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Lewin - TALC

X-RAY DIFFRACTION ANALYSIS FOR ASBESTOS IN TALC

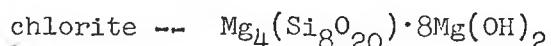
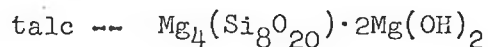
by

S. Z. Lewin, I. Salom, and B. Kraus

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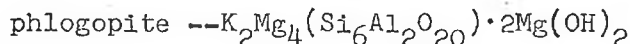
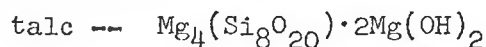
Talc, $\text{Mg}_6(\text{Si}_8\text{O}_{20})(\text{OH})_4$, is a well-defined mineral species that occurs in vast deposits in many localities. Most of the high grade, commercial talcs that are used in cosmetic products contain as accessory minerals relatively small amounts of some or all of the following species:

(a) Chlorite -- $(\text{Mg}, \text{Al}, \text{Fe})_{12}((\text{Si}, \text{Al})_8\text{O}_{20})(\text{OH})_{16}$. It will be noted that a pure magnesian chlorite is related to talc as follows:

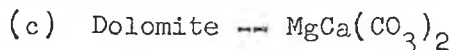


Thus, chlorite may be converted into talc by the leaching away of some of its magnesium hydroxide; and conversely, talc may be converted into chlorite through the action of ground waters or hydrothermal solutions rich in magnesium salts.

(b) Phlogopite -- $\text{K}_2(\text{Mg}, \text{Fe}^{++})_6(\text{Si}_6\text{Al}_2\text{O}_{20})(\text{OH}, \text{F})_4$. It will be seen that a pure magnesian hydroxy-phlogopite is related to talc in the following formal way:



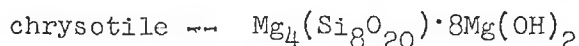
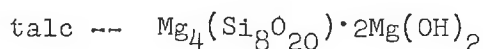
That is, two of the Si in the unit formula have been substituted by two (K, Al) pairs which have the same total formal charge.



(d) α -Quartz $\rightarrow$ SiO_2 .

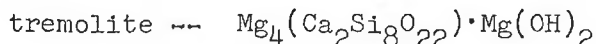
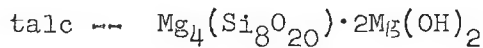
In addition to the above, one or more of the asbestiform minerals is not infrequently encountered. The principal minerals of this type that occur in commercial talcs are:

(e) Chrysotile $\rightarrow$ $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$. It will be noted that the formal analogy between talc and chrysotile may be recognized as shown in the formulas below:



Thus, chrysotile has the same stoichiometry as a magnesian chlorite; these two minerals differ only with respect to the geometry of packing within the silicate layers in the crystal lattice.

(f) Tremolite $\rightarrow$ $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$. A formal analogy between tremolite and talc may be drawn as suggested by the following formulas:



That is, two CaO are present in tremolite in place of one of the $\text{Mg}(\text{OH})_2$ of the talc structure.

(g) Actinolite $\rightarrow$ $\text{Ca}_2(\text{Mg}, \text{Fe}^{++})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$. Actinolite differs from tremolite only in having Fe^{++} replacing Mg^{++} , the degree of replacement being variable.

(h) Anthophyllite $\rightarrow$ $(\text{Mg}, \text{Fe}^{++})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. This mineral differs from tremolite only in the respect that Mg^{++} replaces Ca^{++} .

(i) Amosite $\rightarrow$ $(\text{Mg}, \text{Fe}^{++})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$. Other names for this mineral are Cummingtonite, Grunerite, and Montasite. Amosite is higher in iron content (typically 20-30% FeO) than anthophyllite (typically 3-20% FeO).

(j) Crocidolite $\rightarrow$ $\text{Na}_2\text{Fe}^{++}\text{Fe}^{+++}_2(\text{Si}_8\text{O}_{22})(\text{OH})_2$. This mineral is also known as Riebeckite. Crocidolite differs from anthophyllite in that two $(\text{Na}^+, \text{Fe}^{+++})$ pairs take the place of two $(\text{Mg}^{++}, \text{Mg}^{++})$ pairs in the crystal lattice.

The identification of the minerals accompanying talc is most unambiguously accomplished by means of x-ray powder diffractometry. Figure 1 is a composite powder pattern based upon the average line profiles observed for commercial talcs in the course of over 300 analyses employing a Cu target x-ray tube, a Ni beta-filter, G-M detector, and ratemeter recording. The solid line shows the positions, line shapes, and relative intensities of the talc diffraction peaks. Individual specimens occasionally deviate from this pattern with respect to the shapes and relative intensities of the diffractions occurring at two-theta angles greater than about 34° , due to variations in the degree of crystal perfection. The strongest talc lines are shown as going off-scale on this diagram to indicate that they are much more intense than the lines of the other mineral constituents as normally encountered in commercial talcs. The scale factor of the recording should be adjusted to bring these most intense talc peaks off-scale, in order to bring up the peaks due to the other mineral constituents adequately. These other minerals are shown by dashed or dotted lines, and their relative intensities are indicated for a content of each that is a substantial proportion by weight relative to talc assumed to be the only other constituent. That is, the chlorite peaks, labelled "c", show the relative intensities of chlorite to talc for a 30% chlorite, 70% talc mixture; the phlogopite, labelled "P", is for a 20% mixture with talc; the tremolite, "TRE", represents a 20% mixture; the chrysotile, "CHR", a 10% mixture; the quartz, "Q", a 15% mixture; the dolomite, "D", a 20% mixture. These are the only minerals encountered in over 95% of all the commercial talcs analyzed, and therefore, for the sake of clarity, other mineral species are not included in the diagram of Figure 1.

By continuous-scan recording, at the rate of about 1° two-theta per minute, the principal peaks of the asbestiform minerals can be distinguished at a minimum concentration of about 1-2% by weight. Figure 2 shows a typical recording in the region between 6° and 20° two-theta for a commercial talc containing 2.3% chrysotile and 2.0% tremolite.

