Nevertheless, we have analyzed a few hundred samples (sediments and rocks) in parallel by MWP-OES and ICP-OES. The results are in good agreement, except for Ba. It is indeed possible to make good routine analysis of geological samples with MWP if all the special demands on the sample preparation are fulfilled, including the addition of buffers (*5*, *6*). However, these tricky preparation procedures make MWP-OES a highly awkward analytical method. The fact that the MWP nebulizer can stand higher salt concentration than the ICP nebulizer nevertheless makes it potentially a very interesting source, since nebulizer malfunction is a common source of disturbance in routine analysis.

In many cases it is possible to detect matrix changes from the form and size of the plasma. As the plasma changes, it is obvious that a fixed optical axis through the plasma will observe regions with different energies and thus also different excitation conditions.

ICP-OES. The freedom from matrix effects makes it very easy to prepare both samples and calibration solutions for ICP-OES. Even if different dissolution methods are mixed, it is still possible to make accurate analysis, but the contaminations from reagents can cause trouble if the same amounts of reagents are not used in all samples. The plasma unit itself can generally tolerate very large matrix changes. This led us to recommend that the samples and, if possible, the standard rocks should be uniformly prepared to minimize the effect of contamination due to reagents. There are no difficulties in making synthetic calibration solutions for trace element analysis since the absence of the main elements of a geological matrix in the calibration solutions causes no problems. This makes it easy to prepare calibration solutions for the analysis of trace elements that lack certified values.

The nebulizer and sample transportation can cause several disturbances, but these are not true matrix effects in the plasma. To avoid clogging of the nebulizer, we now use a new preparation method, in which the sample to flux ratio is 1:1. The most critical part in an ICP system is the nebulizer unit, which needs further development. This is of importance for making a good routine analysis system better. The very low detection limits as well as the extended dynamic concentration range makes ICP-OES an ever more superior analytical method than MWP-OES.

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Determination of Microgram Quantities of Asbestos by X-Ray Diffraction: Chrysotile in Thin Dust Layers of Matrix Material

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A method has been developed for the determination of microgram quantities of chrysotile (serpentine asbestos) which is precise, accurate, and rapid. The method utilizes X-ray diffraction techniques and has the capability of measuring microgram amounts of either pure chrysotile or small quantities of chrysotile (typically 1–10% by weight) in the presence of large amounts of matrix material. Detection limits as low as 2 μg/cm^2 (on a filter) are cited. In developing this method, phase analysis procedures, methods of sample preparation, and a technique for X-ray absorption corrections were evaluated.

The detrimental health effects of airborne asbestos particles, notably asbestosis, lung cancer, and mesothelioma (*1–3*), have necessitated the development of analytical techniques that can be used to monitor personal exposures to asbestos fibers. To date, the primary method of asbestos analysis has been fiber counting using optical or electron microscopy, but associated with this method is considerable variability in the measurement of asbestos concentration both within and among laboratories (*4–9*). Representative of this variability is data on analyses of ambient air samples (*4*) which show that differences between laboratories may be as high as two orders of magnitude. Along the same line, appreciable errors also occur in counting fibers collected in occupational environments (*4*, *6*, *7*). This variability is a natural consequence of factors inherent in the counting procedure, i.e., microscope quality, mounting procedure, and the necessity for interpretation by the analyst. While the present U.S. standard is still in terms of fibers per unit volume, the severe analytical problems posed

Table I. Measurement Parameters

component	analytical^a peak(s), ° 2θ	scan range, ° 2θ	step increment, ° 2θ	time per step incr., s
chrysotile	12.08	10.58-13.58	0.02	10
	24.38	22.88-25.88	0.02	10
silver	38.03	37.03-39.03	0.02	0.5
α-quartz	26.66	26.41-26.91	0.01	0.6
talc	9.32	7.82-10.82	0.02	2

^{a} Cu Kα radiation (1.54178 Å).

by the counting method have provided impetus for developing an accurate, precise, rapid, and automated method capable of analyzing microgram quantities of airborne respirable dust. Precedence for measuring asbestos in terms of mass rather than number of fibers has been set in the adoption by West Germany of a mass standard (0.15 mg/m^3) for airborne chrysotile (*10*). The British New Asbestos Regulations, adopted in May 1970, limited chrysotile exposure to 0.1 mg/m^3 or 2 fibers/cm^3 (*10*).

