Asbestiform Amphibole Minerals in Cosmetic Talc

Part I: X-ray Diffraction Method

Part II: Optical Microscopy and Dispersion-Staining Method

Introduction

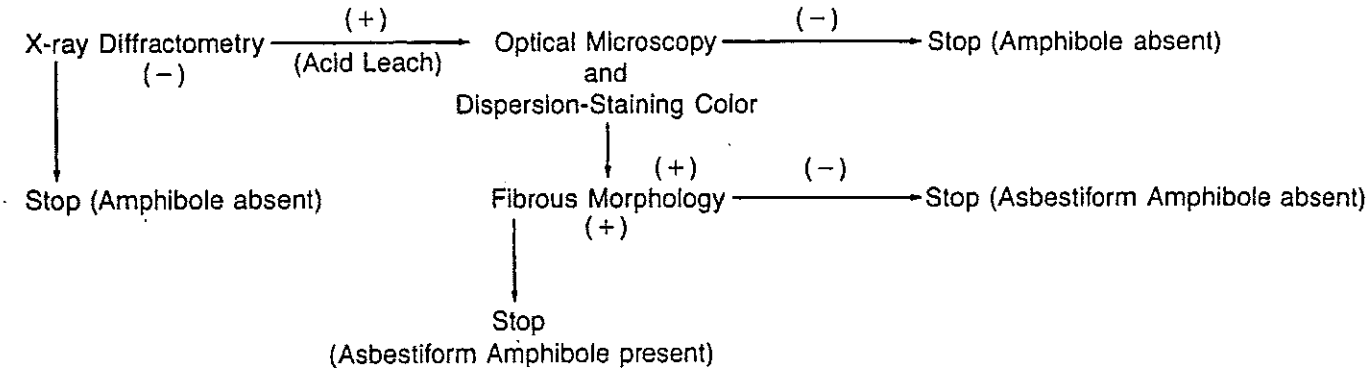
The method which has been adopted for the detection of amphibole minerals in cosmetic talc is the generally accepted method of x-ray diffraction. Methods which appear in the literature for the detection of fibrous amphibole, such as transmission electron microscopy with selected area diffraction[1] and electron microprobe,[2] have also been considered since they are capable of a lower level of detection than by x-ray diffraction. However, they have not been adopted since they suffer from the drawbacks, that the amount of material under examination is quite small (less than a microgram) and the time for analysis, expertise required, and expense of equipment eliminates them as routine methods.

The methodology presented is the most practical available, based on current technology. The use of Transmission Electron Microscopy with Selected Area Electron Diffraction offers greater sensitivity, but is not presented since it is unsuitable for normal quality control application.

Enrichment or concentration techniques using flotation cells have been tried as a means of improving the detection level; however, all efforts so far have been unsuccessful.

Principle

The x-ray diffraction method is based upon the principle that when a crystalline material is placed in an x-ray beam, a portion of the x-rays are diffracted by each set of atomic planes within the crystal. The diffracted rays strike a scintillation counter as the sample is scanned through a prescribed angle with the resulting development of peaks corresponding to each interplanar distance (d). A peak with d value in the range of 8.04 to 8.85Å for a sample talc is strong evidence for the presence of amphibole in that talc. The level of detection of amphibole by this method is 0.5% and above. The variability of detection is caused by such factors as age and manufacturer of x-ray diffractometers, sample homogeneity, specific amphibole mineral present, morphology of amphibole, particle size, preferred orientation, etc. For these reasons the level of detection should be reported for levels above 0.5%, since below this level the data has been found to be not reproducible. If a statistically significant peak is found of intensity equal to or greater than that obtained for the 0.5% standard in the d range for amphibole, described above, then the sample must be put through the following confirming scheme:



Part I: Amphibole Minerals by X-ray Diffractometry

Apparatus

1. X-ray diffractometer, employing nickel-filtered copper K-α radiation, horizontal or vertical goniometer with variable scan speed capability, suitable talc pellet sample holder, variable speed recorder, electronic panel including ratemeter and variable attenuation and time constant settings
2. Hydraulic press, capable of attaining a pressure of 15,000 to 24,000 lb calculated on a 3" ram
3. Mortar and pestle or grinding mill (Note 1)
4. Waring Blendor,* or equivalent blender
5. Spex Mixer/Mill,* or equivalent mechanical mixer
6. Sieve, 325-mesh
7. Optical microscope (Note 2)
8. 1¼" pellet press

Reagents

1. Standard talc sample, containing no detectable amphibole minerals
2. Standard tremolite sample, at least 80% pure
3. Denatured ethanol
4. Boric acid

Procedure

The procedure consists of slow-scanning, under previously determined conditions, a compressed pellet of the sample talc in the 11.0 to 10.0°2θ (8.85 to 8.04 Å) region for the presence of an amphibole peak. There are times when it is difficult to discriminate a possible peak for amphibole over the background noise level.

