

cc: ~~BF-400~~ Dr. Schaffner
~~BF-440~~ Mr. Biermann

We are now in the process of installing an x-ray diffraction unit in the FDA laboratories. When installation is completed, Mr. Stuart will start work using Dr. Stanko's method as a reference. In any, as you suggest, wish to discuss some aspects of the method with Dr. Stanko. If so, we will contact you to make the necessary arrangements.

In closing, I would like to thank you for the research report and to express my appreciation for the effort that you and your staff have devoted to this problem. Only by cooperation of industry and government can the enormous task of protecting the consumer be accomplished.

Sincerely yours,

Robert H. Schaffner, Ph.D.
Director, Office of Technology

Bureau of Foods

R/D:Rvates:jaf:sac:9/28/73
E/D:Approved:RJBiermann/WDavis:9/28/73
W/T:jaf:9/28/73

BE-446 Mr. Davis
BF-446 Mr. Yates

September 28, 1973

Dr. Christopher H. Costello
Associate Director of Research
Research and Development Department
Colgate - Palmolive Company
909 River Road
Piscataway, New Jersey 08854

Colgate - Palmolive Company
New York, New York
AF# 13-716

Dear Dr. Costello:

This is in reply to your letter of September 6, 1973 which included a research report on the x-ray diffraction determination of chrysotile asbestos in talc. In reviewing the enclosed research report, it is obvious that Dr. Sinko and his associates have devoted a great deal of time and effort in this preparation. I am sure the method will be of valuable assistance to us in the development of our technology.

COLGATE-PALMOLIVE COMPANY
Research and Development Department
909 River Road, Piscataway, N. J. 08854

CHRISTOPHER H. COSTELLO
Associate Director of Research

September 6, 1973

Dr. Robert Schaffner
Deputy Director - Office of Technology
Bureau of Foods - FDA Building 8
Food and Drug Administration
5600 Fishers Lane
Rockville, Maryland 20852

Dear Dr. Schaffner:

Ever since the question of asbestos in talc came up approximately two years ago, our Analytical people at Colgate have been studying the problem in an effort to determine meaningful methods of detection of asbestos.

Our people have had several conferences with Dr. Lewin and other experts in this area prior to launching this program. In addition our company has acquired a step-scanning capability for our X-ray diffraction apparatus. Yesterday I received the final report on the development of a method for the determination of crysotile asbestos in talc which is estimated to have a lower limit of detection of 0.2%.

I note from the PINK SHEET of August 27 that FDA has acquired the services of Dr. John W. Stuart to undertake a program to try to identify asbestos in talc through both differential thermal analysis and X-ray diffraction. It occurs to us that the work of our Dr. Simko and his associates would be most helpful to Dr. Stuart in his work and we are therefore sending several copies of our research report on this subject in the hope that you will find it useful.

We intend to publish this work eventually, but in the interim we would be happy to have Dr. Simko discuss his work with Dr. Stuart, or whomever you might designate. Dr. Simko will be willing to go to Washington for this purpose. We would welcome Dr. Stuart here also.

Until a more sensitive method is determined, it is our intention to use this method as a basis for establishing standards for Colgate talc.

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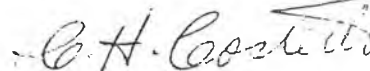
Dr. Robert Schaffner

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September 6, 1973

Please let me hear from you in regard to this matter. I am sending a copy of the research report to Dr. Alfred Weissler as well because of his involvement in this problem in the past. I trust you will both find the report of interest.

Very truly yours,



C. H. Costello

CHC:il
Enc.

cc: Dr. Alfred Weissler

Colgate-Palmolive Company
Research and Development Department
Piscataway, New Jersey

August 15, 1973

Research Report 2675
(Analytical Method)

DETERMINATION OF CHRYSOTILE ASBESTOS IN TALC BY X-RAY DIFFRACTION

Author: Pasquale Briscese

Analytical Section

PC 47 RPA 62130

Referenced Lab Notebook: 5075

Previous Research Report: None

Pasquale Briscese
Submitted: P. Briscese

J. P. Sincich
Approved:

A. Williamson
Section Head:

ABSTRACT

An x-ray diffraction technique for the determination of chrysotile asbestos in talc is described.

Quantitative analysis is made by measuring the area under a selected diffraction peak using the step-scan procedure.

