ASBESTOS, CHRYSOTILE by XRD 9000

$Mg_3Si_2O_5(OH)_4$ MW: ~283 CAS: 12001-29-5 RTECS: CI6478500

METHOD: 9000, Issue 3 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 3: 20 October 2015

EPA Standard (Bulk): 1% by weight

PROPERTIES: Solid, fibrous mineral; conversion to forsterite at 580 °C; attacked by acids; loses water above 300 °C

SYNONYMS: Chrysotile

SAMPLING

BULK SAMPLE: 1 g to 10 g

SHIPMENT: Seal securely to prevent escape of asbestos

SAMPLE STABILITY: Indefinitely

BLANKS: None required

ACCURACY

RANGE STUDIED: 1% to 100% in talc [1]

BIAS: Negligible if standards and samples are matched in particle size [1]

OVERALL PRECISION ($\hat{S}_{rT}$): Unknown; depends on matrix and concentration

ACCURACY: ±14% to ±25%

MEASUREMENT

TECHNIQUE: X-RAY POWDER DIFFRACTION

ANALYTE: Chrysotile

PREPARATION: Grind under liquid nitrogen; wet-sieve through 10 µm sieve

DEPOSIT: 5 mg dust on 0.45 µm silver membrane filter

XRD: Copper target X-ray tube; optimize for intensity; 1° slit; integrated intensity with background subtraction

CALIBRATION: Suspensions of asbestos in 2-propanol

RANGE: 1% to 100% asbestos

ESTIMATED LOD: 0.2% asbestos in talc and calcite; 0.4% asbestos in heavy X-ray absorbers such as ferric oxide

PRECISION ($\bar{S}_r$): 0.07 (5% to 100% asbestos); 0.10 (@ 3% asbestos); 0.125 (@ 1% asbestos)

APPLICABILITY: Analysis of percent chrysotile asbestos in bulk samples.

INTERFERENCES: Antigorite (massive serpentine), chlorite, kaolinite, bementite, and brushite interfere. X-ray fluorescence and absorption is a problem with some elements; fluorescence can be circumvented with a diffracted beam monochromator, and absorption is corrected for in this method.

OTHER METHODS: This is NIOSH method P&CAM 309 [2] applied to bulk samples only, since the sensitivity is not adequate for personal air samples. An EPA test method for the determination of asbestos in bulk insulation samples is similar to this one [3]. NIOSH method 7400 is an optical counting procedure for airborne fibers in personal samples. NIOSH methods 7402 (Asbestos by Transmission Electron Microscopy) and 9002 (Asbestos by Polarized Light Microscopy) are also useful for positive identification of asbestos.

REAGENTS:

1. Chrysotile,* certified reference material.
2. 2-Propanol.*
3. Desiccant.
4. Glue or tape for securing silver filters to XRD holders.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Vials, plastic (for bulk sample).
2. Freezer mill, liquid nitrogen-cooled, grinding vials, and extractor.
3. Ultrasonic bath.
4. Sieve, 10 µm, for wet-sieving.
5. Filters, polycarbonate, 1.0 µm, 37 mm.
6. Filtration apparatus and side-arm vacuum flask with 25 mm and 37 mm filter holders.
7. Oven, drying, 110 °C.
8. Analytical balance, readable to 0.01 mg.
9. Beaker, Griffin, 50 mL, with watch glass cover.
10. Filters, silver membrane, 25 mm diameter, 0.45 µm pore size.
11. Desiccator.
12. Bottles, glass, 1 L, with ground glass stoppers.
13. Wash bottle, polyethylene.
14. Magnetic stirrer.
15. X-ray powder diffractometer with copper target X-ray tube and scintillation detector.
16. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
17. Volumetric pipettes and flasks.

SPECIAL PRECAUTIONS: Asbestos, a human carcinogen, should be handled in a hood [4]. 2-Propanol is flammable.

SAMPLING:

1. Place several grams of the dust to be analyzed in a plastic vial, seal the vial securely, and ship in a padded carton.

