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Project Summary

Bulk Sample Analysis for Asbestos Content: Evaluation of the Tentative Method

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The U.S. Environmental Protection Agency Office of Pesticides and Toxic Substances, Washington, DC, and the USEPA Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, jointly sponsored an effort to produce a practical and objective analytical protocol for the qualitative and quantitative analysis of asbestos in bulk materials. Draft procedures were written for analysis of bulk samples by polarized light microscopy (PLM) and X-ray powder diffraction (XRD). Following review, the Tentative Method for the Determination of Asbestiform Minerals in Bulk Insulation Samples (March 1980) was submitted to a performance testing program that involved multiple laboratory analysis of prepared samples with known asbestos content. This report presents the results of the testing study and provides preliminary observations and characterization of the utility and operational parameters of the Tentative Method.

PLM quantitative analysis employs a point counting procedure to estimate the relative area occupied by asbestos fiber within the microscope fields of view. PLM data must be compared with the known weight of asbestos in the sample in order to characterize the accuracy of the method. Data produced by the point counting procedure are also compared with those produced by the typical quantitation procedures used by some of the participating laboratories. Accuracy and precision of the point counting procedure are considered in two contexts: (1) as PLM is currently used, regarding reported data as a direct estimate of weight percent of asbestos present and (2) allowing adjustments of the data to account for bias and variance in the relationship between the relative area occupied by asbestos and the known weight percent of asbestos in the sample. Information is also presented on within-laboratory variance and the frequency of false negatives and false positives.

A very limited amount of data was returned for characterizing the XRD protocol. Both thin-layer and thick-layer (bulk) techniques were used for quantitative XRD analysis. Because of the small number of XRD reports and the nonequivalence of methods employed, it is not possible to draw any firm conclusions on the precision and accuracy of the XRD protocol. A general comparison of bulk and thin-layer techniques with respect to precision, accuracy, and sensitivity is made.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully

documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

An interlaboratory study was conducted to evaluate the accuracy, precision, and general utility of the Tentative Method for the Determination of Asbestiform Minerals in Bulk Insulation Samples (March 1980). Twenty-two commercial and four government laboratories were each supplied with 11 samples. Eight of the samples were formulated with a known weight of amosite or chrysotile and a matrix material containing primarily gypsum. Within-laboratory duplicates, blanks, and "real-world" samples of sprayed insulation were also included in the materials distributed to laboratories. Four laboratories (two commercial, two government) chose not to participate in the study. The 22 participating laboratories provided a total of 30 polarized light microscopy (PLM) reports and six X-ray powder diffraction (XRD) reports.

The Tentative Method includes procedures for qualitative and quantitative analysis of bulk samples by PLM and XRD. Identification of asbestos fibers by PLM requires the observation of six optical properties: morphology, color and pleochroism, refractive indices (or dispersion staining colors), birefringence, extinction characteristics, and sign of elongation. PLM quantitative analysis uses a point counting procedure to estimate the percent area occupied by asbestos fiber within the microscope fields of view. The prepared samples distributed in this study contained a known weight percent of asbestos. Because PLM analysis produces an estimate of the relative area occupied by asbestos, the relationship between reported area percent and the known weight percent of asbestos was investigated.

Identification of sample components by XRD analysis is accomplished by comparison of the sample diffraction pattern with standard reference powder diffraction patterns. Quantitative analysis involves measuring the integrated areas of diagnostic peaks selected from the full XRD scan of a thin-layer sample. Quantitative analysis must include a correction for matrix absorption effects and comparison with suitable external standards. XRD affords information only on crystal lattice structure and not on crystal morphology. XRD analysis, therefore, cannot distinguish between asbestos minerals and their nonasbestiform varieties. The presence of fibrous particles in a sample must be determined by an optical technique such as PLM.