The (002) chrysotile peak $d = 7.3 \text{ \AA}$ is ideal for this measurement; however, the talc (N.C. Regal Talc used in this study) contains Kaolinite (001) line $d = 7.18 \text{ \AA}$ as a contaminant which interferes with this chrysotile line. Therefore, the (004) line, $d = 2.64 \text{ \AA}$, of chrysotile was used. To compensate for its weaker intensity, a longer exposure for each step was used. This was statistically calculated to be 80 seconds.

The method is estimated to have a lower limit of detection of 0.2% chrysotile in talc.

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DIGEST OF REPORT

Introduction

The characteristics of x-ray diffraction patterns provide a specific method for the identification of crystalline compounds. This technique can be applied either qualitatively or quantitatively to the examination of solid materials.

The allegation that commercial samples of talc contain asbestos minerals contaminants which could be hazardous to health when inhaled led to the development of this method.

Major interest is focused on chrysotile asbestos, a fibrous variety of serpentine, which shows major diffraction peaks at $d = 7.3 \text{ \AA}$ and $d = 3.64 \text{ \AA}$ while the amphibole group, another variety of asbestos, shows a maximum at $d = 8.4 \text{ \AA}$. (1,2)

This report presents details for the quantitative analysis by x-ray diffraction of chrysotile asbestos in talc at the (004) line corresponding to the major diffraction peak at $d = 3.64 \text{ \AA}$.

EXPERIMENTAL DETAILS

1. Instrumental Conditions

Apparatus: Philips Electronics Instruments x-ray generator, type No. 12215/0, was used in combination with a high angle vertical goniometer, scintillation counter and step-scanner.

--CuK α radiation, Nickel filtered, generated at 35 kv and 18 Ma.

Slit system:	divergence	1°
	scatter	0.006 inch
	receiving	1°

Signals from the detector were fed through a pulse height discriminator and the integrated counts per step printed out on a teletypewriter.

The step-scanning arrangement permitted the measurement of small integrated areas of 0.01° per step. A total of 40 steps covering an angle of 0.4° 2 theta from 24.20° up to 24.60° was used for peak area, and an angle of 0.2° 2 theta from 23.50° up to 23.70° and 26.15° up to 26.35° was used for background.

In every sample prior to counting for quantitative analysis, a qualitative scan is necessary over the angle from 23° up to 27° 2 theta to ensure that the area considered for background is free from interferences.

Counting time per step was 80 seconds and total counting time 80 x 40 = 3,200 seconds for peak area and 3,200 seconds for background. (6)

Reagents*: North Carolina Regal Talc from Charles Mathiew, Inc.
Chrysotile Asbestos #410 obtained from Whittaker,
Clark and Daniels, Inc.

* Both materials were supplied through the help of the Skin Products Section.

2. Estimation of Expected Intensities

Talc, a natural hydrous magnesium silicate with the formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, crystallographically is monoclinic and triclinic in form. Geologically, the mineral occurs in rock masses and co-exists with a large number of other hydrated magnesium mineral species.

Chrysotile, a naturally-fibrous mineral, is a hydrated silicate of magnesium which approximates in composition the formula $H_4Mg_3Si_2O_9$. The structure is monoclinic, four molecules of $H_4Mg_3Si_2O_9$ in the unit cell. Each silicon atom is surrounded by four oxygen atoms arranged at the point of a tetrahedron. Together these groups form chains extending parallel to the vertical axis. The binding forces between these chains are weak, thus accounting for the fibrous structure. It includes most of the silky amianthus of serpentine rocks and much of what is popularly called asbestos. (4)

Qualitative examination by x-ray diffraction of N.C. Regal Talc showed mainly talc, with the following minor constituents: chlorite, kaolinite, phlogopite, dolomite and alpha quartz. No detectable quantities of asbestiform minerals, either the amphibole or serpentine group were seen. (2)

Of the above constituents, none absorbed Copper K α radiation strongly in relation to talc, this is known from study of the appropriate chemical elements constituent to each compound. So, absolute counts versus concentration of chrysotile should give a straight line.

The intensity of the (004) line of pure chrysotile $d = 3.64 \text{ \AA}$ gave 540 counts/second net by step-scanning. (In terms of counts per second per percent this = 5.40 c/s/%) Calculation of mass absorption coefficients for Cu K α radiation gave 32.07 for talc and 29.88 for chrysotile.