SAMPLE PREPARATION:

2. Place about 0.5 g of sample dust in a grinding vial and grind in a liquid nitrogen-cooled mill for 2 min to 10 min.
3. Wet sieve the ground dust using a 10 µm sieve and 2-propanol. Place the dust on the sieve and place the sieve directly in an ultrasonic bath or in a wide dish in the bath. Use enough 2-propanol to cover the dust (put water in the bath if a dish is used to contain the 2-propanol). Apply ultrasonic power to sieve the dust.
   NOTE: It may take some time to obtain several mg of dust. Heating of the 2-propanol is likely and cooling periods may be required.
4. Recover the sieved sample dust from the 2-propanol by filtering the suspension through a non-fibrous filter (polycarbonate) or by driving off the 2-propanol on a hot plate. Dry the sieved sample in 110 °C oven for 4 h or more.
5. Weigh out about 5 mg of the sieved material onto a small square of tared weighing paper. Record the actual sample weight, W_s, to the nearest 0.01 mg. Transfer the dust to a 50 mL beaker, washing the weighing paper with several mL of 2-propanol. Add 10 mL to 15 mL 2-propanol to the beaker.
6. Cover the beaker with a watch glass. Agitate in an ultrasonic bath at least 3 min until all agglomerated particles are dispersed. Wash the underside of the watch glass with 2-propanol, collecting the washings in the beaker.

7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 mL to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel and apply vacuum. During filtration, rinse the beaker several times and add rinsings to the funnel.
   NOTE: Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add 2-propanol to the funnel when the liquid level is lower than 4 cm above the filter. Leave the vacuum on after filtration for sufficient time to produce a dry filter.
8. Remove the filter with forceps and attach it to the sample holder for XRD analysis.

CALIBRATION AND QUALITY CONTROL:

9. Prepare and analyze working standard filters:
   a. Prepare two suspensions of chrysotile asbestos in 2-propanol by weighing 10 mg and 100 mg of the dry powder to the nearest 0.01 mg. Quantitatively transfer each to a 1 L glass-stoppered bottle using 1.00 L 2-propanol.
      NOTE: Depending on the particle size of the standard, it may need to be ground and wet sieved (step 3). Dry the standards in a 110 °C oven for 4 h or more. Store in a desiccator.
   b. Suspend the powder in the 2-propanol with an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally-insulated top and add a stirring bar to the suspension. Cool the solution to room temperature before withdrawing aliquots.
   c. Mount a filter on the filtration apparatus. Place several mL 2-propanol on the filter surface. Turn off the stirrer and shake vigorously by hand. Within a few seconds of setting the bottle down, remove the lid and withdraw an aliquot from the center of the 10 mg/L or 100 mg/L suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, return all of the suspension to the bottle, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the filter. Keep the tip of the pipet near the surface but not submerged in the delivered suspension.
   d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times. Prepare working standard filters, in triplicate, by this technique, at e.g., 0 µg, 20 µg, 30 µg, 50 µg, 100 µg, 200 µg, and 500 µg.
   e. Apply vacuum and rapidly filter the suspension. Leave vacuum on until filter is dry. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the filter. Transfer the filter to the sample holder.
   f. Analyze by XRD (step 12). The XRD intensities (step 12.d) are designated I_x^o and are then normalized (step 12.e) to obtain $\hat{I}_x^o$. The intensities for standards greater than 200 µg should be corrected for matrix absorption (steps 12.f and 13).
   g. Prepare a calibration graph by plotting $\hat{I}_x^o$, as a function of the deposited asbestos mass, W_A, µg, of each standard.
      NOTE: Poor repeatability (relative standard deviation greater than 10% above 40 µg chrysotile) indicates that new standards should be made. The data should lie along a straight line. It is preferable to use a weighted least squares with $1/\sigma^2$ weighing, where σ^2 is the variance of the data at a given loading.
   h. Determine the slope, *m*, of the calibration curve in counts per microgram. The intercept on the abscissa should be 0 µg ± 5 µg.
      NOTE: A large intercept indicates an error in determining the background, i.e., an incorrect baseline has been calculated or interference by another phase.
10. Select six silver membrane filters as media blanks (for determination of sample self-absorption, step 13) randomly from the same box of filters to be used for depositing the samples. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 mL to 10 mL of 2-propanol through the filter. Remove, let dry, and mount on sample holders. Determine the net normalized count for the silver peak, $\hat{I}_{Ag}^o$, for each media blank (step 12). Obtain an average value, $\overline{B}_{Ag}$, for the normalized silver peak intensities of the six media blanks.