Conclusions

Linear regression in natural logarithmic coordinates was used to study the relation between the reported data, in terms of percent asbestos by area, and the known values, in terms of percent asbestos by weight. The fact that a considerable amount of the variation in the data was removed by regression in logarithmic coordinates is consistent with the assumption that area percent and weight percent are related by a power function. Analysis of the regression shows that variation in the area-weight relationship is attributable to differences between laboratories, differences between asbestos types (chrysotile and amosite), and interactions between laboratory and asbestos type.

Reported PLM data were divided into three groups based on the quantitation procedure(s) used by the reporting laboratory.

Group P—(Point count) PLM asbestos area percent determinations by the point count procedure (Tentative Method).

Group B—(Both) PLM asbestos area percent determinations by the laboratories' own methods for laboratories that also provided data by the point count method.

Group O—(Other) PLM asbestos area percent determinations by the laboratories' own methods for laboratories declining to use the point count method.

Considering reported PLM results as direct estimates of the weight percent of asbestos (i.e., ignoring the problem of relating area percent and weight percent), it was found that Group O is significantly more biased than Group P. Groups P and B are similarly biased. Point counting has a greater positive bias on amosite samples than on chrysotile samples. For a sample containing 10 percent chrysotile by weight, the average bias (b) of Group P is 18.5 percent; for 50 percent chrysotile, b = −24.2 percent; for 10 percent amosite, b = 118.5 percent; for 50 percent amosite, b = 12.1 percent.

A regression relating standard deviations and means of reported PLM results, when performed in natural logarithmic coordinates, did not establish any differences among Groups P, B, and O with respect to precision. The standard deviation of Group P is directly related to the mean reported value. Precision may be expressed as the coefficient of variation (CV). The CV is less than 100 percent on samples containing more than approximately 6 percent asbestos by area, and less than 50 percent on samples containing more than approximately 32 percent asbestos by area. At a mean reported value (MP) of 10 percent asbestos, CV ≅ 79 percent; at MP = 20 percent, CV ≅ 61 percent; at MP = 50 percent, CV ≅ 41 percent.

Analyses were performed on transformed data to investigate improvements in data quality that might be made by adjusting (calibrating) individual laboratory results. If the parameters of the area-weight relationship are used to transform reported area percent data to predicted weights, a considerable gain in accuracy is achieved, as measured by the average percent absolute error. By this measure of accuracy, Group O has a greater error than Group P on samples containing less than 20 percent asbestos by weight. Residual variance in the transformed data is measured by the mean squared error about the regression line. By this measure of variance, Group P was found to be significantly more precise than Groups B and O. Further analysis of adjusted data indicates that laboratories using point count analysis are better able to distinguish samples containing more than 7 percent from those with less than 7 percent asbestos by weight than they are able to distinguish samples with more than 1 percent from those with less than 1 percent asbestos by weight.

Samples from the chrysotile series were included as within-laboratory duplicates. Although a more extensive effort would be required to adequately evaluate the precision of the PLM protocol on repeated analysis of the same sample, a gross estimate using the present data indicates that within-analyst variability accounts for less than 25 percent of the total variance.

One of the important characteristics of the point count procedure to be evaluated is the likelihood of its generating false positives and false negatives.

A false positive occurs when an analyst reports asbestos present in a sample that does not contain asbestos. A false negative occurs when an analyst reports no asbestos present in an asbestos-containing sample. Data produced by point counting included five false negatives out of a total of 19 analyses of the 1.2 percent chrysotile sample. One false negative out of 19 analyses was reported for the 4.9 percent chrysotile sample. No false negatives were reported for any amosite samples or for any samples containing more than 5 percent chrysotile by weight. The reporting of false negatives is more likely due to the variability of sample and slide preparation steps than to the point counting procedure *per se*. One false positive out of 19 analyses was reported for the series of blank samples and was probably due to contamination. The probability of a false negative on the 4.9 percent chrysotile sample was 0.05 (1/19). EPA currently recommends the analysis of at least three samples of a suspect material. The rate of false negatives is such that the analysis of three samples, if each contained at least 5 percent asbestos by weight, would result in three false negatives with a probability less than 0.03 and possibly as low as 0.001.