The following equation gives the c/s/% expected in a mixture of talc and chrysotile.

$$c/s/\% = \frac{5.4 \times 29.88}{32.07} = 5.03 \quad \text{and} \quad \frac{5.03}{5.40} \times 100 = 94\%$$

Practically no correction is needed due to absorption in the mixture of talc and chrysotile. (3,5)

The value obtained for the mass absorption coefficients are based on the formulas for talc, $Mg_3Si_4O_{10}(OH)_2$, and chrysotile $Mg_3Si_2O_5(OH)_4$. (Card No. 19-770 for talc and 9-444 for chrysotile edited by the Joint Committee on Powder Diffraction Standards.)*

* Joint Committee on JCPDS
Powder Diffraction Standards
1601 Park Lane, Swarthmore, Pennsylvania 19081

3. Procedure

No special sample preparation was necessary for the talc. North Carolina Regal talc is already finely-ground to pass a 325 mesh sieve, 44 microns opening, as received.

The chrysotile asbestos obtained from Whittaker, Clark & Daniels, Inc., #410, was partially ground and needed further grinding to diminish the particle size to an average of 50 microns. This was accomplished by 2 hours grinding in a Waring Blender.* The ground fibers were checked by microscope for size.

* The blending assembly can be obtained from Waring Products Service Center, New Hartford, Connecticut 06057, Model No. 5018.

An exactly-known weight of chrysotile was added to the talc. The mixture, tightly closed in a weighing bottle, was placed in another jar and insulated with tape in the jar to avoid breakage. This jar was placed in a mixer/mill* and each sample mixed for 1 hour with the help of two plastic balls.

* Spex Model 1810, Spex Industries, Metuchen, New Jersey.

Each sample, after being properly mixed, was loaded in a flat aluminum x-ray sample holder. Care was taken to ensure proper loading of the powder.

To minimize orientation effects and to standardize the procedure for each sample, the following three steps were found necessary:

1. Load the sample holder and press the powder with a spatula.
2. Remove the excess with a Gillette razor blade.
3. Make the surface flat and smooth by pressing with a ground glass plate.

Finally, place the sample in the x-ray instrument and take counts over the peak and background areas.

4. Calibration Curve

Chrysotile can be detected with a high degree of assurance by a qualitative x-ray scan when present at approximately 5% and higher. Consequently, a calibration curve covering the range from 1 to 5% only was necessary. Samples used for calibration are listed in Table 1.

Table 1

Standard Components Weights in Grams

<u>Talc</u>	<u>Chrysotile</u>	<u>Total</u>	<u>% Chrysotile</u>
2.475	0.025	2.500	1.0
2.450	0.050	2.500	2.0
2.425	0.075	2.500	3.0
2.400	0.100	2.500	4.0
2.375	0.125	2.500	5.0

Results obtained by x-ray analysis are listed in Table 2 and plotted in Figure 1.

Table 2

Results: Intensity Net Counts in 0.4° Angle
vs. Concentration in Weight % Chrysotile

<u>Concentration Weight % Chrysotile</u>	<u>Intensity Net Counts 0.4° Angle</u>
1.0	26.400
2.0	39.100
3.0	61.870
4.0	86.430
5.0	102.550

Net Counts = Total Counts (Peak Area - Background Area)

Using the method of least squares, the following equation was found for the relationship between intensity and concentration.