X-ray diffraction (XRD) was deemed the method most feasible for analyzing minute quantities of chrysotile and, while a number of other investigations have been made concerning the quantitative measurement of chrysotile by XRD, the quantities examined were generally in the milligram rather than microgram range. Working in a range of 1–10 mg, Crable et al. (*11–13*) clearly demonstrated the viability of XRD for the quantitative measurement of asbestos. Goodhead (*14*) used film techniques for determining percent chrysotile in a silicon matrix, and Rickards (*15*) cited 10 μg as the detection limit for chrysotile by XRD and postulated that 50–100 μg could be measured in the presence of an interference.

In the process of developing an effective method a number of factors had to be examined and evaluated. Of pivotal importance were the following: (1) the effects of the ultrasonic treatment used in sample preparation on X-ray response and particle size, (2) the cogency of the various phase analysis methods, (3) corrections for X-ray absorption by the analyte and any co-existent matrix, (4) techniques for preparing thin layers of dust on filters, (5) an evaluation of analytical bias resulting from ashing of the collection filter followed by redeposition of the analyte and (6) the detection limit and analytical parameters associated with the method. Each of these areas was thoroughly examined or developed so that, based upon the results obtained from this study, a well-documented statement can now be made about the feasibility of XRD for chrysotile analysis. Of equal importance is the fact that the fundamentals developed during the course of this work can now be extended to other serpentine and amphibole minerals, both pure and in interfering matrices.

EXPERIMENTAL

Apparatus. A Philips APD-3500 automated powder diffractometer was used with a Philips XRG-3000 X-ray generator and a scintillation counter. Small integrated peak areas were reliably measured through the use of a step scanning mode. Silver membrane filters were used as a support for the samples and, in conjunction with a pulse height selector and a focusing graphite monochromator, were used to reduce background. All measurements were obtained using a Philips long fine focus copper X-ray tube run at a power level of 1400 W. The instrumental configuration employed in this study included a 1° receiving slit and a 2θ compensating divergence slit. The positions (2θ) of the analytical peaks for the various analytes examined along with the associated scan ranges, step increments and count times per step increment are summarized in Table I.

Reagents. Chrysotile, obtained from Union Carbide was designated as Calidria asbestos, high purity open. Talc was obtained from the Sierra Talc and Chemical Company, a division of Cyprus Mines Corporation. Silver membrane filters (Selas Flotronics), Millipore AA filters, and Gelman DM-450 filters were used at various stages in this study. Dispersions were produced using reagent grade isopropyl alcohol (Fisher).

Grinding, Sieving, and Particle Sizing. Chrysotile (0.8 g) was placed in a freezer mill (SPEX, Inc.), cooled to liquid nitrogen temperature and ground for 7 min at a grinding rate of ca. 5 impacts per second. Because dry grinding may lead to some decomposition of the chrysotile, the grinding rate and grinding time were kept to a minimum. The ground material was wet sieved through a 10 ± 2 μm sieve following the general method of Kupel (*16*). The talc was dry sieved as received through a 10-μm sieve using an Allen-Bradley Sonic Sifter. All particle size determinations were performed with an RCA-EM3H transmission electron microscope.

Preparation of Suspensions. A weighed amount of the sieved chrysotile or talc was placed in 50 mL of isopropyl alcohol and the mixture subjected to an ultrasonic cell disruptor (Ultrasonics, Inc., Model W140) at an output power level of 5 W until a stable suspension was obtained. The resulting suspension was diluted to 1 L with isopropyl alcohol in a standard volumetric flask to give the desired final concentration. To prepare suspensions containing both talc and chrysotile, separate dispersions of the two minerals were first generated in the manner given above, then combined. The final concentrations of chrysotile ranged from 5–10 μg/mL while the talc ranged from 100–1000 μg/mL.