The six laboratories reporting XRD results were grouped into two general categories for purposes of data analysis. These categories, thin-layer and bulk, were defined on the basis of the XRD technique used for quantitative analysis. Three of the laboratories performed the requested analyses using some variation of the thin-layer method of quantitation included in the Tentative Method. The remaining three laboratories used alternative bulk or thick-layer methods of quantitation. It should be emphasized that within categories none of the methods used were strictly equivalent. Moreover, within the thin-layer group, no laboratory followed the Tentative Method protocol exactly.

Because of the small number of participating laboratories reporting XRD results, and the nonequivalence of methods employed, it is not possible to draw any firm conclusions from the reported results about the accuracy and precision of the XRD method. However, from a general comparison of bulk vs. thin-layer methodology, two observations can be made.

First, bulk methods appear to be at least as accurate and precise as thin-layer methods over the range of samples included in this study and significantly more accurate for the analysis of chrysotile.

Second, there is a suggestion that thin-layer methods of analysis may be more reliable (i.e., more sensitive) than bulk methods at the 1 percent level of chrysotile in a simple matrix.

Data produced by thin-layer methods of analysis included one false negative out of three analyses of the 4.9 percent chrysotile sample. The same laboratory reported chrysotile false positives for all amosite samples and for the blank sample with reported chrysotile values ranging from <1 to 8 percent. A second laboratory reported one false negative out of three analyses in the 19.4 percent chrysotile sample.

Data produced by bulk methods of analysis included two false negatives out of three analyses of the 1.2 percent chrysotile sample. One of these laboratories also reported a false positive amosite in the 4.9 percent chrysotile sample.

Recommendations

The study presented in this report is a preliminary evaluation designed to determine the precision and accuracy of the Tentative Method as applied to carefully prepared samples. It should be emphasized that the samples analyzed consisted of only two types of asbestos fiber and a single matrix material. Only one type of asbestos was included in any given sample. One of the main obstacles to reliable analysis of bulk samples is the variability of sample composition. Complete characterization of the method requires that several issues be addressed, as discussed below. The highest priority, however, should be assigned to investigations that will extend the application of the method to a range of real-world samples involving different fiber types and matrices.

Polarized Light Microscopy

Several aspects of the PLM method require further investigation. Briefly, future studies should be designed to determine the following:

1. The feasibility of specifying definitive sample preparation procedures to be used for quantitative PLM analysis;
2. The proportion of total variance attributable to individual procedures of the method, i.e., sample preparation, sub-sampling, and point counting;
3. The proportion of total variance contributed by within-laboratory variability;
4. The effect of specific variables within the point counting procedure, including the number of points to be counted, magnification used, and the possible bias introduced by the use of a 25-point reticle instead of a cross-hair reticle;
5. The possibility of introducing a staged point counting process that would allow fewer counts to be determined on samples with a high percentage of asbestos;
6. The effect of the presence of more than one type of asbestos in a bulk sample;
7. The feasibility of individually calibrating PLM laboratories with information derived in round robin sample analysis programs.

Recommendations for specific changes to the method include elimination of the confidence interval calculation and revision of the rule for reporting 1 percent asbestos.

It is apparent from the results of this study that some type of training would be required to achieve comparable application of the PLM protocol between laboratories. While point counting is a classical petrographic technique, it is not a standard procedure in the majority of laboratories currently analyzing bulk samples for asbestos. Training alternatives might include regional courses and distribution of split samples analogous to the NIOSH program for the asbestos air sampling method.

It should also be noted that the PLM method presented, although an improvement over subjective techniques, is still a procedure for estimating the relative *area* occupied by asbestos fiber and matrix material. Alternative analytical techniques that measure weight percent directly or that provide an empirically more satisfying relationship to relative weight of asbestos fiber should be sought and investigated.

X-Ray Powder Diffraction

There are two major areas in the application of XRD techniques to quantitative analysis of asbestiform minerals in bulk materials that require further investigation: identification and charac-

terization of standard reference materials, and further development and evaluation of thin-layer and bulk methods of analysis.

