Asbestiform Amphibole Minerals in Cosmetic Talc

Part I: X-ray Diffraction Method
Part II: Optical Microscopy and Dispersion-Staining Method

Introduction

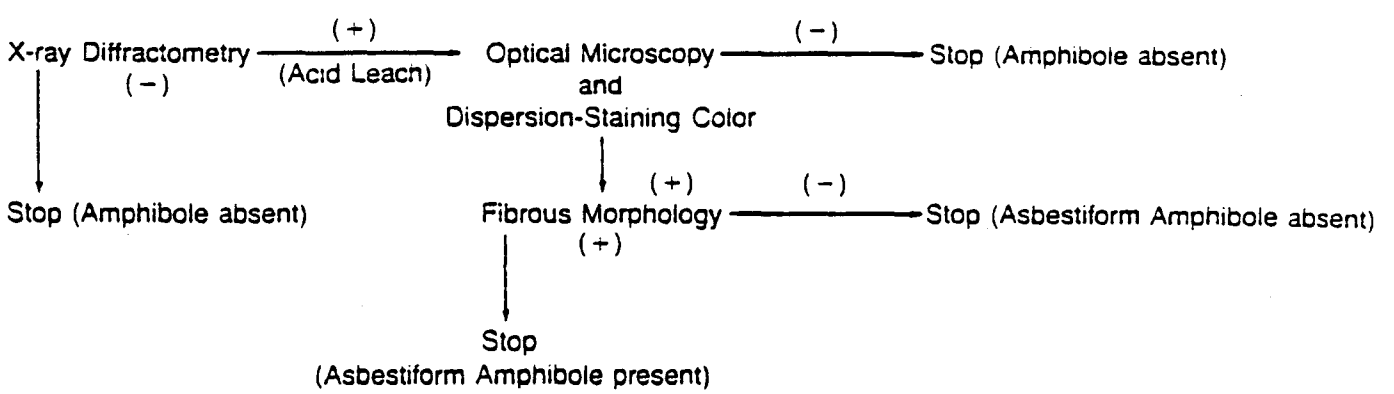
The method which has been adopted for the detection of amphibole minerals in cosmetic talc is the generally accepted method of x-ray diffraction. Methods which appear in the literature for the detection of fibrous amphibole, such as transmission electron microscopy with selected area diffraction[1] and 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

$\sigma = N$

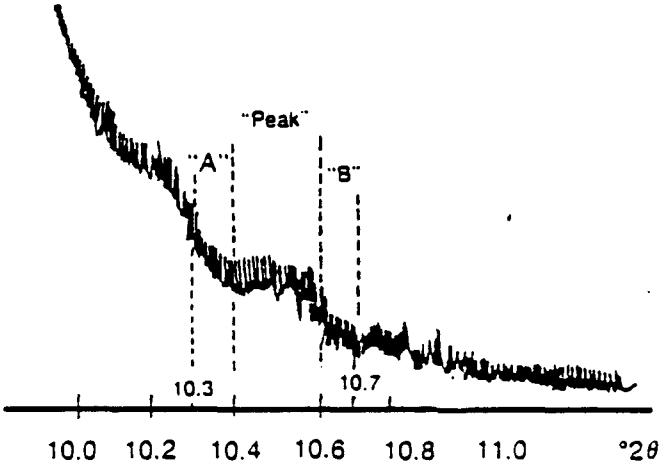


Figure 1.

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

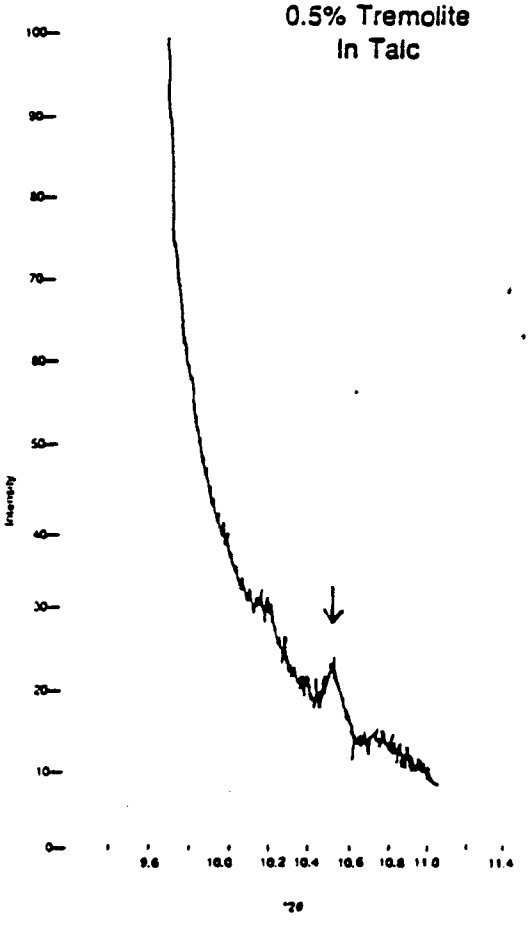


Figure 2

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

* * * * *

Free Crystalline Silica (Quartz) in Talc

(DTA Method)