Deposition of Thin Dust Layers on Silver Filters. Two pore sizes of silver membrane filters were used in this study, 0.45 and 0.80 μm. The former was used to maximize sensitivity (see Table II) and the latter for those large depositions that would clog the 0.45-μm membranes. Two techniques were used in preparing thin dust layers on the silver filters. In the first, pipetted aliquots of the suspensions were filtered through silver membrane filters following a carefully developed procedure as follows: prior to removal of an aliquot, the suspension was first stirred for 1 min with a magnetic stirrer, then vigorously hand shaken, stirred a second time for 1 min and finally hand shaken again. The aliquot was withdrawn immediately after the second agitation during which time the dispersion was *not* stirred. A positioning collar placed on the pipet ensured that each aliquot was taken from the center of the dispersion. Three milliliters of isopropyl alcohol were then placed in the reservoir of a 2.5-cm Gelman vacuum funnel prior to the addition of the aliquot. After delivery, the pipet was rinsed into the reservoir and the mixture rapidly filtered. The sides of the reservoir were *not* rinsed after filtration. Two types of pipets were used in this method, a class A transfer pipet and a class A transfer pipet with the capillary tip removed (recalibrated).

In the second method of dust layer preparation, the required amount of material was weighed out, dispersed in isopropyl alcohol and subsequently filtered through a silver membrane filter. This method was designed to avoid the use of a pipet.

In both methods, the suspensions were filtered using the Gelman vacuum filter funnel giving an effective area of deposition of 3.46 cm^2; a rectangular area 1.41 cm × 1.59 cm (2.24 cm^2) is actually irradiated by the X-ray beam.

Filter Ashing. The Millipore AA or Gelman DM-450 filters (with deposited talc and chrysotile) were ashed in an International Plasma Corporation low temperature asher for 4 h at a radio frequency (RF) power level of 100 W with an oxygen flow of 70 cm^3/min.

THEORY

Corrections for X-ray Absorption. If absolute amounts of analyte are to be quantitatively measured, then corrections for X-ray absorption by the analyte and by any surrounding matrix must be made; i.e., the measured intensity I_m must be multiplied by a correction factor Γ to give the corrected intensity I_c

$$I_c = \Gamma I_m \tag{1}$$

For samples of less than "infinite thickness" (*17*), Williams (*18*) devised a method whereby the absorption coefficient of a powder could be determined at the same time as analytical intensities were being measured. This was accomplished by mounting the powder on the surface of a metal and measuring the attenuation of the X-ray beam from the metal after it had passed through the powder. Williams went on to successfully use this method for determining quartz in various ceramics (*18*). Along similar lines Leroux (*19, 20*) derived an equation for evaluating the above correction factor based on the amount of attentuation observed for the intensity of a diffraction peak from an underlying silver filter. This correction factor is expressed as follows:

$$\Gamma = \frac{-R \ln T_n}{1 - T_n^{R}} \tag{2}$$

where $R = \sin \theta_{Ag}/\sin \theta_X$ (X represents analyte) and $T_n = I_{Ag}/I_{Ag}^0$ where I_{Ag} and I_{Ag}^0 represent the intensities of the attenuated and unattenuated silver peaks, respectively.

Combining Equations 1 and 2

$$I_c = I_m \frac{-R \ln T_n}{1 - T_n^{R}} \tag{3}$$

By plotting intensity as a function of weight for standards prepared from pure analyte (negligible absorption effects when less than 200 μg/filter), a calibration curve is generated from which slope (m_o) and intercept (b_o) may be calculated. Substituting these parameters into Equation 3 gives a general expression for the corrected, absolute weight of analyte (X_c).

$$X_c = \frac{1}{m_o}(I_c - b_o) \tag{4}$$

Calculation of Detection Limits as a Function of the Amount and Nature of a Matrix. Using some of the equations established above, an expression has been derived by this laboratory for use in calculating detection limits for an analyte at any specified concentration in various matrices. The theoretical ratio of the intensities of a silver reflection from a filter with and without the thin layer of sample is given (*21*) by the equation

$$T_n = I_{Ag}/I_{Ag}^0 = \exp\frac{-2\mu_s^* t\rho}{\sin \theta_{Ag}} \tag{5}$$

where t = sample thickness (cm), ρ = bulk density of the sample (g/cm^3), and

$$\mu_s^* = \Sigma f_i \mu_i^* \tag{6}$$

(f_i and μ_i^* are the weight fraction and mass absorption coefficient of the ith component).