The most common concern of laboratories participating in the evaluation of the XRD protocol was the lack of well-characterized, readily available reference materials. A thorough, systematic investigation of asbestiform materials for use as standard materials should be undertaken. This should include identification of major sources; determination of availability and cost; and complete mineralogical characterization and determination of purity, particle size distributions, and powder diffraction patterns of materials from these sources.

Since asbestos minerals vary in composition depending on the source and exhibit different behaviors in grinding, peak positions and/or relative intensities of XRD patterns may vary from sample to sample. This variability is particularly problematic for the amphibole minerals. A quantitative study to assess the comparability of X-ray response of asbestos minerals from different sources should be conducted. If possible, observed differences between different samples of the same asbestos variety should be correlated with specific sample characteristics (e.g., chemical composition and particle size).

The need for further development and evaluation of both thin-layer and bulk methods of XRD analysis is underscored by the following observations: few laboratories are currently set up to routinely perform the thin-layer analysis as prescribed; the proposed thin-layer method of quantitation is considerably more time-consuming and costly than bulk or thick-layer methods; and for samples analyzed in the methods evaluation study, the bulk method was at least as accurate and precise as the thin-layer method.

In particular, a comparison of the bulk and thin-layer methods should be made over a variety of asbestos types and matrix materials, with attention given to sample preparation requirements, instrument requirements, sensitivity, precision, accuracy, and speed and cost of analysis.

For both bulk and thin-layer methods, the following areas of investigation are proposed:

1. Assessment of sample preparation requirements;
2. Assessment of preferred orientation effects on quantitative analysis;
3. Assessment of the effect of the use of the step-scanning mode of analysis on the limits of detection; and
4. Assessment of absorption correction requirements and techniques.

Results and Evaluation

Polarized Light Microscopy

Eleven sample series were distributed to laboratories. Eight of the series were targeted at specific weight percents of asbestos fiber. Two species of asbestos were used, chrysotile and amosite. One matrix material, containing primarily gypsum, was used in all prepared samples. Target weights were designed to cover a wide range of asbestos concentrations approximately equally spaced on a logarithmic scale. Blanks (Series F) were provided as controls and for determining the method's potential for producing false positives. The "real-world" sample (Series J) was included for comparison of between-laboratory variance. Duplicates (Series K) were included to estimate the average within-laboratory variance. Target weights and allowable limits for matrix and asbestos fiber in each sample series are presented in Table 1.

Group means and standard deviations are summarized in Table 2. Note that in six of nine cases the mean (MP) of the point count group is closer to the nominal weight than the mean (MB) of Group B. This is not a significant difference, and it appears that Groups P and B are comparably biased. Note also in Table 2 that estimates by Group O are consistently higher than those by Groups P and B. Sign tests suffice to show that Group O is significantly more biased than Groups P and B. Ninety-percent confidence intervals were calculated for Group P data. Using the midpoints of the confidence intervals, the average percent bias was calculated at several weight percent levels. These are presented in Figure 1. The percent bias varies with weight percent of asbestos similarly for amosite and chrysotile samples. Point counting has a greater positive bias on amosite samples than on chrysotile samples and, in fact, underestimates asbestos content in samples containing more than about 18 percent chrysotile by weight.

The standard deviation of reported PLM data increases as the mean reported area percent of asbestos increases for all groups. Precision may be expressed as the percent-relative standard deviation or CV. CV is related to means (MP) for Group P in Figure 2. The CV is less than 100 percent on samples with more

Table 1. Sample Composition

Series	Target Wt. %	Actual Wt. %	Fiber Type	Wt. of Asbestos (g)	Wt. of Matrix (g)
C	1	1.2	Chrysotile	0.05 ± .005	4.95 ± .05
A	4	4.9	Chrysotile	0.20 ± .01	4.80 ± .05
E	16	19.4	Chrysotile	0.80 ± .01	4.20 ± .05
I	64	74.5	Chrysotile	3.20 ± .01	1.80 ± .05
H	2	2.5	Amosite	0.10 ± .01	4.90 ± .05
G	8	9.8	Amosite	0.40 ± .01	4.60 ± .05
D	16	19.4	Amosite	0.80 ± .01	4.20 ± .05
B	32	38.8	Amosite	1.60 ± .01	3.40 ± .05
F	0	0	None	None	3.0 – 5.0
J	–	50.0*	Chrysotile	–	–
K†	Varies	Varies	Chrysotile	–	–

*Mean of reported area percents, Groups P and B.