MEASUREMENT:

11. Obtain a qualitative X-ray diffraction scan (e.g., 10 degrees to 80 degrees 2-theta) of the sample to determine the presence of chrysotile and interferences. The expected diffraction peaks are as follows:

	Peak (2-Theta Degrees)	
Mineral	**Primary**	**Secondary**
Chrysotile	12.08	24.38
Silver	38.12	44.28

12. Mount the filter (sample, standard, or blank) in the XRD instrument and:
    a. Determine the net intensity, I_r, of the reference specimen before each filter is scanned. Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses.
    b. Measure the diffraction peak area of a chrysotile peak that is free of interference. Scan times should be long, e.g., 15 min.
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
    d. Calculate the net intensity, I_x (the difference between the peak integrated count and the total background count).
    e. Calculate and record the normalized intensity, $\hat{I}_x$, for the sample peak on each sample and standard:

$$\hat{I}_x = \frac{I_x}{I_r} N.$$

    NOTE: Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently; net intensities should be normalized to the most recently measured reference intensity.
    f. Determine the net count, I_{Ag}, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (for example, 5% of scan time for analyte peaks) throughout the method. Normalize I_{Ag} (step 12.e) to obtain $\hat{I}_{Ag}$.
    g. Scan each field blank over the same 2-theta range used for the analyte and silver peaks. These analyses serve only to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blanks.

CALCULATIONS:

13. Calculate the percentage, C, of chrysotile in the bulk dust sample:

$$C = \frac{(\hat{I}_x \times \mathrm{f}(T) - b) \times 100}{m \times W_S}, \%,$$

where: $\hat{I}_x$ = normalized asbestos peak intensity for sample peak,
b = intercept of calibration graph ($\hat{I}_x^{\circ}$ vs. W_A),
m = slope of calibration graph (counts per µg),
$\mathrm{f}(T) = \frac{-R\ln(T)}{1-T^R}$ = absorption correction factor (see Tables 1a and 1b),
$R = \sin(\theta_{Ag}) / \sin(\theta_x)$,

T = $\hat{I}_{Ag} / \overline{B}_{Ag}$ = transmittance of sample,

$\hat{I}_{Ag}$ = normalized silver peak intensity from sample,

$\overline{B}_{Ag}$ = average normalized silver peak intensity from media blanks (average of six values), and

W_S = mass, µg, of deposited sample.

NOTE: For a more detailed discussion of the absorption correction procedure, see references 5, 6, 7, and 8.

EVALUATION OF METHOD:

This method is based on the work of B.A. Lange in developing P&CAM 309 [1,2]. Samples in the range of 1% to 100% chrysotile in talc were studied to establish the feasibility of an XRD method for airborne asbestos. Analytical precision was as follows:

% Chrysotile in Talc	$\overline{S}_r$ (%)
100	6.9
10	4.7
7	9.8
5	8.2
3	10.1
1	12.5

This work also showed that bias of results after absorption corrections are made is negligible.

REFERENCES:

[1] Lange BA, Haartz JC [1979]. Determination of microgram quantities of asbestos by x-ray diffraction: chrysotile in thin dust layers of matrix material. Anal Chem *51*(4):520–525.

[2] NIOSH [1979]. Chrysotile asbestos (bulk): P&CAM 309. In: Taylor DG, ed. NIOSH manual of analytical methods. 2nd ed. Vol. 5. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 79-141, available as accession No. PB83-105445 from NTIS [www.ntis.gov].

[3] Perkins RL, Harvey BW [1993]. Test method: method for the determination of asbestos in bulk building material. Washington, DC: US Environmental Protection Agency, Office of Research and Development, EPA/600/R-93-116 [www.nist.gov/nvlap/upload/EPA-600-R-93-116.pdf].