Since $t = X/Af\rho$ where X = weight of pure analyte (g), A = area of deposition (cm^2), and f = weight fraction of pure analyte, then

$$T_n = \exp\frac{-2X\mu_s^*}{Af \sin \theta_{Ag}} \tag{7}$$

Defining the lower limit of detection (LLD) as the amount of material required to produce a *measured* intensity equal to three times the standard deviation of the background intensity (*22, 23*), then at the LLD

$$3s = I_m = I_c/\Gamma = \frac{m_o X + b_o}{\Gamma} \tag{8}$$

Substituting Equations 2 and 7 into 8 yields the expression

$$3s = (Xm_o + b_o)\,\frac{1 - [\exp(-2X\mu_s^*/Af \sin \theta_{Ag})]^{R}}{-R(-2X\mu_s^*/Af \sin \theta_{Ag})} \tag{9}$$

By determining a 3s level from background measurements and by specifying both the weight fraction of analyte in the matrix (f), and the mass absorption coefficient of the sample (μ_s^*), Equation 9 can be solved for X by numerical means (*24*) to give the lower limit of detection for the analyte in the given matrix.

Table II. Relation of Sonification Time to Sensitivity and Lower Limit of Detection (LLD)

sonification time	sensitivity, counts/μg	LLD, μg/cm^2
2.5 h	61 (1)[c]	4
10 min[a]	95 (2)	3
10 min[b]	108 (2)	2

[a] 0.8-μm pore size filters. [b] 0.45-μm pore size filters. [c] Figures in parentheses represent one standard deviation for least squares line.

RESULTS AND DISCUSSION

With reference to the areas of proposed investigation outlined in the introduction, definitive statements can now be made concerning the effects, importance and applicability of these areas on this method for chrysotile. (1) While prolonged sonification does change X-ray response and probably particle size, those short periods of sonic treatment used in preparing dispersions have negligible effects. (2) The best method for phase analysis involves measuring integrated peak areas and normalizing by means of an external standard. (3) Corrections for X-ray absorption can readily and effectively be made when the analyte is present in a matrix such as talc at levels as low as 1% by weight. (4) Thin dust layers can be reproducibly generated by filtering suspensions containing particulate matter at concentrations as high as 1000 μg/mL. (5) Ashing of the collection filter and subsequent redeposition of the analyte introduces no analytical bias into the method. (6) The detection limit for chrysotile by this method is at a level of 2 μg/cm^2 on silver membrane filters, and the overall precision of the method ($\overline{\text{RSD}}$) is 6.9%. A detailed discussion of these salient points is presented below.

Effects of Ultrasonic Treatment on Particle Size. To obtain stable dispersions of chrysotile and talc, ground and sieved samples of these minerals were placed in isopropyl alcohol and subjected to the action of an ultrasonic cell disruptor. Concern about the possible reduction in the length and/or diameter of the relatively brittle chrysotile fibers as a result of the sonification prompted a study on the actual effects of the sonic treatment. This concern is particularly germane should it become necessary to use ultrasonic techniques to redisperse the chrysotile after the original collection filter has been ashed so that the asbestos may be redeposited on silver membrane filters. In this study, comparable amounts of chrysotile were "sonified" for widely varying periods of time and subsequently both sized by electron microscopy and used in generating calibration curves. The results of this investigation indicate that prolonged ultrasonic treatment (>10 min) may be reducing particle size although insufficient sizing data have been gathered to state unequivocally that the apparent decrease in size is statistically significant. The supposition of decreased particle size is borne out by the X-ray responses of the sonified material. Calibration curves generated using the sonically treated samples show increased detection limits and decreased sensitivity (counts/μg) with increased sonification time (Table II). These observations are probably a consequence of the fact that with increased sonification time a larger fraction of the sample is becoming small enough to either pass through the filter or lodge in the interior of the silver filter where it is shielded from X-rays. A more detailed study is presently being conducted to add statistical credence to the observation that sonification decreases particle size. At any rate, the marked response of the