†Series K samples were provided as duplicates and included samples from series C, A, E, and I.

Table 2. *Means and Standard Deviations of Reported PLM Results, by Group (P, B, O)*

(percent asbestos by area)

Series	Type	Weight %	Means			Standard Deviations		
			MP	MB	MO	SP	SB	SO
C	Chrysotile	1.2	4.2	5.3	7.4	4.5	5.3	7.3
A	Chrysotile	4.9	7.3	4.9	24.8	6.3	2.9	27.5
E	Chrysotile	19.4	21.7	19.0	42.0	14.8	5.9	24.6
I	Chrysotile	74.5	64.3	63.0	85.6	19.6	17.3	4.7
H	Amosite	2.5	12.5	18.0	24.0	8.6	13.9	18.3
G	Amosite	9.8	26.2	29.3	40.0	16.9	17.3	12.7
D	Amosite	19.4	37.8	42.3	41.4	17.7	17.5	12.4
B	Amosite	38.8	48.9	57.7	65.0	19.5	17.4	21.5
F	None	0.0	0.2	0.0	1.0	0.9	0.0	2.2
J	Environmental	-	50.7	49.3	65.0	16.1	14.7	11.2

than approximately 6 percent asbestos by area and less than 50 percent on samples with more than approximately 32 percent asbestos by area. At MP = 10 percent asbestos, CV ≅ 79 percent; at MP = 20 percent, CV ≅ 61 percent; at MP = 50 percent, CV ≅ 41 percent.

It is of interest to evaluate the accuracy of the PLM methods after adjusting for the relationship between reported area percent and the known weight percent of the samples. This allows not only a better understanding of what reported PLM data mean but also indicates what improvements might be made in data quality by adjusting PLM area percent estimates to better represent weight percent. Area percent data were adjusted for laboratory and asbestos-type effects to yield predicted weight percent values for each individual result. The most obvious and expected result in comparing the average percent absolute errors of treated and untreated data is the considerable gainin accuracy (reduction of error) that results from the transformation. After transformation, the average Group P inaccuracy is only one-fifth of the original. Adjusted Group P data are significantly more precise than those of Groups B and O. If laboratories had access to information with which they could calibrate their results (according to the area-weight relationship for each laboratory and asbestos type), considerable gains in accuracy and precision of results could be achieved. The gains in precision would be greater for laboratories using the point counting quantitation procedure than for laboratories using alternative procedures.

X-Ray Powder Diffraction

Means and standard deviations of all reported XRD results are shown in Table 3. Average reported values for XRD are shown for bulk methods, thin-layer methods, and both methods together. Except for Series G, the means of the bulk method are closer to the reference values than those of the thin-layer method. Estimates of precision, given by the coefficient of variation, showed no significant difference between bulk and thin-layer methods. Considering individual CVs, those for bulk are all less than or equal to those for thin-layer, except for Series C and B, further suggesting that bulk methods are at least as precise as thin-layer methods, as applied by laboratories in this study.

Comparison of the bulk and thin-layer methods by asbestos type indicates that for analysis of chrysotile, bulk methods are significantly less biased than thin-layered methods. No significant difference in slopes (bias) was observed between bulk and thin-layer methods for amosite.

The results do give evidence that XRD is capable of detecting chrysotile at the 1 percent level in a simple matrix and suggest that at this level the thin-layer method may be more reliable. Further investigation is required to determine reliable detection limits over a variety of sample materials for both procedures.

Bulk methods appear to be at least as accurate and precise as thin-layer methods over the range of samples included in this study and significantly more accurate for the analysis of chrysotile.