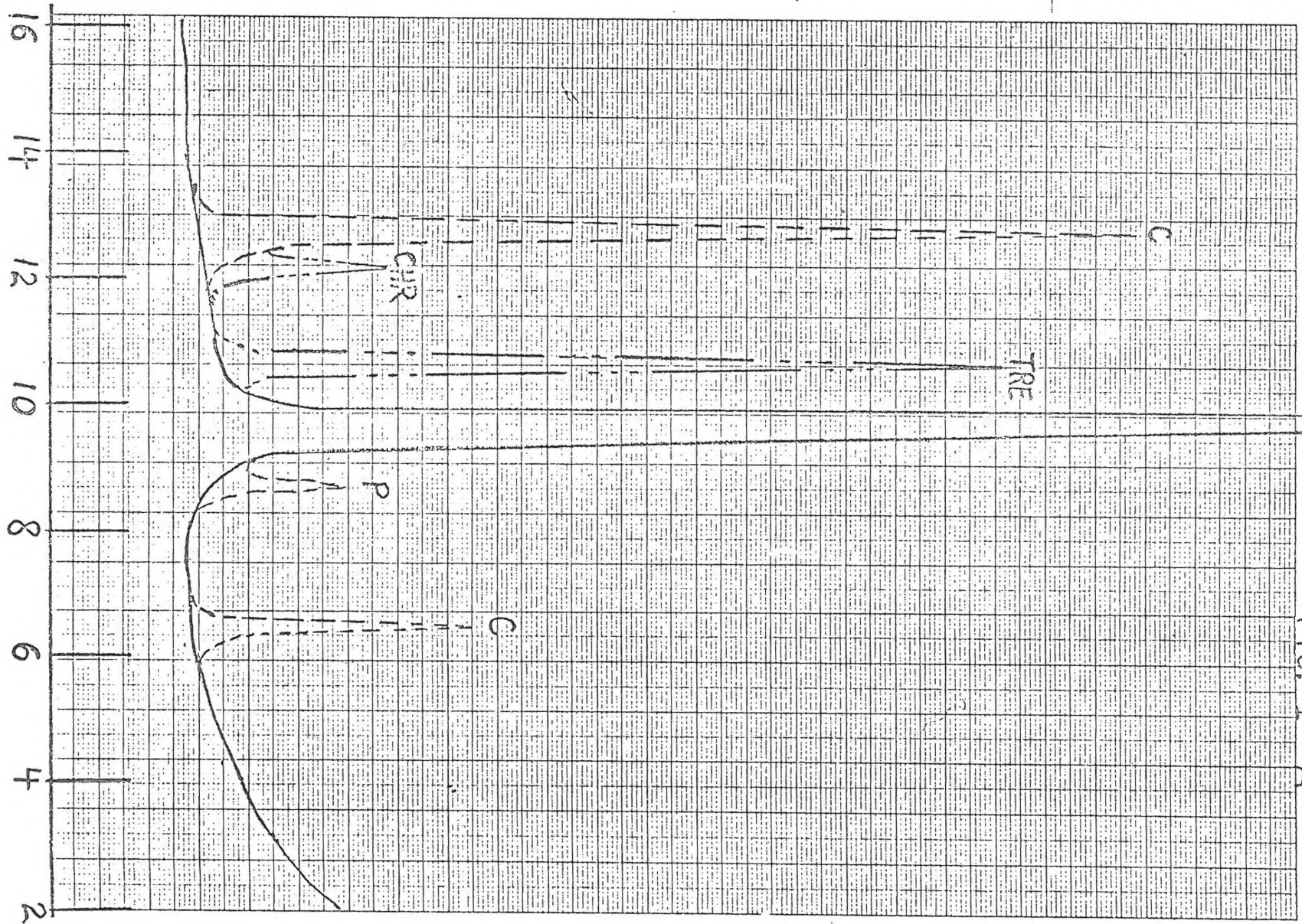


FIG. 1-A

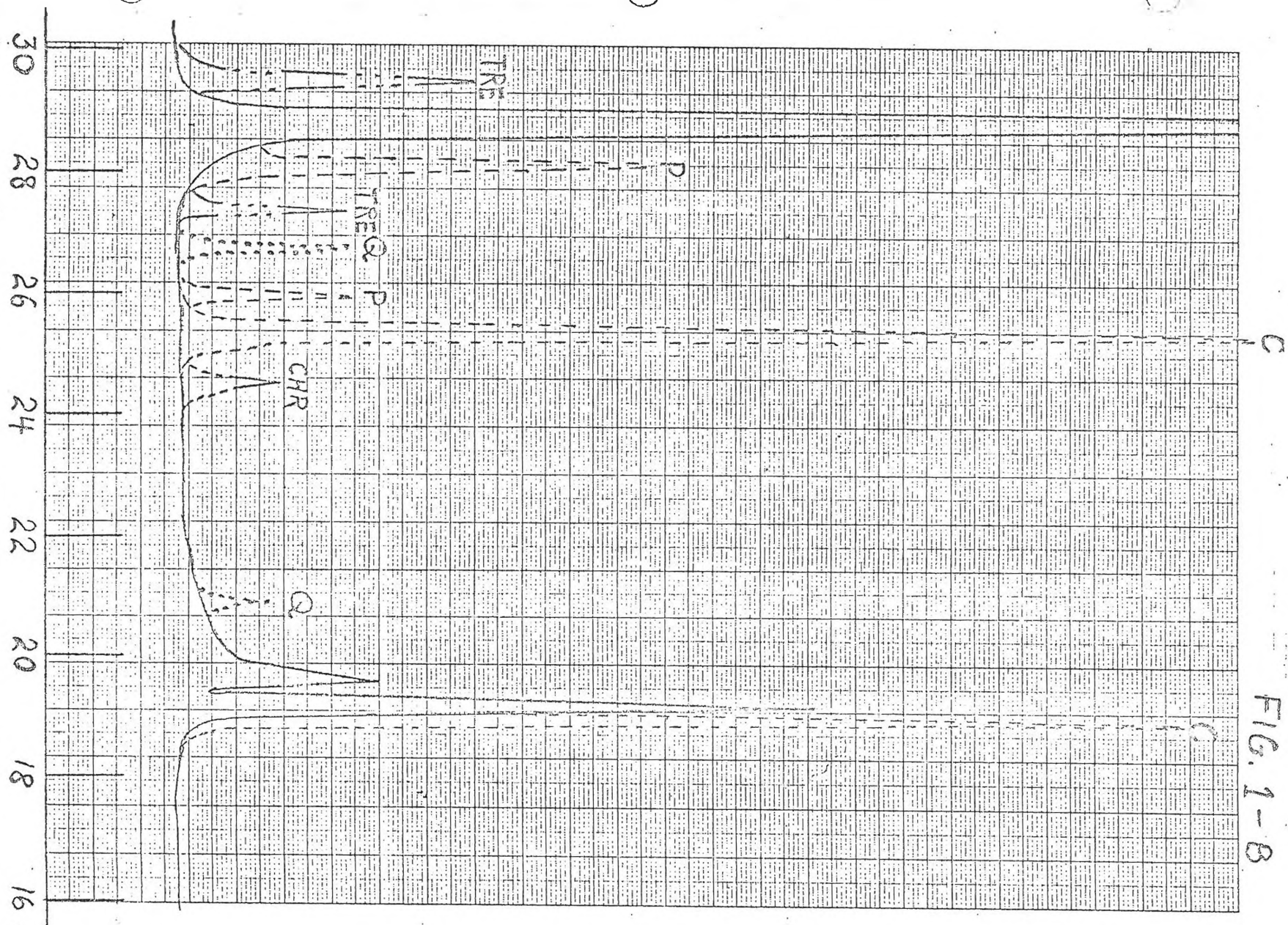


FIG. 1-B

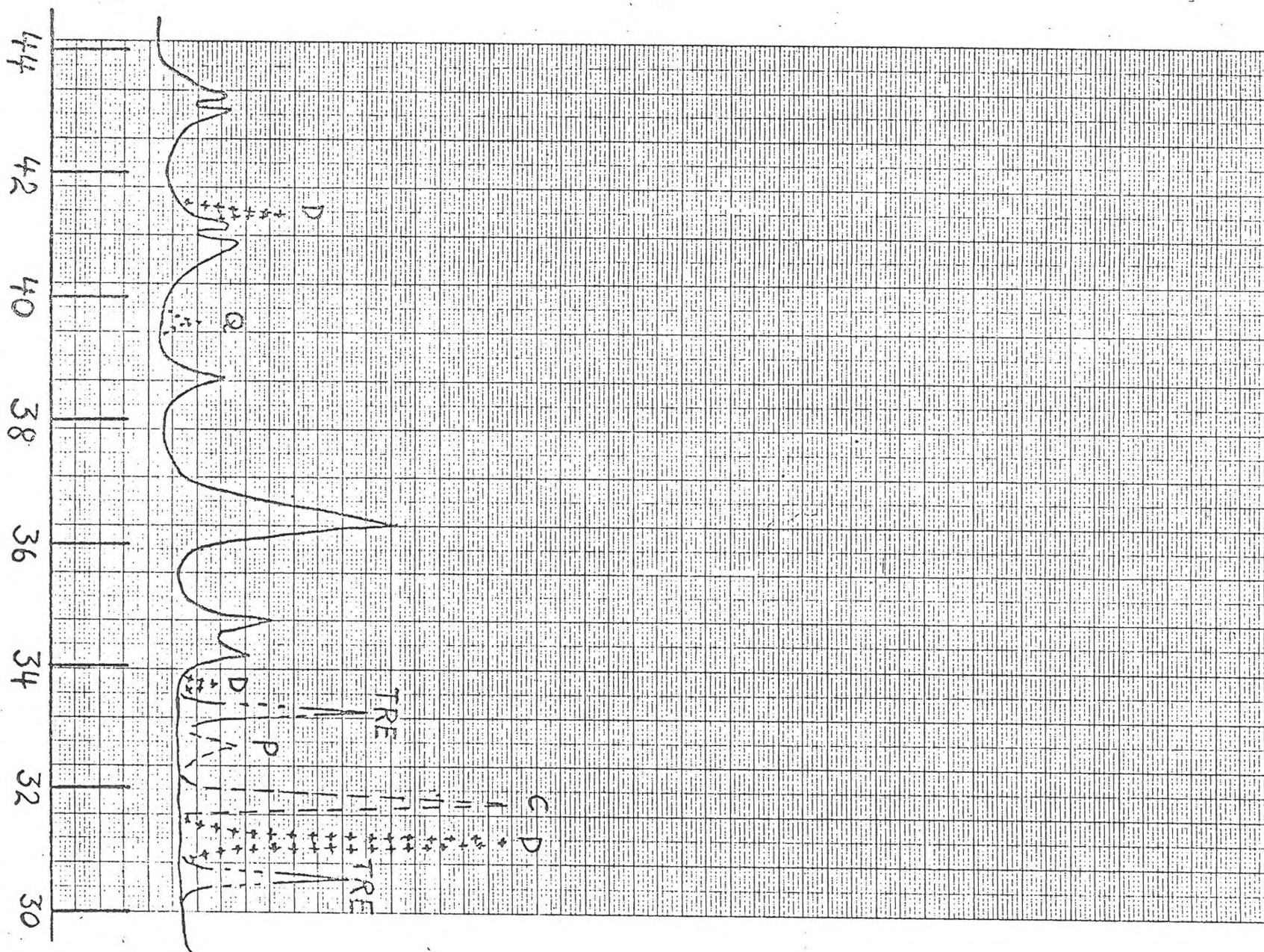


FIG. 1-C

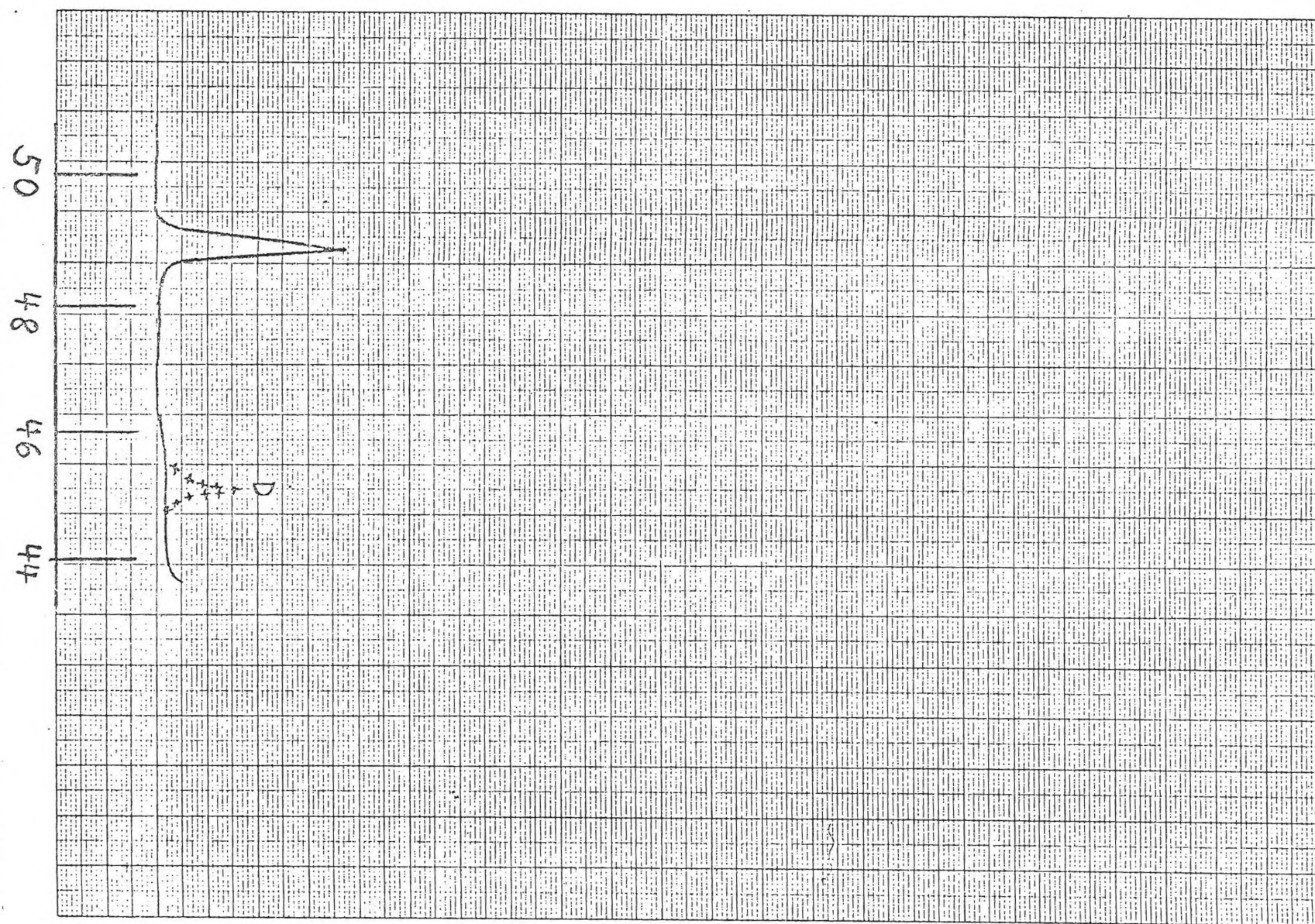


FIG. 1-D

For greater sensitivity of detection of the asbestiform minerals, and for quantitative precision in determination of the concentration it is necessary to utilize a step-scanning procedure. The improvement obtainable in detectability of the asbestiform minerals by step-scanning is shown in the comparison between Figures 3 and 4.

Figure 3 shows the continuous-scan diffractogram, with evidence of a tremolite peak in the vicinity of 10.6° two-theta. In Figure 4, the region from 10.00° to 11.00° was measured at 0.01° intervals, integrating the x-ray photon count for 5 minutes at each angle setting in order to give improved counting statistics. The Figure shows that there are, in fact, two distinct tremolite peaks, differing in d-value by 0.223 ± 0.011 Angstroms. This shows that tremolite is somewhat variable in composition, as is to be expected from its crystallography alluded to in the preceding, and the difference observed here is associated with the variability in the degree of replacement of Mg by Ca in the amphibole lattice. Hence, measurement of a peak height may give a misleading impression of the concentration of the mineral; for reliable quantitative assessment these results show that total peak areas must be employed.

Another important feature of the problem of determining the asbestiform minerals in the presence of other minerals commonly present in commercial talcs is illustrated by the data shown in Figure 5. This Figure presents the step-scans in the tremolite (10.20° to 10.80°) and chrysotile (11.80° to 12.80°) regions for a commercial talc which contains in addition to these minerals a moderate amount of chlorite (about 4% by weight). The curves marked "A" were obtained on the original sample; "A'" is a repeat run of the same specimen, packed anew in the same sample holder. The large discrepancy in quantitative respects between A and A' demonstrates the critical role played by packing and preferred orientation effects. This shows that the quantitative estimation of these minerals must be based upon the determination of the ratios of a given peak area to that of a known concentration of an internal standard.

The curves marked "B" were obtained on the same talc, but to which 2.0% by weight of chrysotile had been added. It is not easy to obtain a uniform mixture of the added chrysotile with the talc, because of the fibrous and somewhat elastic nature of the former. A procedure that we have found to be satisfactory is as follows. Mix the talc and