Should the presence of a small amphibole peak above the background "noise" be in question, it will be necessary to statistically evaluate the scan. A timer/scaler is required on the electronic panel of the x-ray diffractometer. In order for a peak to be statistically significant, the peak intensity must equal or exceed three standard deviations (3σ) above the average background intensity (N):

*Registered Trademark

Where $N + 3\sigma$ = minimum peak intensity

N = average background count

$\sigma = N$

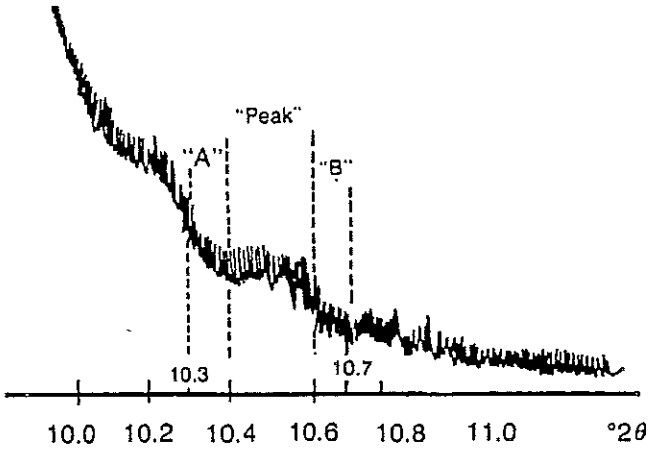


Figure 1.

Determine the region of the scan in question: in the Figure 1 scan, a peak appears to be present in the 10.40 to 10.60°2θ region.

Slow scan with cumulative pulse counting through the peak region three separate times and average the number of counts.

Determine a background count by scanning a region equal to ½ of the °2θ region covered by the peak, immediately, before and after the peak. The counting time for each of these background regions will equal ½ the total counting time used for the peak. Count each background region three times. Then average each region and add the two averages to obtain the background count (N).

Example:

In Figure 1.

	Region (°2θ)	*Time (sec.)*
Peak	10.40 to 10.60	120
Background		
Region A	10.30 to 10.40	60
Region B	10.60 to 10.70	60

Peak 10.40 to 10.60°2θ		*Background* Region A 10.30 to 10.40°2θ		Region B 10.60 to 10.70°2θ	
time secs.	*counts*	*time secs.*	*counts*	*time secs.*	*counts*
120	60,332	60	28,784	60	28,506
120	59,870	60	28,943	60	28,368
120	60,105	60	28,634	60	28,204
Average	60,102		28,787		28,359

$$N = 28{,}757 + 28{,}359 = 57{,}146$$
$$\sigma = \sqrt{57{,}146} = 239 \quad 3\sigma = 717$$
$$N + 3\sigma = 57{,}146 + 717 = 57{,}863$$

The actual number of counts obtained for the integrated peak intensity was 60,102; therefore, the "suspect" peak is statistically present in the scan.

Standard Preparation

Optimal instrument conditions must first be determined with the use of tremolite standards: 1.0%, 0.75%, 0.5% tremolite by weight, prepared in a standard talc which is free of interfering peaks in the 11.0 to 10.0°2θ region.

Weigh out appropriate amounts of standard talc and tremolite both of which have been ground to pass a 325-mesh sieve. Transfer to a Waring Blendor.* Add 100 ml of ethanol to the blender and blend at low speed for 5 minutes.

Carefully transfer the contents of the blender, with repeated ethanol washings, into a large beaker. Evaporate the ethanol on a steam bath.

Shake the sample in a plastic vial for 5 minutes on a Spex Mixer/Mill* to remove clumps and caked sample resulting from the evaporation of ethanol.