y = intensity (net counts)
x = concentration in wt. % chrysotile

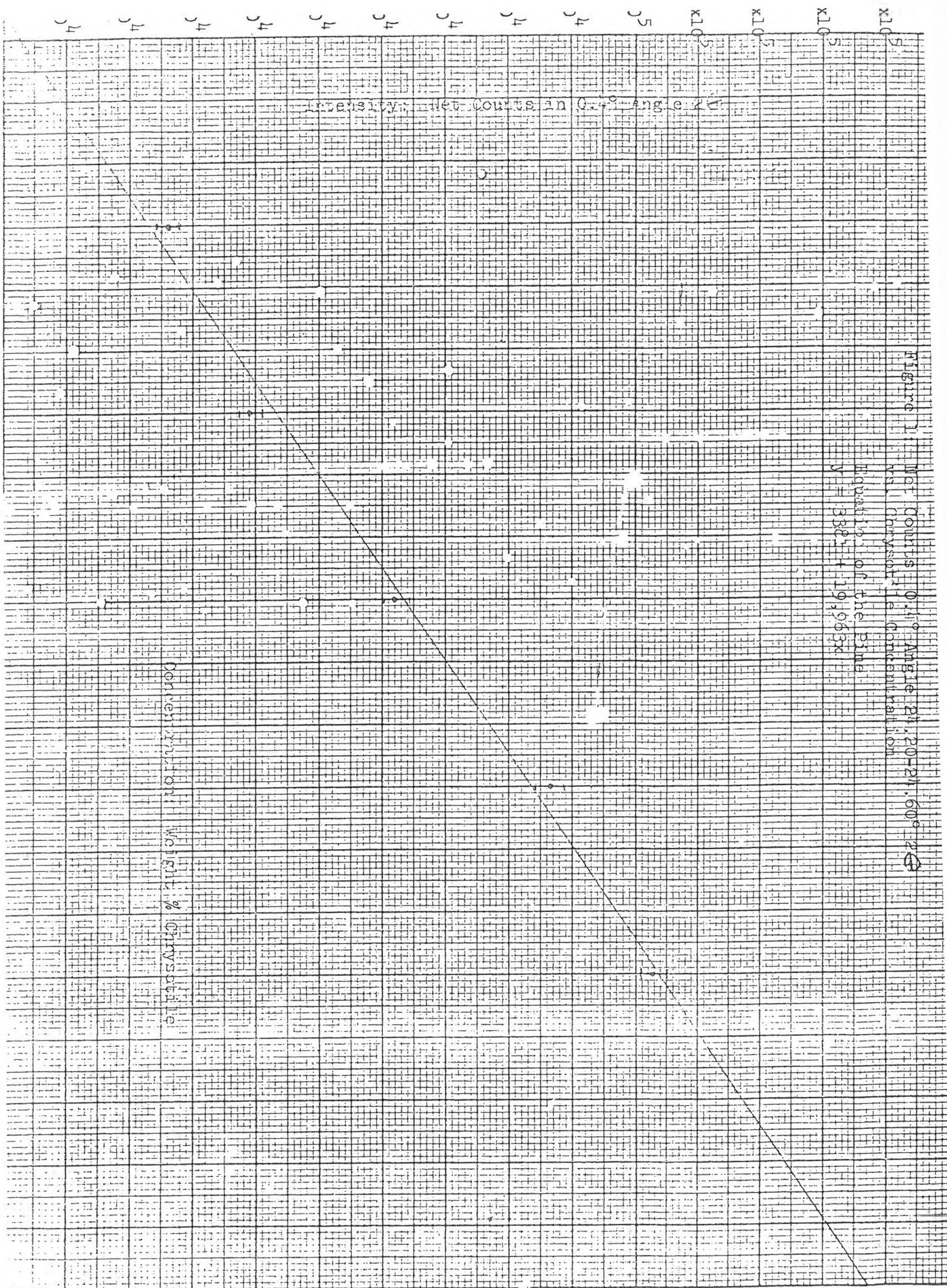
Equation of the line: $y = 3381 + 19.963 x$.

5. Analytical Error Due to Counting Statistics (5)

A series of measurements for 1, 2, 3, 4 and 5% chrysotile in talc gave the following counts. Table 3, columns 2 and 3.

Figure 1. Net Counts 0.47° Angle 24.20-24.60° 2θ
 vs. Crystallite Concentration

Equation of the line
 $y = 382.14 + 19.963x$



The standard deviation (G) in percent of a measurement involving a given number of counts at peak area N_p and a given number of counts at background area N_b is

$$G(\%) = 100 \frac{\sqrt{N_p + N_b}}{N_p - N_b}$$

In Table 3, $2G$ is shown as counting error and in terms of % chrysotile, columns 4 and 5.

Table 3

Analytical Error Due to Counting Statistics

<u>Concentration</u>	<u>N_p</u>	<u>N_b</u>	<u>Counting Error $2G$</u>	<u>Error $2G$ % Chrysotile</u>
1%	353,080	326,440	6.2%	0.062%
2%	360,740	321,640	4.2%	0.084%
3%	386,390	324,520	2.7%	0.076%
4%	429,190	342,760	2.0%	0.080%
5%	433,390	330,840	1.7%	0.085%

6. Variation of Standard Deviation With Counting Time (5,6)

A series of measurements of a sample containing 1% chrysotile in talc gave a total count 353,080 for the peak area and 326,440 for the background area. (40 steps, 80 seconds per step).