Table III. Analytical Results as a Function of Phase Normalization Method

sample set	normalization procedure	$\overline{RSD}$[a] A[b]	$\overline{RSD}$[a] B[c]	RSD of slope A	RSD of slope B	linear correlation coefficient A	linear correlation coefficient B
I	external	8.7	7.9	2.5	2.6	0.9988	0.9986
	substrate	8.4	8.0	3.1	3.3	0.9982	0.9972
	none[d]	8.8	7.9	2.4	2.7	0.9988	0.9986
II	external	6.9	9.0	2.1	3.1	0.9991	0.9980
	substrate	6.6	9.3	2.7	3.7	0.9986	0.9972
	none[d]	6.9	9.0	1.3	1.8	0.9997	0.9993

[a] $\overline{RSD} = [\Sigma n_i(RSD_i)^2/\Sigma n_i]^{1/2}$; all relative standard deviations were tested and shown to be homogeneous before being pooled (Bartlett's test at 1% significance level). [b] 7.33-Å peak of chrysotile (primary). [c] 3.65-Å peak of chrysotile (secondary). [d] Raw intensity (counts).

X-ray sensitivity to sonification time indicates that the treatment time must be kept to a minimum.

Evaluation of Phase Analysis (Normalization) Methods. Two methods of normalizing the raw, net intensities of the diffraction peaks from pure chrysotile (no matrix) were evaluated to determine their effect on the analytical results. In the first method, corrections were made for instrumental instabilities by referencing the raw intensities to an α-quartz peak from a reference stone (external normalization). In the second method, the raw intensities were first externally normalized then referenced to a silver peak (also externally normalized) from an underlying filter to correct for any variations in the chrysotile intensity due to the orientation, height, and variability in flatness of the silver filter in the sample holder (substrate normalization). To obtain the necessary data, two sets of raw intensities were collected using two different pore size silver filters and chrysotile suspensions that had been ultrasonically treated for 10 min. The 7.33- and 3.65-Å peaks of chrysotile, the 2.36-Å peak from the underlying silver filter, and the 3.34-Å peak from the quartz reference stone were measured. The first set of data was taken using chrysotile deposited on 0.45-μm pore size silver filters (I) and the second with chrysotile deposited on 0.80-μm pore size silver filters (II). The overall analytical precision ($\overline{RSD}$, pooled relative standard deviation), the linear correlation coefficients, and the relative standard deviations (RSD) of the slopes of the calibration curves were determined using each of the two methods and also the raw data. A Bartlett's test at a 1% level of significance shows that within each set of data (I or II) the $\overline{RSD}$s and RSDs of the slopes are equal, demonstrating that both phase analysis methods give comparable results (Table III), and indicating that the physical condition of the filter is reproducible and is not a critical factor when *integrated* intensities are being measured. Convenience dictates the use of the external method unless a filter is heavily loaded (greater than ca. 2 mg) at which point the substrate method should be employed as it provides the means for X-ray absorption correction (see later section). Examination of Table III also reveals that in all instances the raw data give results comparable to both types of normalized data (Bartlett's test, 1% level). However, it is felt that this is simply a consequence of the excellent instrumental stability observed over the relatively short time period during which this study was conducted. Long-term stability has been found to be significantly less, and corrections should be made continuously for instrumental instability.

X-Ray Absorption Corrections. To evaluate the viability of the X-ray absorption correction method (theory section), thin dust layers containing 10%, 7%, 5%, 3%, and 1% (w/w) chrysotile in a talc matrix were deposited on silver filters and the intensities of the chrysotile and silver peaks measured.

