene Association Journal 51(8):447-452.

4. Jankovic, J.T., J. Clere, W.T. Sanderson and L.A. Piacitelli. 1988. Estimating quantities of asbestos in building materials. National Asbestos Council Journal (Fall):47-51.

5. Perkins, R.L. 1990. "Visual Estimates and Point-counting: Points to Consider." Professional development seminar paper presented at the National Asbestos Council's Fall Technical Conference and Exposition, Phoenix, Ariz. September.

6. I. Stewart. 1988. U.S. Environmental Protection Agency: Asbestos Content in Bulk Samples: Visual Estimates and Weight Composition (EPA 560/5-88-011). Office of Toxic Substances, Washington, D.C. September.

7. Perkins, R.L., and B. W. Harvey (in preparation). 1990. U.S. Environmental Protection Agency: Test Method for the Determination of Asbestos in Bulk Building Materials. Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, N.C.