FIG. 3

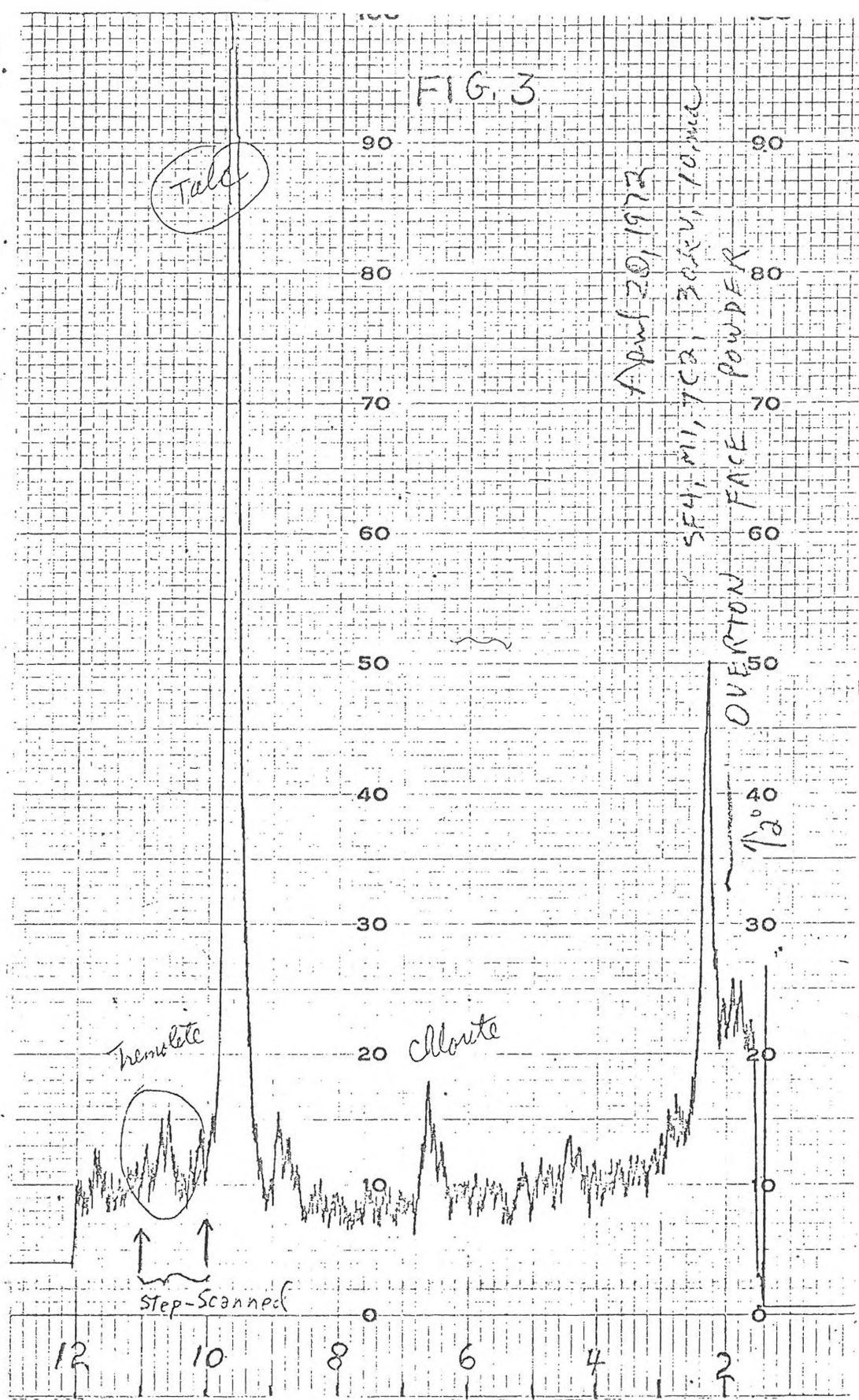
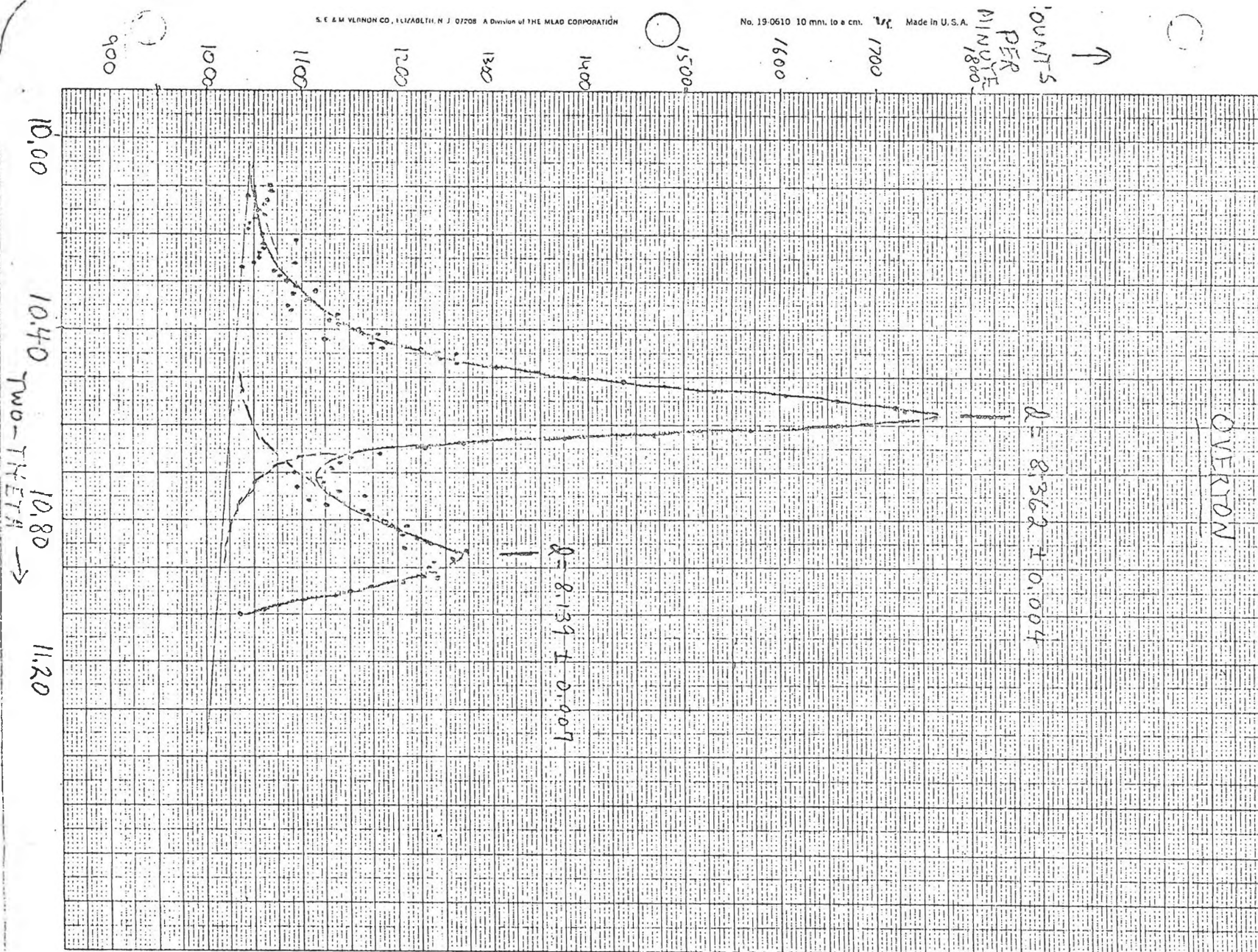