Since chrysotile is the most commonly occurring asbestos mineral in bulk insulation materials, and since most laboratories routinely performing quantitative analysis of asbestos in insulation samples use bulk methods of analysis, use of bulk methods of XRD analysis (ancillary to PLM) should be given further consideration.

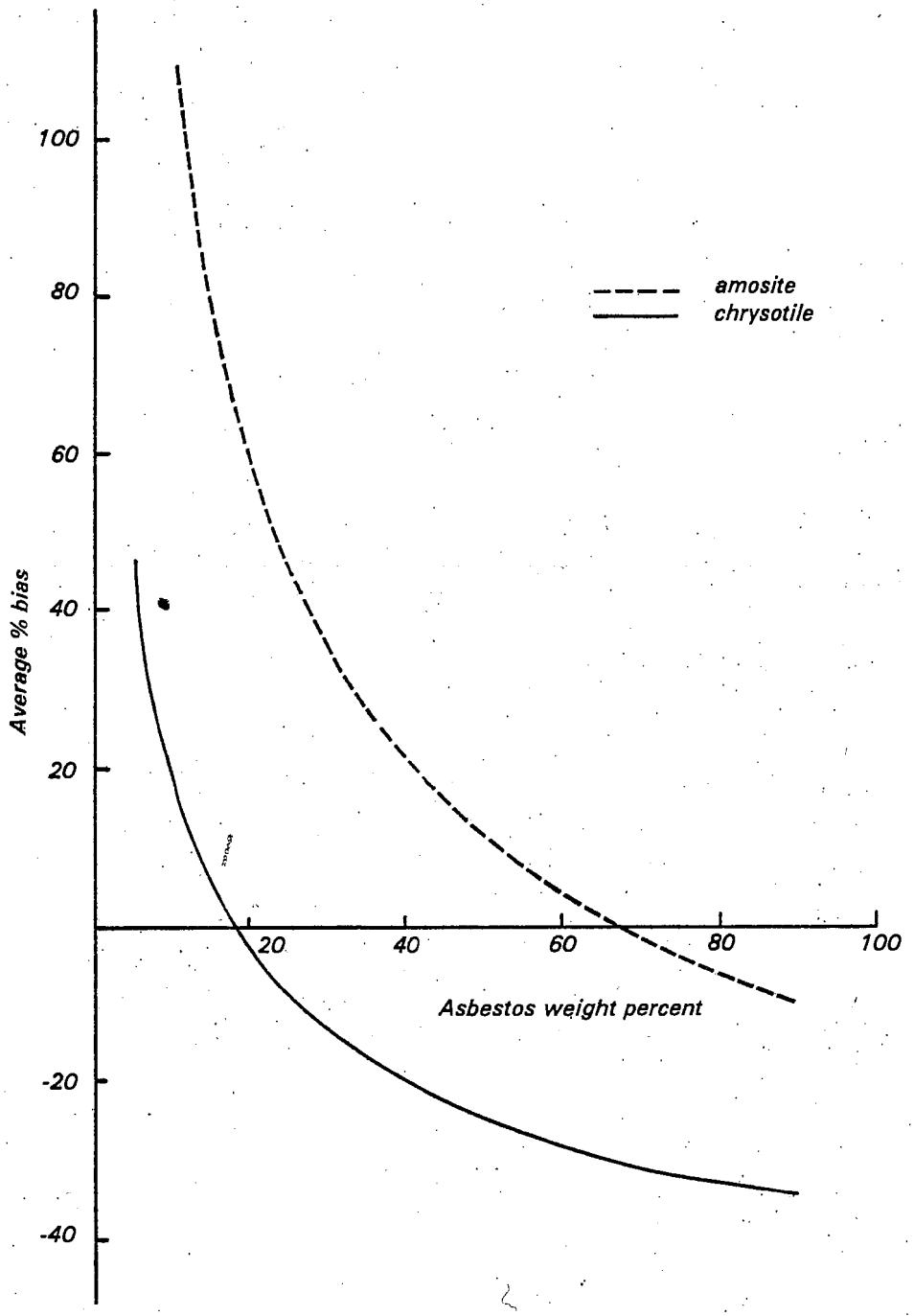

Figure 1. Average percent bias of Group P (point count) data.