Principle

Differential thermal analysis (DTA) involves the measurement of thermal reactions which are induced in a sample as it is being heated at a constant rate. First-order thermal transitions are denoted as endothermic or exothermic depending upon whether the process is accompanied by the absorption or release of energy in the form of heat. The sample holder includes a reference thermocouple and a differential thermocouple, which detect thermal reactions by continuously monitoring any difference in temperature between the sample material and a thermally inert reference substance (calcined alumina) contained in another cavity or sample dish of the holder.

The DTA method permits the unequivocal detection of quartz (free crystalline silica) in talc at a 0.5 to 1.0% w/w minimum detectable level. The method utilizes the thermal transition representing the reversible alpha to beta crystal inversion of quartz at 573 ° C. On heating, the latent heat of inversion gives rise to an endothermic reaction; on cooling, an exothermic transition is obtained. The talc is first calcined at approximately 800 ° C for the purpose of inducing irreversible thermal transitions attributable to mineral impurities. The cooling curve then shows a flat baseline, thus improving detectability for quartz. Studies have shown that the intensity of this thermal peak is affected by the particle size distribution of the quartz. Therefore, DTA is not recommended for the quantitative determination of quartz.

Apparatus

1. Differential Thermal Analyzer, including either a high temperature powder sample holder of nickel or stainless steel construction with exposed-loop differential thermocouple (such as Platinel II) or sample holder employing a ring type differential thermocouple with platinum dishes, with equipment to heat to at least 800 ° C
2. Spex Mixer/Mill,* or equivalent mechanical mixer with plastic vial and plastic ball
3. Sieve, 325-mesh
4. Mortar and pestle, or grinding mill

Reagents

1. Standard talc sample, containing no detectable quartz
2. Standard quartz sample, at least 95% pure

Procedure

Standard Preparation

Grind standard talc and quartz samples to pass a 325-mesh sieve. This will give a particle size distribution of 0 to 44 μm.

Weigh appropriate amounts of the ground standard talc and quartz into a plastic vial to prepare 1.0% w/w quartz-talc standard. Mix with a plastic ball approximately 10 minutes in Spex Mixer/Mill.*

*Registered Trademark

Instrumental Parameters

Experimental conditions for a typical DTA unit (Stone Model RC-202C or LA-XYH) are as follows:

Sample holder: high temperature powder type, of nickel or stainless steel construction (Model SH-8BE2), with exposed-loop differential thermocouple (Platinel II), imbedded reference thermocouple (Platinel II or Chromel/Alumel)

Temperature range: ambient to 800 ° C

Sample: 130 to 150 mg talc, using a loose, consistent packing technique

Reference material: alumina, ground to pass 325-mesh sieve

Atmosphere: static air

Heating rate: 10 ° C/min

Sensitivity: 40 μvolts full scale

Furnace: LTF, water-cooled to 1200 ° C

Instrumental parameters must be determined for a particular differential thermal analyzer such that 0.5 to 1.0% w/w quartz in talc may be detected in the cooling curve subsequent to calcining the talc at 800 ° C. Once these experimental parameters have been determined, they must not be altered during the analysis of talc samples in order to assure instrument sensitivity.

It is emphasized that reproducibility of the method is based on standardizing the experimental conditions.

Run the prepared quartz-talc standard to optimize sensitivity of the instrument.

If the quartz inversion endotherm at 573 ° C is masked by thermal transitions of mineral impurities in the talc, it is necessary to rely on a cooling curve for quartz detection. If there is no provision on the DTA instrument for programmed cooling, heat the talc to 800 ° C, cool to room temperature, and record the thermogram on reheating for detection of quartz.

Grind talc or talc ore samples to pass 325-mesh sieve to give particle size distribution comparable to standard sample. Run the prepared talc sample under the same identical conditions as the standard. Detect the quartz by means of the crystal inversion at 573 ° C on heating or cooling (Notes 1 & 2).