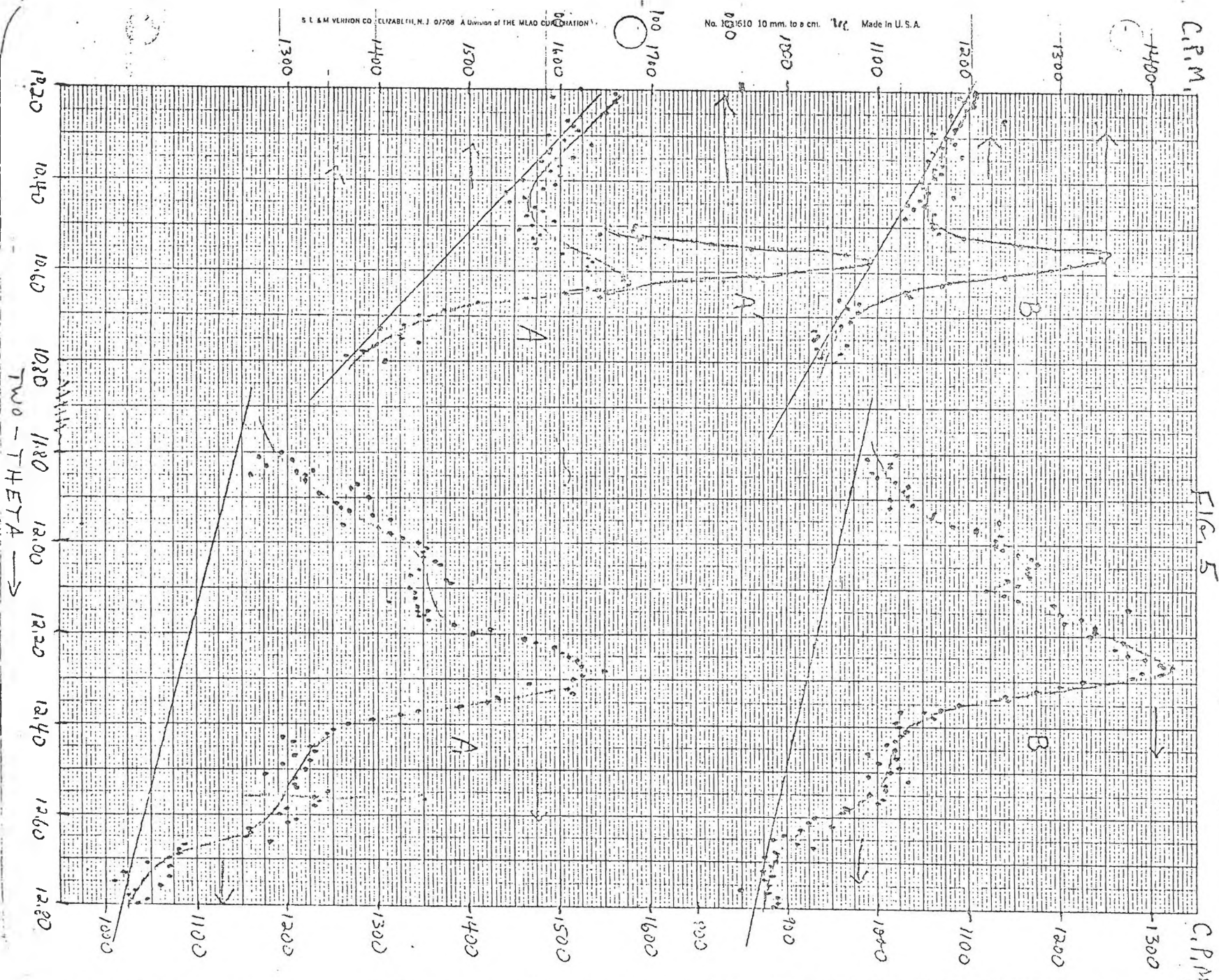
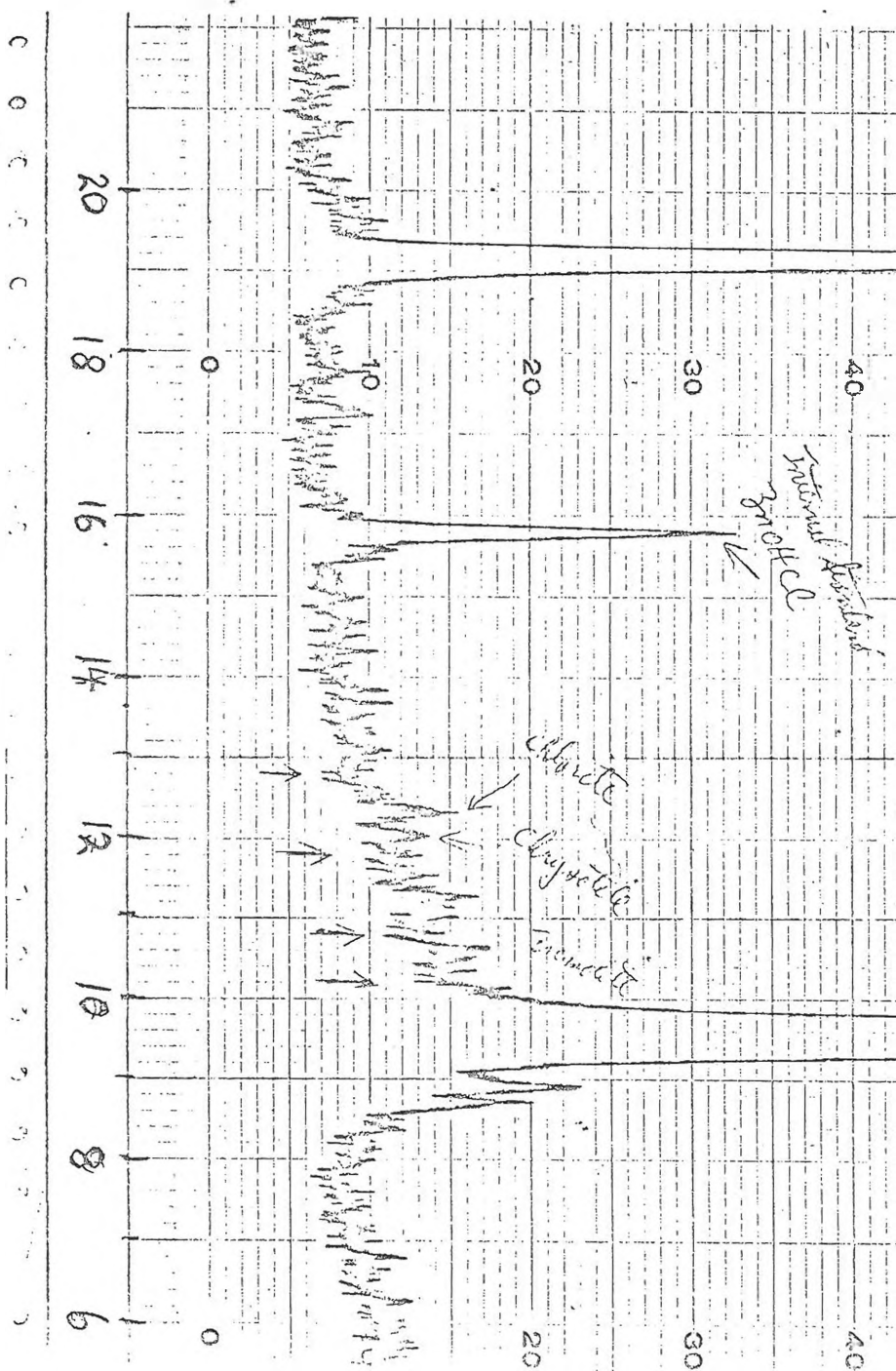