The average silver peak intensity was determined using clean filters, and the chrysotile intensities were corrected for X-ray absorption using Equation 3. The slope (m_0) and intercept (b_0) values found for a calibration curve of pure chrysotile (negligible absorption effects) were then used to calculate the corrected weights according to Equation 4. A comparison of the uncorrected weights to the actual weights reveals that errors in accuracy can be significant if absorption corrections are not made. For example, at a level of 1% chrysotile in talc, a 100-μg sample of chrysotile would give an apparent weight of 49 μg before absorption correction and 102 μg after correction.

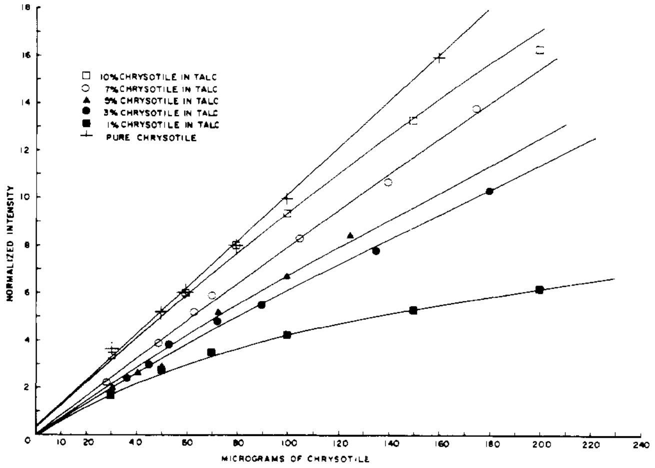

Figure 1. Intensities of the diffracted beam from chrysotile samples *before* X-ray absorption corrections (7.33 Å peak)

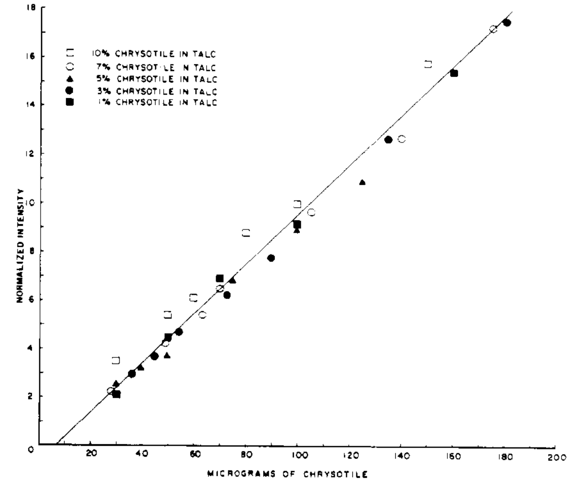

Figure 2. Intensities of the diffracted beam from chrysotile samples *after* X-ray absorption corrections (7.33 Å peak)

The effectiveness of the correction method is shown graphically in Figures 1 and 2 where the intensities of the primary chrysotile peak are plotted before and after absorption corrections. The curves in Figure 1 correspond well with those

Table IV. Calibration Curve Slopes Derived from Plots of Corrected[a] Intensity vs. Weight of Chrysotile (μg)

chrysotile in talc, %	slope, counts[d]/μg	linear correlation coefficient
100[b,c]	108	0.9991
100[b]	95	0.9988
10	98	0.9984
7	111	0.9978
5	92	0.9961
3	101	0.9993
1	102	0.9938

[a] Corrected for X-ray absorption. [b] No X-ray absorption corrections. [c] 0.45-μm pore size silver filters used, all other results are for 0.80-μm pore size silver filters. [d] Externally normalized.

Table V. Detection Limits for Chrysotile in Different Matrices

matrix	chrysotile, %	detection limit,[a] μg/cm^2
. . .	100	2
. . .	100	3 (secondary peak)
talc	10	3
talc	7	3
talc	5	3
talc	3	3
talc	1	3
ZnO_2	1	3.5
$CaCO_3$	1	3.5
ZrO_2	1	4.0
TiO_2	1	3.5
Fe_2O_3	1	4.5

[a] Determined using the primary peak (7.33 Å) unless otherwise noted.

predicted by theory (*20*), and the linearity of points in Figure 2 demonstrates the ability of the correction technique to compensate for absorption effects. The slopes of the corrected intensity vs. weight curves for the various percentages of chrysotile in talc are given in Table IV and by their comparable values further demonstrate the excellent correspondence between intensities that differed initially by as much as a factor of three due to X-ray absorption.