Report results as "None detected," or as "Equal to or greater than 0.5 to 1.0% w/w."

Notes

1. The value of the DTA method lies in the specificity of the determination over that attainable by x-ray diffraction in the silicate mineral matrix. No other mineral has been reported in the literature to have a thermal transition peak at 573 ° C. Semi-quantitative DTA is feasible only under fixed experimental conditions and with some knowledge of quartz particle size.
2. If semi-quantitative estimation of the quartz content is desired, this may be achieved under fixed experimental parameters by comparison of quartz peak intensities obtained for additional quartz-talc standards (Figure 1). The particle size distribution of the quartz in talc samples and standards must be as consistent as possible.

* * * * *

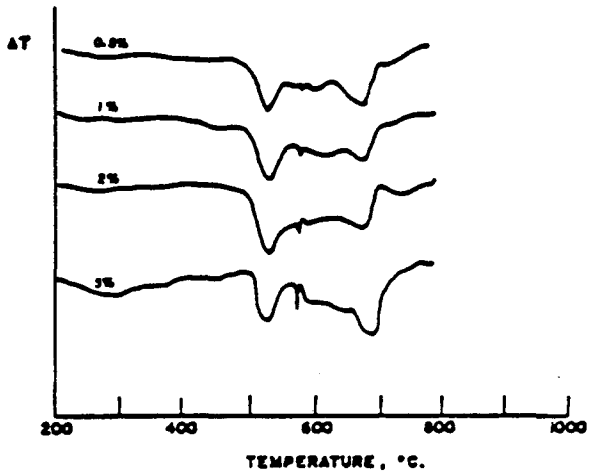


Figure 1

Free Crystalline Silica (Quartz) in Talc

(X-ray Diffraction Method)

Principle

X-ray diffraction is a convenient method for determining the presence of crystalline impurities, such as free crystalline silica (quartz), in talc. It is necessary that at least the three strongest diffraction lines of quartz be present in the x-ray pattern to confirm the presence of quartz in the talc: 3.34_x, 4.26_4, 1.82_2dÅ.

It has been experimentally determined that compression of a talc sample containing quartz into a pellet results in an x-ray diffraction pattern having more intense quartz peaks than the pattern obtained from a packed-powder sample of the same talc. Using this pressed pellet technique, it is possible to detect the three strongest quartz peaks at a minimum level of 2% w/w.

Apparatus

1. X-ray diffractometer with nickel-filtered CuKα radiation and a suitable 1¼" circular sample holder for the pelletized sample
2. Hydraulic press capable of maintaining from 15,000 to 24,000 lb (as calculated on a 3" ram)
3. 1¼" pellet press

Reagent

Boric acid

Procedure

Sample Preparation

Transfer approximately 2 g of sample talc to the die-holder and distribute evenly on a polished, scratch free die; then distribute approximately 4 g of boric acid on top of the talc layer. Compress the two layers into a pellet whose talc face is free of flaws (Note).

Instrumentation

Scan the sample pellet by x-ray through the three analytical quartz regions under instrumental conditions which have previously been determined sensitive to the 2% w/w quartz level.

As an example, the following conditions have been employed on the Siemens Diffractometer (Model No. M386-X-A4) and Siemens Counter and Recorder (Type T):

Radiation: Cu with K_B filter at 40 KV and 24 ma
Divergence slit: ½° Receiving slit: 0.2 mm
Goniometer speed: ½°2θ/minute
Recorder speed: 600 mm/hour
Attenuation = 1 x 10^3 impulses/second
Time constant, T[S] = 1
Rise time = 0.18 Attenuator = 20

X-Ray Diffraction Scans

First scan the sample pellet from 25.5 to 27.5 °2θ for the presence of a peak at 26.7 (±0.1) °2θ. If no peak is detected, quartz is absent at the lower limit of detection.

If a peak is observed in the above scan, then scan the pellet through the 19.5 to 21.5 °2θ region for a quartz reflection at 20.8 (±0.1) °2θ. The absence of a peak confirms the absence of quartz at or above 2% w/w.

If both peaks are observed, scan the sample from 49.0 to 51.0 °2θ for the presence of a peak at 50.1 (±0.2) °2θ.

The presence of all three peaks confirms that the talc contains quartz at a level equal to or greater than 2% w/w.

Report results as "None detected," or as "Equal to or greater than 2% w/w."

Note

The amount of pressure necessary for a good talc face may vary from talc to talc and can only be determined experimentally.

* * * * *