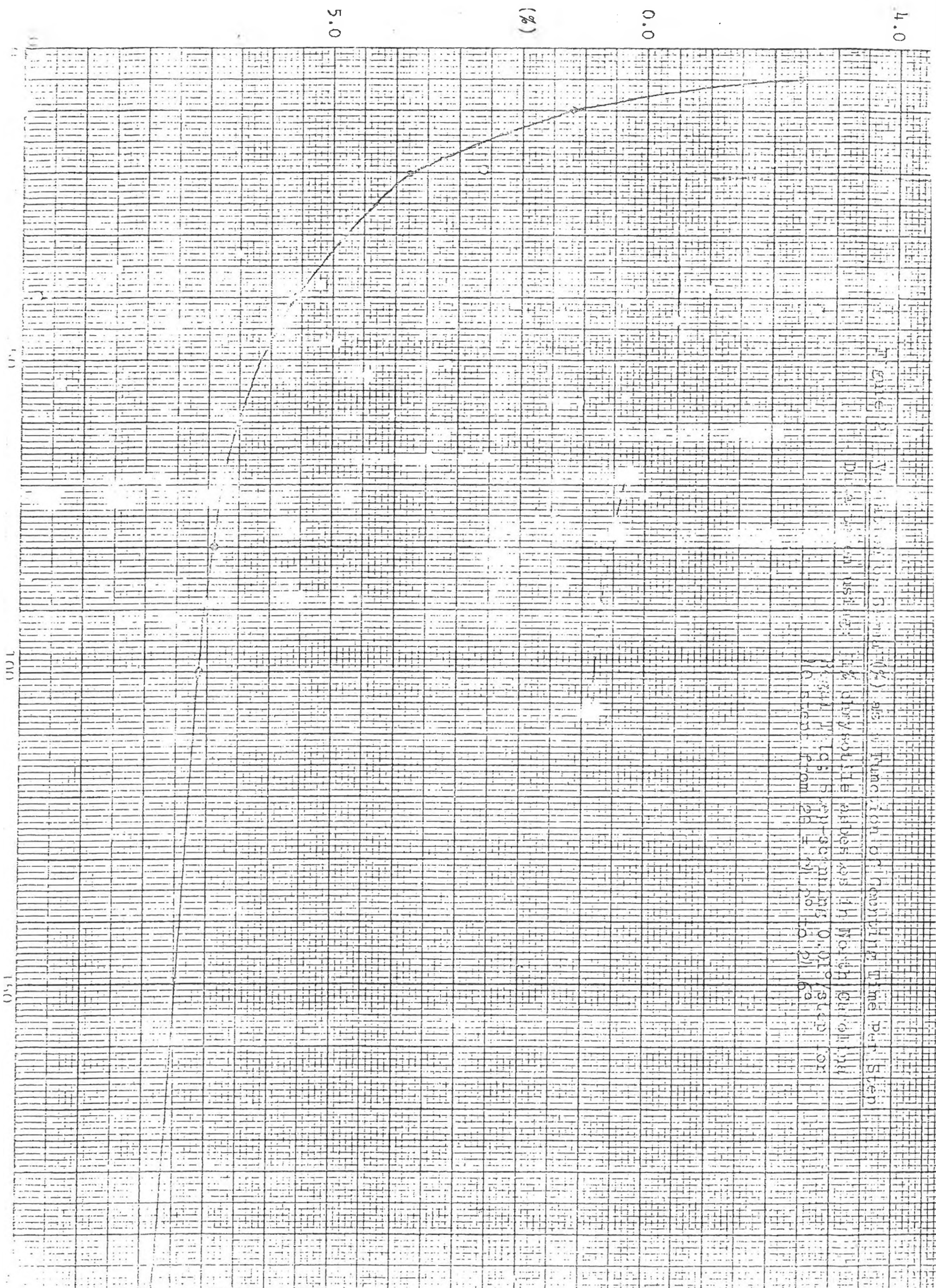
Taking the same number of steps, i.e., 40, and different counting time, i.e., 5, 10, 20, 40, 60, 80, 100 and 200 seconds per step, the following equations are applicable.

$$\frac{\text{Total Counting Time}}{3200} \times 353,080 = \text{Counts for peak area} = N_p$$

$$\frac{\text{Total Counting Time}}{3200} \times 326,440 = \text{Counts for background} = N_b$$

$$\text{where: } G(\%) = 100 \frac{\sqrt{N_p + N_b}}{N_p - N_b}$$

From the data obtained, a curve is constructed in Figure 2 showing the standard deviation as a function of counting time. No great advantage occurs by increasing the counting time above 80 seconds.