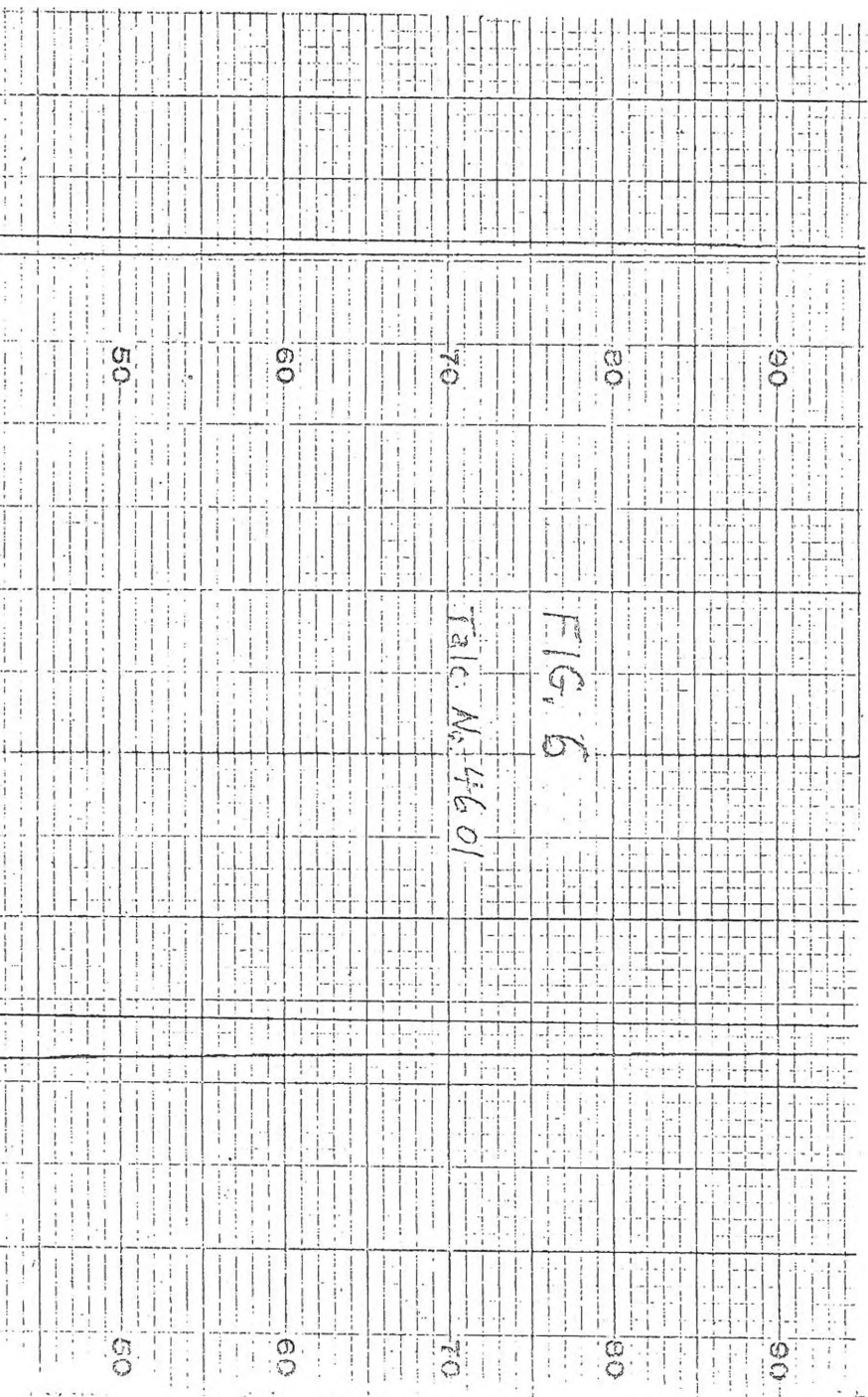
FIG. 4



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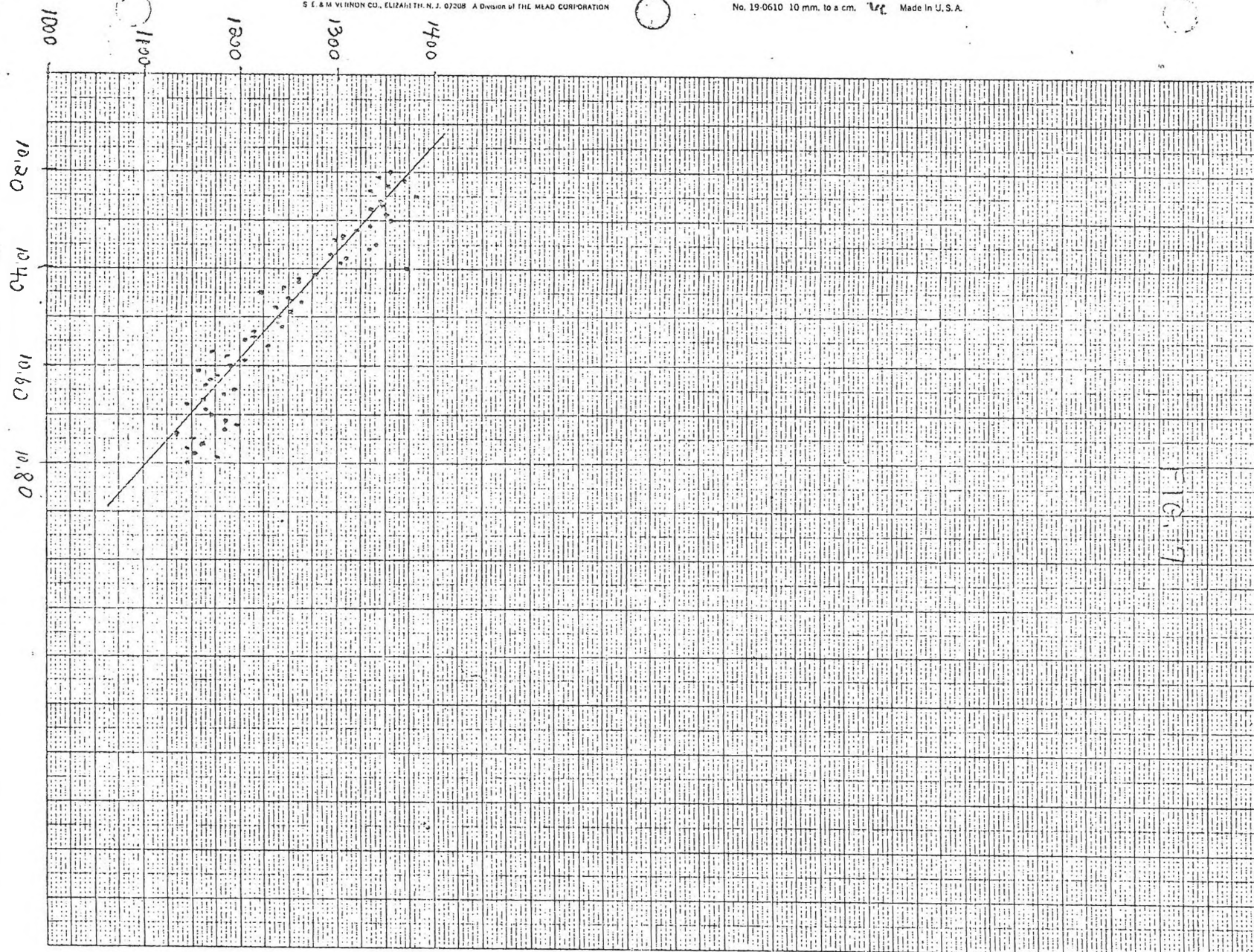
chrysotile by hand with an equal weight of mucilage (e.g., LePage's glue), and shape the resulting plastic mass into rods. Allow these to dry thoroughly; then reduce to a fine powder by abrading on emery paper. The mucilage is then removed from the powder by leaching with water.

In the present case, the chlorite peak at 12.28° two-theta can serve as the internal standard, and the area of the chrysotile peak at 12.05° can be determined relative to it. Comparison of the ratios of these two peaks for the "A" sample (containing "x"% chrysotile), and the "B" sample (containing "x"+2.0% chrysotile) reveals that $x = 2.3 \pm 0.6$ % chrysotile by weight.

For the general case, in which an added internal standard is necessary we have found the compound ZnOHCl to be most suitable. If added in low concentration, it contributes a single sharp peak at 15.8° , a location in the diffractogram which is completely free of the lines of any other mineral encountered in talc specimens. Figure 6 shows the diffractogram of a sample of talc containing 4.2% by weight of this internal standard.

Figure 7 shows the step-scan data in the tremolite region for a talc specimen containing no tremolite, illustrating the linear character of the base line. The step-scanning technique permits as little as 0.02% of tremolite to be distinguished from the background within the 50% confidence limit. Similar detection limits apply to the other asbestiform minerals.

Other regions of the diffractogram are less suitable for determination of the asbestiform minerals, because of interference from nearby intense lines. This is illustrated by Figure 8, which shows the step-scan data for the region from 28.00° to 29.80° , in which a tremolite peak (at 29.50°) occurs close to a talc peak (at 28.75°).

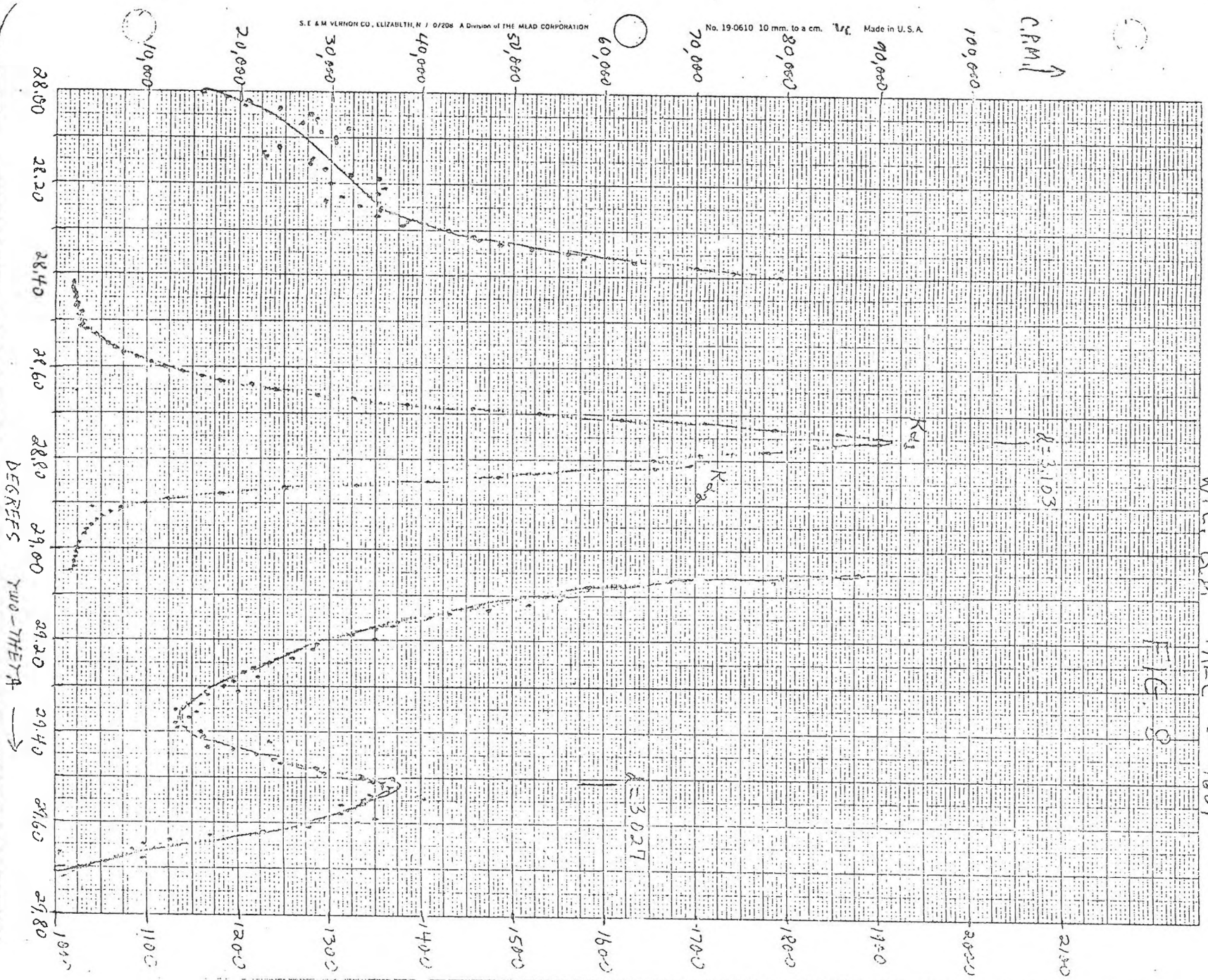


W.C. & D. TALE # 187

-10.7

W.C. & D. TMLC # 4601

FIG. 3





Johns-Manville

Research & Engineering Center

P. O. Box 159
Manville, N. J. 08835
(201) 722-9000

August 24, 1971

Dr. A. Weissler, Acting Director
Division of Colors & Cosmetic Technology
Office of Product Technology
Department of Health, Education & Welfare
Food & Drug Administration
Washington, D. C. 20204

Dear Dr. Weissler:

Attached is a discussion of the methods which could be used to identify and quantify asbestiform minerals in talc. I believe one point which cannot be emphasized too strongly is the fact that X-ray diffraction cannot be used to identify a specific amphibole species when present in only small amounts in a talc matrix. It is necessary, therefore, to resort to petrographic techniques in order to establish the identification.