[4] NIOSH [1976]. Revised recommended asbestos standard. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-169 [www.cdc.gov/niosh/docs/77-169/].

[5] Leroux J, Powers CA [1970]. Direct x-ray diffraction quantitative analysis of quartz in industrial dust films deposited on silver membrane filters. Occup Health Rev *21*(1):26–34.

[6] Williams PP [1959]. Direct quantitative diffractometric analysis. Anal Chem *31*(11):1842–1844.

[7] Abell MT, Dollberg DD, Lange BA, Hornung RW, Haartz JC [1981]. Absorption corrections in x-ray diffraction dust analyses: procedures employing silver filters. In: Russell PA, ed. Electron microscopy and x-ray applications to environmental and occupational health analysis. Vol. 2. Ann Arbor, MI: Ann Arbor Science Publishers, Inc., pp. 115–118.

[8] Dollberg DD, Abell MT, Lange BA [1980]. Occupational health analytical chemistry: quantitation using x-ray powder diffraction. In: Dollberg DD, Verstuyft AW, eds. Analytical techniques in occupational health chemistry. Washington, DC: American Chemical Society, ACS Symposium Series No. 120, pp. 43–65.

METHOD REVISED BY:

M. T. Abell, NIOSH/DPSE.

Table 1a. Absorption correction factor as a function of transmittance (1.00 to 0.70) for chrysotile primary and secondary peak combinations with silver primary peak

	Absorption Correction Factor	
Transmittance	Primary Peak	Secondary Peak
1.00	1.0000	1.0000
0.99	1.0157	1.0078
0.98	1.0317	1.0157
0.97	1.0480	1.0237
0.96	1.0647	1.0319
0.95	1.0817	1.0402
0.94	1.0991	1.0486
0.93	1.1168	1.0572
0.92	1.1350	1.0659
0.91	1.1535	1.0747
0.90	1.1724	1.0837
0.89	1.1917	1.0928
0.88	1.2114	1.1021
0.87	1.2316	1.1115
0.86	1.2522	1.1212
0.85	1.2733	1.1309
0.84	1.2948	1.1409
0.83	1.3168	1.1510
0.82	1.3394	1.1613
0.81	1.3624	1.1718
0.80	1.3859	1.1825
0.79	1.4100	1.1933
0.78	1.4346	1.2044
0.77	1.4598	1.2157
0.76	1.4856	1.2272
0.75	1.5120	1.2389
0.74	1.5390	1.2508
0.73	1.5666	1.2630
0.72	1.5949	1.2754
0.71	1.6239	1.2881
0.70	1.6536	1.3010

Table 1b. Absorption correction factor as a function of transmittance (0.69 to 0.39) for chrysotile primary and secondary peak combinations with silver primary peak

	Absorption Correction Factor	
Transmittance	Primary Peak	Secondary Peak
0.69	1.6839	1.3142
0.68	1.7151	1.3277
0.67	1.7470	1.3414
0.66	1.7797	1.3555
0.65	1.8132	1.3698
0.64	1.8475	1.3845
0.63	1.8827	1.3995
0.62	1.9188	1.4148
0.61	1.9558	1.4305
0.60	1.9938	1.4465
0.59	2.0328	1.4629
0.58	2.0728	1.4797
0.57	2.1139	1.4969
0.56	2.1560	1.5145
0.55	2.1993	1.5325
0.54	2.2438	1.5510
0.53	2.2895	1.5700
0.52	2.3365	1.5895
0.51	2.3848	1.6095
0.50	2.4344	1.6300
0.49	2.4855	1.6510
0.48	2.5380	1.6727
0.47	2.5921	1.6950
0.46	2.6478	1.7179
0.45	2.7051	1.7414
0.44	2.7642	1.7657
0.43	2.8251	1.7907
0.42	2.8879	1.8165
0.41	2.9526	1.8431
0.40	3.0195	1.8705
0.39	3.0885	1.8989