Determine by microscopy the homogeneity of the prepared standard previous to the x-ray diffraction analysis.

Press the homogeneous standard into a 1¼" pellet with a backing of boric acid. Transfer 2 (±0.2) g of standard to the die-holder and evenly distribute on a polished, scratch-free die. Distribute 4 (±0.2) g of boric acid evenly on the talc layer. Press the mixture into a pellet under conditions suitable for obtaining a smooth planar surface (for example, a pressure of 15,000 to 24,000 lb calculated on a 3" ram has been found to produce suitable pellets). The resulting pellet must have a talc face which is free of flaws; if not, the pellet must be discarded (Note 3). Prepare two acceptable pellets from each standard.

*Registered Trademark

Sample Preparation

Prepare two pellets from each sample in the manner described for the standard pellets. Make a qualitative scan from 4 to 50°2θ on one of these pellets to ascertain the presence of amphibole above the 2% level or the presence of mineral impurities having interfering peaks in the 11.0 to 10.0°2θ (8.85 to 8.04 Å) region of the scan. The presence of such interference will eliminate use of the x-ray diffraction method for the sample, and one will have to proceed directly to the microscopical procedure.

Instrumentation

Instrumental variables are optimized on the 1% standard. Lower standards are then analyzed under the optimum conditions to determine the lower level of detection. Of major importance in obtaining maximum instrument sensitivity are a slow diffractometer speed combined with compatible recorder speed, and high attenuation combined with a statistically acceptable time constant on the ratemeter. Under appropriate instrumental conditions the peak obtained for the 0.5% standard should be detectable above background noise as shown in Figure 2.

Typical instrumental conditions employed for the Siemens Diffractometer (Model No. M386-X-A4), and Counter and Recorder Unit (Type T) are:

Radiation:	Cu with K_b filter at 40 KV and 24 ma
Divergence slit:	1° Receiving slit: 0.2 mm
Goniometer speed:	$^1/_{10}$°2θ/minute
Recorder Speed:	300 mm/hour
Attenuation:	1 x 10^3 impulses/second
Time constant:	T(s) = 4

Statistical error of 1.1% under these conditions

Rise Time = 0.18
Attenuator = 20

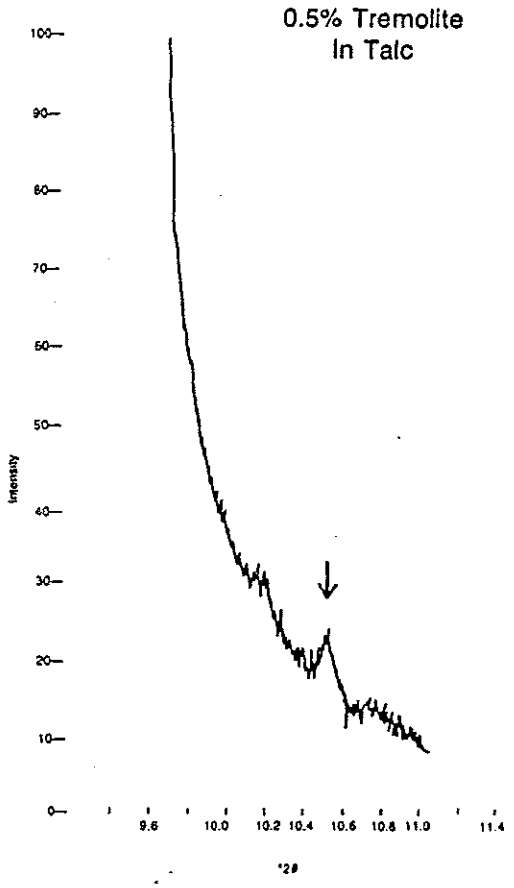


Figure 2

X-Ray Diffraction Scans

Place the standard or sample pellet in a suitable holder and slowly scan between 11.0 and 10.0°2θ. Then rotate the pellet 90° with respect to its original position in the goniometer and rescan between 11.0 and 10.0°2θ since pellet orientation may affect peak intensity. The presence of a reproducible peak (or peaks) is due to the presence of amphibole mineral (or minerals); the absence of peaks in this region indicates the absence of amphibole in the sample, within the limit of detection of this technique.