I hope this information is satisfactory and if I can be of any further assistance, please do not hesitate to contact me.

Sincerely,

Dr. Sidney Speil, Director
Corporate, Mining & Pipe Divisions

JPL/jr

Attachment

IDENTIFICATION OF ASBESTOFORM MINERALS IN TALC

Asbestoform minerals which may be present in talc can be detected by X-ray diffraction techniques. The amphibole minerals will show a diffraction peak at about 8.4 Å, while chrysotile will show a peak at 7.3 Å. These diffraction peaks are sufficiently separated from talc peaks so that there is no problem with interference. It should be pointed out that when small amounts of these minerals are present in a talc sample the X-ray diffraction technique merely indicates their presence and may not allow for a positive identification. Furthermore, one cannot distinguish between the fibrous and massive forms of amphibole minerals by X-ray diffraction. When small quantities are involved it is also impossible to distinguish between chrysotile fiber and other serpentine minerals.

For quantitative work a series of standards can be prepared using pure minerals. The following procedure which is described for talc and tremolite is recommended for any of the asbestoform minerals:

Finely ground talc is suspended in ethyl alcohol at a concentration of 0.1 g in 100 ml. The use of alcohol is necessary since talc is naturally hydrophobic and cosmetic grades may also be contaminated with water repellent oils. Good dispersion is achieved by 2 minute agitation in an ultrasonic bath.

A similar suspension of finely ground tremolite is prepared at a concentration of 0.01 g per 100 ml of alcohol. If a mineral specimen is used, it should be ground in an agate mortar to the extent that it would be normally ground for X-ray diffraction examination.

The mixtures are prepared by adding aliquots of the tremolite suspension to different 100 ml talc suspensions to give tremolite levels ranging upward from 0.1 per cent. Each mixed suspension is agitated ultrasonically and then filtered through an 8 u Millipore solvint filter. Unfortunately the sample cannot be used in this form because there is some segregation of the tremolite during filtration.

To insure good mixing, the filter is ashed at 800F for 20 hr and the ash dispersed by grinding in a small agate mortar. The powder is then mounted for X-ray diffraction in the normal manner. The samples are examined by scanning at a slow speed over the 8.4 Å peak with the instrument settings adjusted for maximum sensitivity. We have used a Phillips diffractometer with a simulation detector and a curved crystal monochromator with nickel filtered $\text{CuK}\alpha$ radiation. The rate meter settings were 50, 10, 0.

Using a simple diffractometer scan it is possible to detect as little as 0.2 per cent tremolite in talc by this method. For smaller amounts two possibilities are suggested. One of these is to use a repetitive scanning technique obtaining total counts which are statistically significant. This technique involves scanning under the 8.4 Å peak several times until a sufficiently high count is obtained. This is then compared with the count obtained from a tremolite or amphibole free specimen.

The second technique suggested is an addition method which involves adding small amounts of tremolite to the talc. This is done at several different levels of addition and the area under the 8.4 Å peak measured for each addition. The results are plotted as shown in the attached graph and the amount present in the original sample estimated by extrapolation to the base line.

For general information, the X-ray diffraction patterns of talc and typical asbestoform minerals are also attached.

Petrographic Examination

As mentioned earlier, the presence of asbestoform minerals is indicated by the presence of the 8.4 Å diffraction peak. This does not, however, constitute a positive identification of these minerals. If their presence is indicated, it is necessary to examine the sample by petrographic techniques in order to establish whether or not the minerals are truly present and if they are present in their fibrous forms. The optical properties of talc, chrysotile and several of the common amphibole minerals are as follows:

Talc - Flakes and scales

Flakes lying in plane of slide, RI = 1.589

Flakes seen end-on, parallel to vibration direction of light, RI = 1.539

Flakes seen end-on, perpendicular to vibration direction of light, RI = 1.539

Tremolite - Splinters, blade shaped, etc., due to prismatic cleavage. Tremolite is the only common amphibole which does not show "parallel extinction". The extinction angle is approximately 17°.

Max. RI when splinter is lying at 17° to vibration direction of light, 1.625 to 1.634.

Min. RI when splinter is lying 17° to vibration direction of light 1.599 to 1.613.

Tremolite is differentiated from talc by its shape, higher refractive indices, and lower birefringence.

Chrysotile - Fibers lying parallel to vibration direction of light have RI = 1.504 to 1.557 or greater.

Most Canadian chrysotiles have RI near 1.556
birefringence 0.011.

Chrysotile differs from talc in shape; and has much lower birefringence.

Amosite - Color: straw

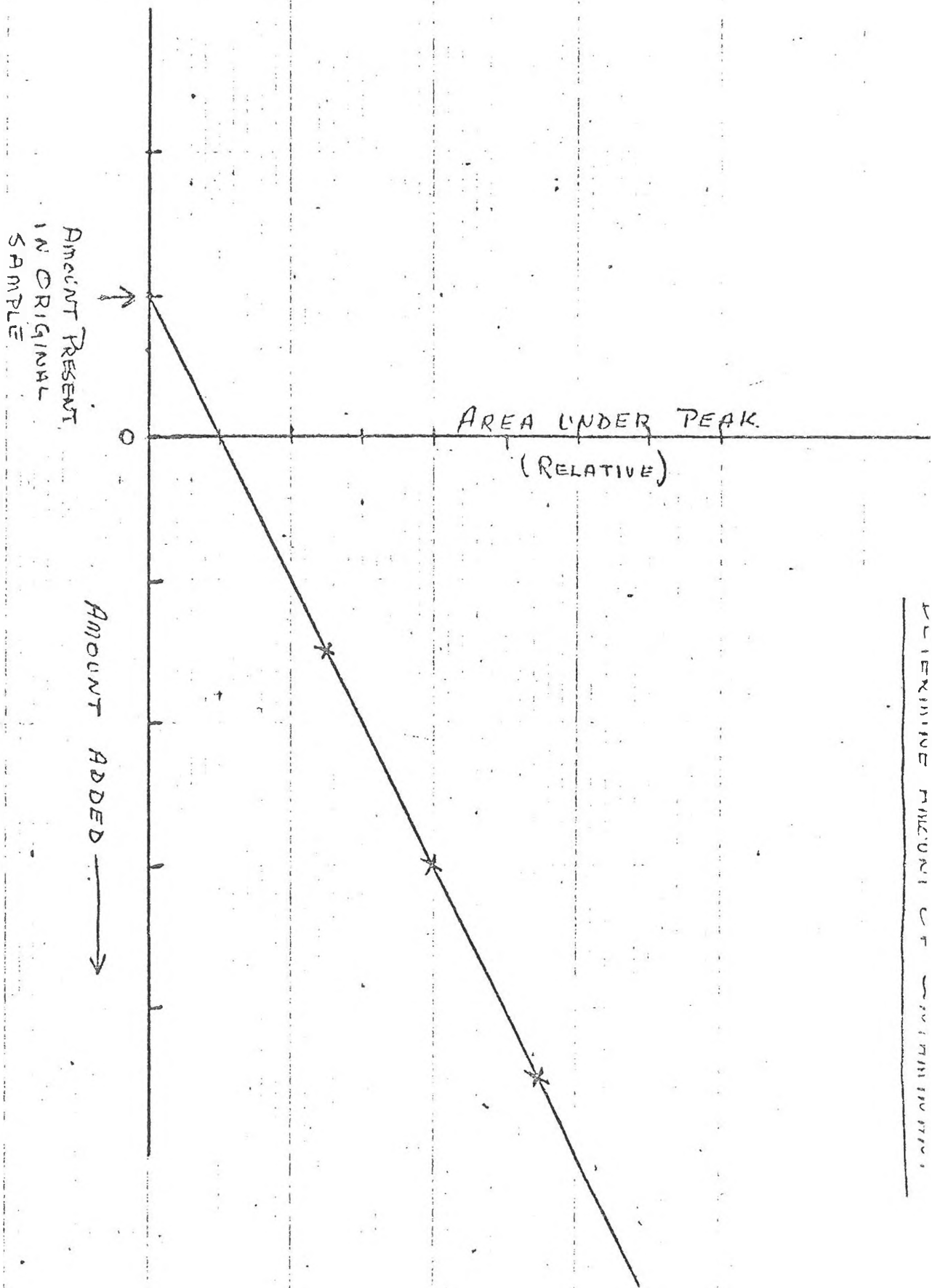
Max. RI (fibers lying parallel to vibration direction
of light) 1.664 - 1.69

Crocidolite - Color: smoky-blue

Max. RI (fibers parallel to vibration direction of
light) approx. 1.70 to 1.74.