As an additional check on the principle of this correction technique, a portion of the data accumulated in this study was used in determining the mass absorption coefficient (μ^*) for talc (Equation 7). The experimentally determined value of 33.62 cm^2/g compares favorably with the calculated value of 31.2 (*25*) and adds further credibility to the results obtained.

Evaluation of Techniques Used for Depositing Thin Dust Layers. The thin dust layers used in this study were generated by filtering pipetted aliquots of suspensions containing particulate matter, specifically talc and chrysotile. However, there has been concern at this laboratory that errors which could significantly affect the precision and accuracy of the results may be incurred by pipetting from particulate dispersions. The primary concerns have been that the capillary tip of the pipet might foster poor precision by promoting variable amounts of particulate aggregation, and filter out a fraction of the particles, thereby introducing a bias into the analytical accuracy. To test for effects on the accuracy and precision, three different techniques were used in placing 10 mg of pure talc on three sets of 10 silver filters each. (Talc was used as it represented the mineral component that was used in highest concentration during the entire course of this investigation.) In the first technique, 10.00 ± 0.01 mg samples of talc were weighed out, suspended in isopropyl alcohol, and the entire suspension was filtered through the silver filters. In the second and third techniques, a transfer pipet and a transfer pipet with the capillary tip removed (recalibrated) were used to draw 10-mL aliquots from a suspension containing 1000 μg/mL of talc. The average talc diffraction peak intensities and associated standard deviations were used to assess and compare the precision and accuracy of the three techniques. The values of the mean and standard deviation found for the diffracted intensities from the weighed samples were then assumed to be the true and best values respectively.

A statistical F-test (two tailed) show that, at a 5% level of significance, the standard deviations associated with the samples prepared using either the regular transfer pipet or the tipless transfer pipet were not different from the standard deviation found for the weighed samples ($P = 0.638$ and 0.653, respectively). A statistical t-test (two tailed) showed that at a 5% level of significance the average intensity of the diffracted beam from the weighed talc samples is not different from the average beam intensities of the samples that were generated with either the regular pipet or the tipless pipet ($P = 0.151$ and 0.055, respectively). Thus this demonstrates that transfer pipets can be used in taking aliquots from suspensions containing particulate matter in concentrations as high as 1000 μg/mL.

Detection Limits. The detection limit for chrysotile was defined as the amount of material required to give a diffracted X-ray intensity equal to three times the standard deviation of the background (*22, 23*). Using this definition in the form of Equation 9 the lower limits of detection for pure chrysotile and for the various percentages of chrysotile in talc were established (Table V). By measuring the background radiation levels of the other matrices given in Table V at angular positions comparable to those used for chrysotile background measurements, Equation 9 was also used to predict the minimum mass of chrysotile that could be detected in these matrices assuming 1% chrysotile by weight.

One of the conclusions reached during the course of this investigation is that the analysis of bulk samples for relative percent analyte should be made on samples that are less than "infinitely thick" (*17*). The procedure involves the deposition of a known weight of sample on a silver filter, the determination of the actual weight of analyte using the absorption correction method, and finally the calculation of percent analyte. The advantages of analyzing bulk samples in this manner are: (1) both relative and absolute amounts of analyte can be determined simultaneously, (2) it becomes unnecessary to prepare calibration curves based on varying percentages of analyte in a matrix; a single calibration curve for the pure analyte suffices, and (3) the method does not require a prior knowledge of the identity or nature of the matrix (assuming it is not an interference), it is merely required that the amount of sample placed on the filter be less than that which will absorb all of the diffracted X-rays from the underlying silver filter. By comparison, the nature of the matrix *is* critical in analyzing "infinitely thick" bulk samples *unless* an internal standard is used.