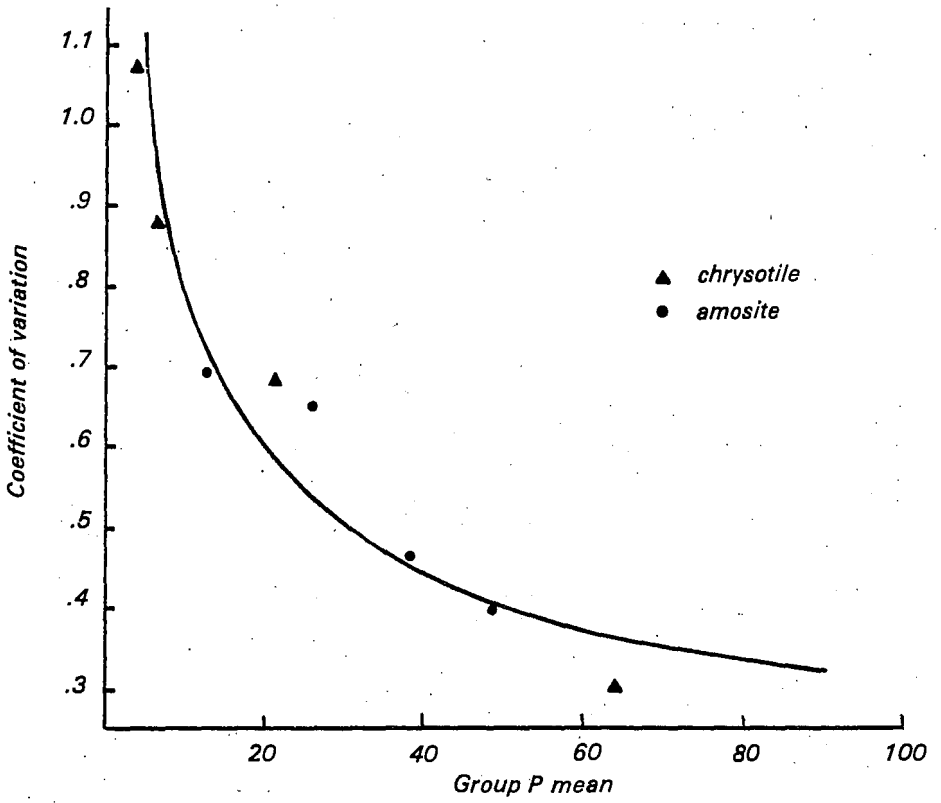

Figure 2. Coefficient of variation of Group P (point count) data.

Table 3. Means and Standard Deviations of Reported XRD Results

(percent asbestos)

Series	Type	Weight %	Thin-Layer M	Thin-Layer S	Bulk M	Bulk S	Pooled M	Pooled S
C	Chrysotile	1.2	3.0	2.0	1.0	1.7	2.5	1.8
A	Chrysotile	4.9	3.3	3.5	4.3	4.2	4.3	3.3
E	Chrysotile	19.4	3.7	3.5	18.0	11.4	10.8	10.9
I	Chrysotile	74.5	50.0	7.1	74.5	0.7	62.2	14.7
H	Amosite	2.5	1.5	0.7	3.0	1.4	2.8	1.0
G	Amosite	9.8	7.0	5.7	21.7	4.2	15.8	9.0
D	Amosite	19.4	28.0	12.7	24.0	6.9	25.6	8.3
B	Amosite	38.8	61.0	11.3	52.0	22.5	55.6	17.6
F	None	0	0.2	0	0	0	0	0

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The complete report, entitled "Bulk Sample Analysis for Asbestos Content: Evaluation of the Tentative Method," (Order No. PB 82-196 841; Cost: $13.50, subject to change) will be available only from:
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