Anthophyllite - Similar to tremolite, but shows parallel extinction.

DETERMINE AMOUNT OF SUBSTANCE



A°	I/I_0	A°	I/I_0	A°	I/I_0	A°	I/I_0	DA°	I/I_0	A°	I/I_0	DA°	I/I_0	A°	I/I_0
.3	25	8.97	10	9.34	100					9.02	4	9.12	50		
.9	30														
.25	55	8.40	100					8.41	100	8.4	100	8.3	100		
.48	7					7.31	100							7.15	50
.04	13	5.09	20					5.01	50			5.09	20		
.9	9	4.87	16												
.62	13	4.79	16	4.66	90					4.89	10	4.83	20	4.46	75
.50	25													4.34	85
		4.49	30	4.55	30	4.52	50	4.45	50	4.51	16	4.55	40	4.14	65
.13	20											4.14	40	4.11	40
.9	13	4.01	10					3.89	25	3.88	10	3.87	30	3.83	50
		3.87	30					3.7	25					3.72	20
.65	35					3.65	70			3.66	10	3.65	35		
		3.39	60					3.43	100	3.42	12	3.45	30	3.56	50
.36	30													3.37	12
.24	60	3.28	60					3.27	60	3.27	14	3.26	80		
.05	100	3.14	95	3.116	100			3.11	80	3.12	55	3.06	90	3.148	4
.87	20	2.99	65					2.94	60	2.98	10	2.99	20		
		2.956	60												
.84	40	2.82	20							2.8	18				
		2.79	70												
.74	20	2.71	100					2.71	100	2.72	40	2.75	70	2.73	4
								2.59	50						
.68	30	2.58	30	2.6	30	2.56	40	2.53	60	2.60	14	2.54	10	2.55	85
.59	30														
.54	40	2.52	70							2.54	12	2.50	30	2.52	50
.43	13			2.48	65	2.45	60							2.48	85
.32	20	2.33	35	2.34	16			2.33	40	2.32	12	2.36	10	2.38	25
.30	20	2.29	30					2.27	20	2.3	4	2.29	30	2.33	95
.25	13	2.27	30	2.21	20					2.21	10	2.24	15	2.28	16
.17	9	2.20	12							2.20	4	2.21	15	2.24	20
.14	30	2.16	40					2.16	40	2.18	16	2.19	50		
.07	9	2.11	35			2.09	20	2.04	30	2.08	6	2.1	15		



MINERALS, PIGMENTS & METALS DIVISION

PFIZER INC., 640 NORTH 13TH STREET, EASTON, PENNSYLVANIA 18042

215 253-6261

September 23, 1971

Dr. Alfred Weissler
Division of Colors and Cosmetic Technology
FDA
Washington, D.C. 20204

Dear Dr. Weissler:

Following is our procedure for the determination of asbestos like materials in talc by x-ray diffraction.

1. Equipment used is [REDACTED] x-ray diffractometer using 4000 watt constant potential generator, copper fine focus x-ray source, scintillation counter and step-scanner.
2. Samples are prepared for presentation to the diffractometer by grinding to less than 325 mesh (44 microns). The powder is packed into an aluminum plate which contains a cavity. The sample is leveled in the cavity and then compressed with one downward motion of a spatula. The spatula should not be rotated in the least. If this is done, the sample may become highly oriented causing errors in the line intensities.
3. The diffractometer scan is made with 1° divergence slits and .1 mm receiving slits. The step scan is done in steps of $0.05^\circ 2\theta$ from $28^\circ 2\theta$ to $8.5^\circ 2\theta$. Each point is counted for a time of 24 seconds. The actual diffraction patterns are obtained by plotting the discrete 0.05° increments versus intensity by using a modified plotting routine in a Wang Model 700 mini-computer with Model 702 plotter.
4. Standards are prepared by adding known amounts of chrysolite and tremolite to talc which has been proven to be free of these minerals by x-ray and electron microscopy techniques.



MINERALS, PIGMENTS & METALS DIVISION

Dr. Alfred Weissler
September 23, 1971
Page 2

5. The 8.4° peak for amphiboles and 7.0° peak for serpentines and chrysotiles from the samples are compared with those from the standards and percentages are calculated directly.

If you require any more specific information on this, please contact me at your convenience.

Very truly yours,

Robert E. Norwood
Group Leader
Physical and Chemical Testing

REN:bls

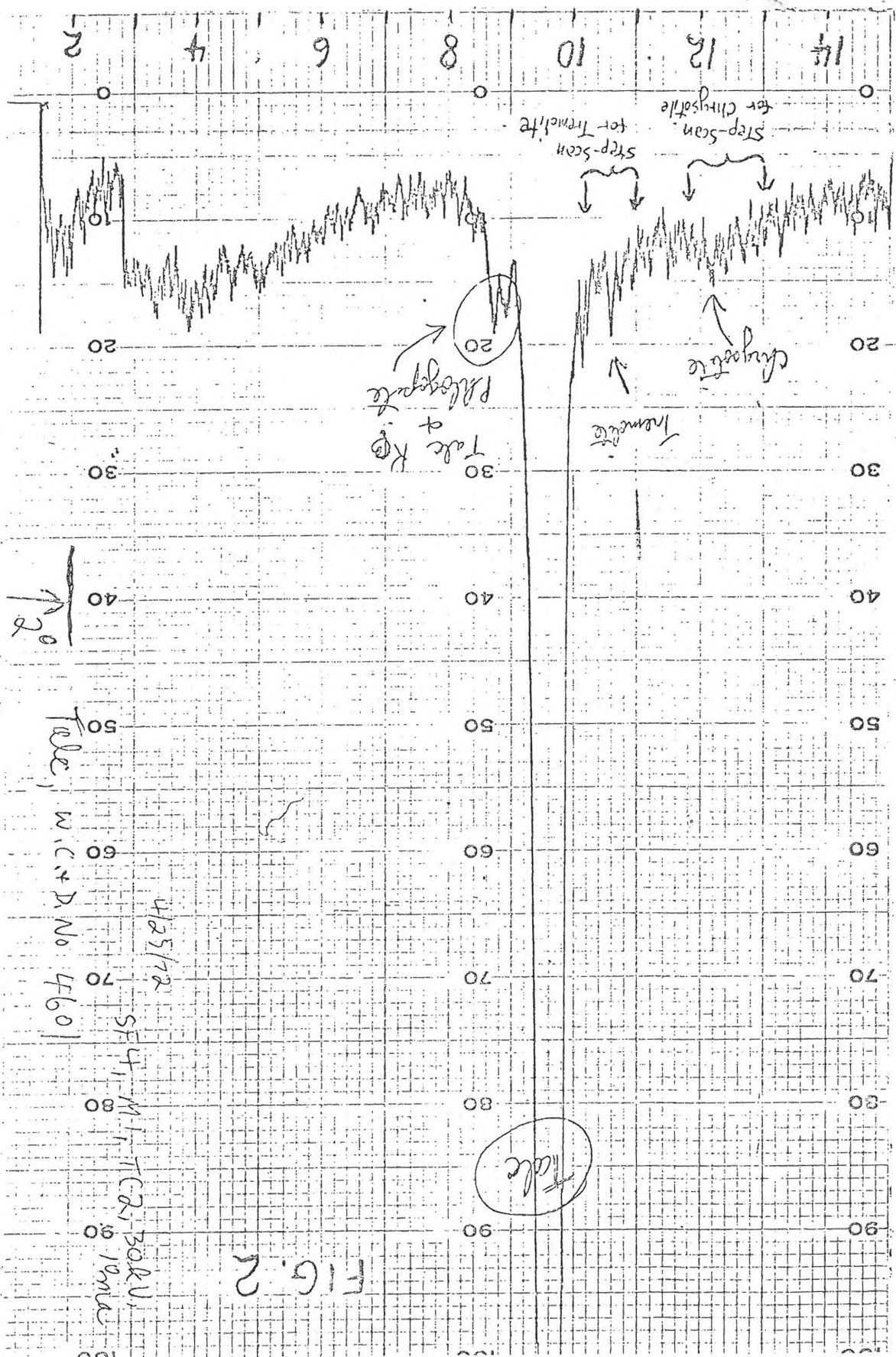


FIG. 2