Recovery Studies. The applications of the method described in this paper are directed primarily toward the analysis of samples collected by small personal air samplers, attached to workers, which draw air through a filter at ca. 1.7 L/m. Worker movement, air currents, partial blockage of the face of the filter cassette, particle size discriminators attached to the cassette, and cassette positioning may lead to inhomogeneous deposits of analyte on the filter. The principles of the method described above require (1) homogeneous depositions of uniform thickness and (2) silver filters as support material. Therefore, to assure optimum results, the collection filters must be ashed and the chrysotile redeposited on silver membrane filters. Since concern about deposition homogeneity precludes direct sampling with silver filters, a study was carried out to evaluate the possibility of bias being in-

Table VI. Count to Mass Conversion Factors for Chrysotile

fibers/μg[a]	source	mass of 8-h sample,[b] μg	ref.
0.67×10^4	textile products	244	(*27*)
1.39×10^4	friction products	117	(*27*)
2.25×10^4	pipe products	73	(*27*)
5.2×10^4	commercial buildings	31	(*5*)
2.0×10^4	"general standard"	82	(*28*)
2.0×10^4	hygiene standard	82	(*10*)

[a] Fibers >5 μm in length. [b] 1.7 L/m sampling rate.

troduced into the analytical results as a consequence of the ashing and redeposition.

Equal amounts of chrysotile were deposited on 12 Millipore AA filters and 12 silver membrane filters (six filters at each of two levels; 100 and 150 μg). The AA filters were then ashed in a low temperature asher and the residues redeposited on silver membrane filters. The average intensities of the diffracted beams from the 12 redeposited samples were compared with those of the 12 direct deposition samples and a two tailed t-test showed that at a 5% level of significance ($P = 0.466$, 0.426, respectively) there was no difference in the means at either of the two levels of loading. Similarly, both sets of filters for each of the two levels gave comparable standard deviations (two tailed F-test, 5% level of significance $P = 0.058$, 0.182, respectively) indicating that ashing and redeposition does not introduce analytical bias or affect the precision of the method.

Count to Mass Conversion. On July 1, 1976, the Occupational Safety and Health Administration (OSHA) promulgated a standard for occupational exposure to asbestos containing an 8-hour time-weighted average (TWA) concentration exposure limit of 2 fibers/cm^3 longer than 5 μm (*26*). To determine if this level is commensurate with the detection limit of the above method, it is necessary to obtain a count-to-mass conversion factor for chrysotile fibers. The results of several studies in which conversion factors were reported are summarized in Table VI. Quite clearly, the results are at variance and reflect not only the variety in the sources or uses of the fibers but also the differences in techniques used by the original investigators. However, based on these correction factors, the minimum amount of material that would be collected in a personal sample exceeds by at least a factor of three the detection limit determined for chrysotile at a level of 1% in talc and exceeds by at least a factor of five the detection limit for pure chrysotile.

CONCLUSIONS

This study clearly demonstrates the substantial potential of XRD as a routine technique for the quantitative determination of microgram quantities of serpentine asbestos. The utility of this method for both personal samples collected on filters and bulk samples is evident in its (1) specificity for chrysotile, (2) low detection limits, (3) excellent precision, particularly in comparison to the interlaboratory precisions of 30–100% (or greater) found using fiber counting methods for non-occupational (*4*, *5*, *8*), occupational (*6*, *7*), and laboratory generated samples (*9*), (4) capability of making precise and accurate quantitative measurements on small quantities of chrysotile in the presence of large amounts of matrix material, a situation where the counting method is at best difficult, (5) potential for automation, and (6) ready adaptability of the method to other asbestiform materials (e.g., tremolite) in different matrices.

No method is without its drawbacks, the primary one of which in this case is the problem of interferences. Minerals such as antigorite, lizardite, members of the kaolinite group (kandites), and possibly chlorite are potentially serious interferences with chrysotile. Sample pretreatment and X-ray line profile analysis are two approaches presently being explored in an attempt to reduce the adverse effects of interferences.

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