Report results as "None detected" or as "Detected approximately X% level," where "X" equals the level detected.

Part II: Asbestiform Amphibole Minerals by Optical Microscopy and Dispersion-Staining

Apparatus

1. Polarizing microscope. Best results will be obtained if the instrument includes the following:
   a. Individually centering objectives
   b. Bertrand lens
   c. High-intensity light source
   d. Centering condenser/substage
2. Dispersion-staining device (Note 4)
3. Vacuum filtration equipment, including either a porcelain cone with glass fiber filter mat or a porous glass bottom cup

Reagents

1. Hydrochloric acid, 10% v/v
2. Cargille immersion liquid Series HD, $n_D^{25^\circ} = 1.605$ (Note 5)

Procedure

Acid Treatment

Because of the interference caused by some carbonates (e.g., calcite) in the detection of asbestiform amphiboles in talc by optical microscopy/dispersion-staining, it is necessary to first remove these carbonates by a simple acid leaching procedure:

Weigh out 2 g of the talc into a 100 ml beaker. Add 25 ml of 10% v/v HCl slowly (to prevent excessive evolution of gas if carbonates are present) and heat, with occasional stirring on a steam bath for 30 minutes.

Filter with vacuum filtration equipment, and wash several times with hot water. Dry the talc.

Optical Microscopy and Dispersion-Staining

Carefully disperse 0.1 mg of talc in one drop of Cargille HD liquid, $n_D^{25^\circ} = 1.605$, and cover with a clean cover slip.

Examine the sample in the dispersion-staining central stop mode. The substage diaphragm should be almost completely closed, the field diaphragm may be partially closed to enhance color contrast, and the polarizer should be in position.

Tremolite, actinolite and presumably other amphibole minerals, under these conditions, will show the following dispersion-staining colors: yellow changing to blue with rotation of the sample relative to the polarizer *or* yellow changing to orange with rotation. The variation of the color change is due to the fact that the tremolite may lie in one of two positions relative to its principal optical orientation.

Examine the sample for asbestiform fibrous amphibole minerals.

In order for an amphibole mineral to be considered asbestiform fibrous it must meet the following OSHA definition (Reference 4).

1. Particles must appear to be fibrous rather than as crystals or slivers.
2. The maximum diameter of a fiber to be counted in 3 microns.
3. The maximum length of a fiber to be counted in 30 microns.
4. The length to width ratio must be 5 or more to 1, that is, 5 times or more longer than wide.
5. The separate or individual fibers must contain fibrils or the "bundle of sticks" effect, unless they are at a nondivisible stage. A fibril cannot be subdivided and would be counted, if it meets the other criteria. The length to width ratio of 5 or more to 1 is not meant to imply that other particles are not hazardous.

Report results as "Asbestiform Amphibole Present" or as "Asbestiform Amphibole Absent."

> It is imperative that both dispersion-staining color *and* fibrous morphology criteria be satisfied before identifying a particle as asbestiform amphibole, since other substances may show colors similar to those described.

Notes

1. Talcs to be analyzed and the tremolite used to prepare standard samples must be finer than 325 mesh (maximum particle size of 44 microns). The Tekmar Analytical Mill (Model A-10) is available from:

   Tekmar Company
   P.O. Box 37202
   Cincinnati, Ohio 45222

2. It is important that the homogeneity of the prepared talc-tremolite standard samples be verified by optical microscopy.
3. This requirement is critical since excessive surface scatter will cause abnormally high background count.
4. The only commercially available dispersion-staining device is available from:

   Walter C. McCrone Associates, Inc.
   2820 South Michigan Avenue
   Chicago, Illinois 60616

5. Available from:

   R. P. Cargille Laboratories, Inc.
   Cedar Grove, New Jersey 07009

   —or from laboratory suppliers.

References

1. Rohl, A. N., Langer, A. M., *Environmental Health Perspectives 9*, 95 (1974)
2. Rubin, I. B., Maggiore, C. J., *Environmental Health Perspectives 9*, 81 (1974)
3. L. S. Birks, X-Ray Spectrochemical Analysis, pages 54–55, Interscience Publishers (1959)
4. "Tremolite and Talc." U. S. Department of Labor, Occupational Safety and Health Administration, Field Information Memorandum #74-92, November 21, 1974

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