7. Lower Limit of Detection (L.L.D.) (5,6)

The lower limit of detection is normally defined as that concentration which gives a count rate equivalent to a background reading plus twice the standard deviation of the background. This assumption will be correct in 95% of cases studied (95% confidence limit).

where: $N_b = 326,440$ net counts of background

$$\sqrt{N_b} = 571.35 \text{ counts for } 1(6)$$

$$2\sqrt{N_b} = 1142.70 \text{ counts for } 2(6)$$

Equation of the line $y = 3381 + 19,967 x$

Let $y = 0$

$$x = -0.17\%$$

Let $y = 1143$ counts = 2(6) above background

$$x = -0.11\%$$

$$\begin{aligned} \text{L.L.D.} &= \Delta x = x \text{ at } y = 1143 - x \text{ at } y = 0 \\ &= 0.06\% \end{aligned}$$

As a figure of merit, it is better to multiply the L.L.D. by 3, where 3 is a factor which corrects for instrumental drift. Therefore,
L.L.D. = + 0.18% chrysotile.

RESULTS

1. Reproducibility and Precision of the Instrument

The reproducibility of the x-ray instrument was checked by daily analyses on a standard for 6 consecutive days. The standard used contained 5% chrysotile.

Table 4

Reproducibility and Precision of the Instrument Standard: 5% Chrysotile in Talc

<u>Day</u>	<u>Intensity: Net Counts 0.4° -Angle</u>	<u>% Chrysotile</u>
1	102,550	5.13%
2	102,230	5.12%
3	103,979	5.21%
4	100,039	5.01%
5	97,264	4.87%
6	101,554	5.08%
Av. =		5.07%
SD =		+ 0.12
RSD =		2.3%

2. Recovery Study

A sample of M6670 #450 finished product Cashmere Bouquet Talc was checked for chrysotile with the present method and gave zero % chrysotile.

Chrysotile was added to it for a recovery study. The results are listed in Table 5.

Table 5

Recovery Study

<u>Total Weight in Grams of Talc and Chrysotile</u>	<u>% Chrysotile Added</u>	<u>% Chrysotile Found</u>	<u>% Recovery</u>
2.5	0.2	0.33	165
2.5	0.5	0.61	122
2.5	1.0	0.93	93
2.5	2.0	1.73	86
2.5	5.0	4.9	98

The very high recovery at the 0.2% level and the more acceptable results at the 0.5% level, limit the technique to the order of 0.5%.

DISCUSSION

The method presented can be applied satisfactorily to detect chrysotile asbestos in talc. It was developed especially for the evaluation of chrysotile asbestos. In principle, however, it can be applied to any other type of asbestos subject to the limitation of producing suitable calibrations.

The lower limit of detection was calculated as 0.2%. Further improvement of the detection limit for this method will require the use of a more powerful x-ray tube, generator and improved revolution provided by the use of a crystal monochromator.

It was an unfortunate case that talc invariably contains, among other contaminants, kaolinite, making it difficult to use the more intense line (002) of chrysotile due to the proximity of kaolinite, $7.18 \text{ \AA}^\circ$, and chrysotile, $7.3 \text{ \AA}^\circ$ lines.

An early attempt to use this line after thermally destroying kaolinite at 500°C proved that along with kaolinite some chrysotile was also destroyed. (3)

Carrying the method further to use the 002 line can be very rewarding for the sensitivity that can be attained, calculated to be 46% better. However, this is not without sacrificing a lot of time since the parameters involved are many.

By looking at the less intense chrysotile line (004), free of interference, and by selecting the proper parameters, favorable results were obtained.

Total time required for the analysis of a single sample is estimated at 3-1/2 hours.

CONCLUSION AND RECOMMENDATIONS

X-ray diffraction offers a specific, accurate and precise method for the determination of chrysotile asbestos in talc at 0.5% and above.

INDEX TERMS

1. X-ray Diffraction
2. Chrysotile Asbestos
3. Talc

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