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16. ABSTRACT
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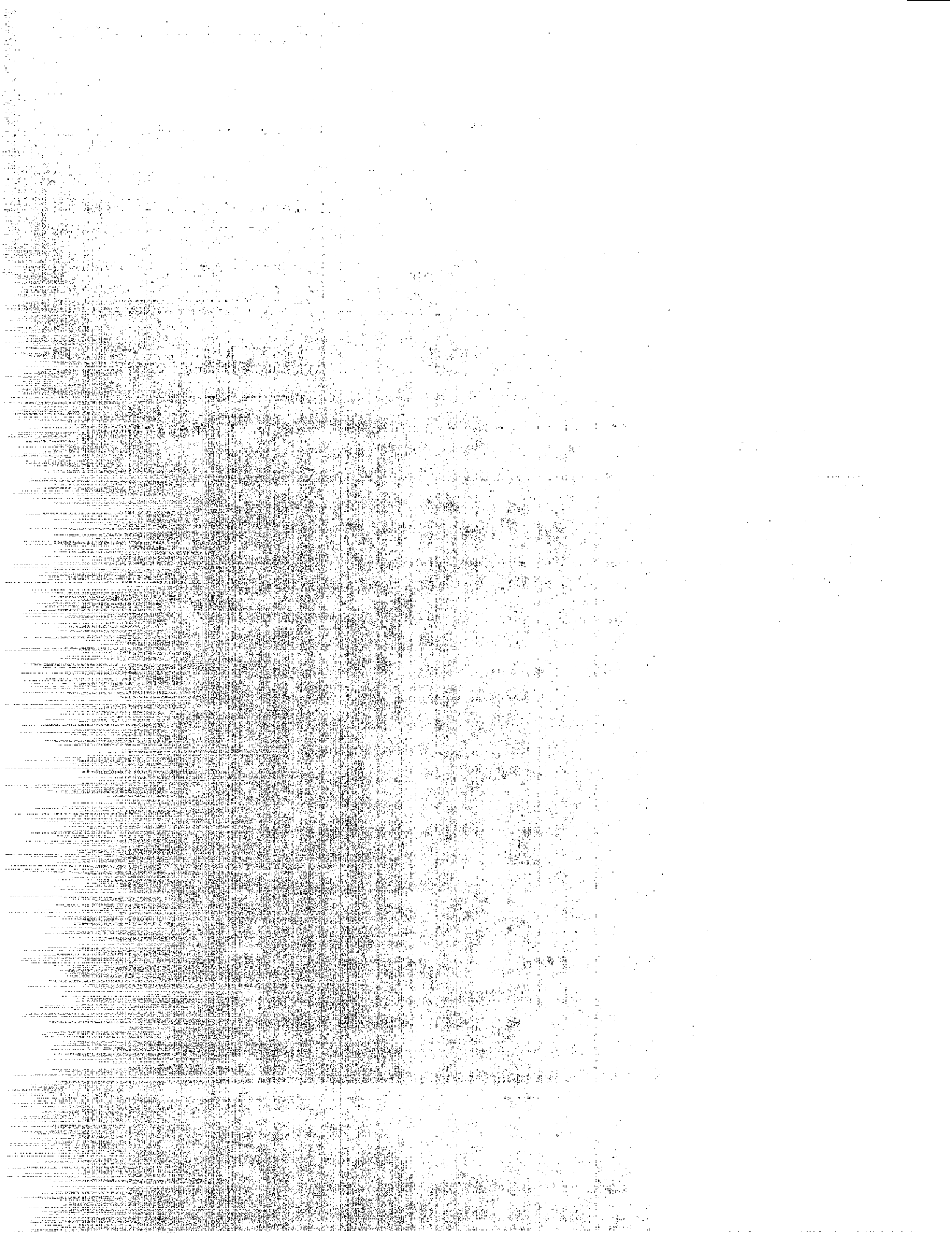

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STATE OF CALIFORNIA
DEPARTMENT OF TRANSPORTATION
DIVISION OF CONSTRUCTION
OFFICE OF TRANSPORTATION LABORATORY

March 1979

FHWA No. D-5-48
TL No. 635314

Mr. C. E. Forbes
Chief Engineer

Dear Sir:

I have approved and now submit for your information this final research project report titled:

X-RAY DIFFRACTION ANALYSIS OF
SELECTED PAINT PIGMENTS

Study made by . . . . . Enviro-Chemical Branch

Under the Supervision of . . . . . E. C. Shirley
and
T. L. Shelly

Principal Investigator . . . . . B. J. Chapman

Report Prepared by . . . . . B. J. Chapman

Very truly yours,

NEAL ANDERSEN
Chief, Office of Transportation Laboratory

Attachment
BJC:cj

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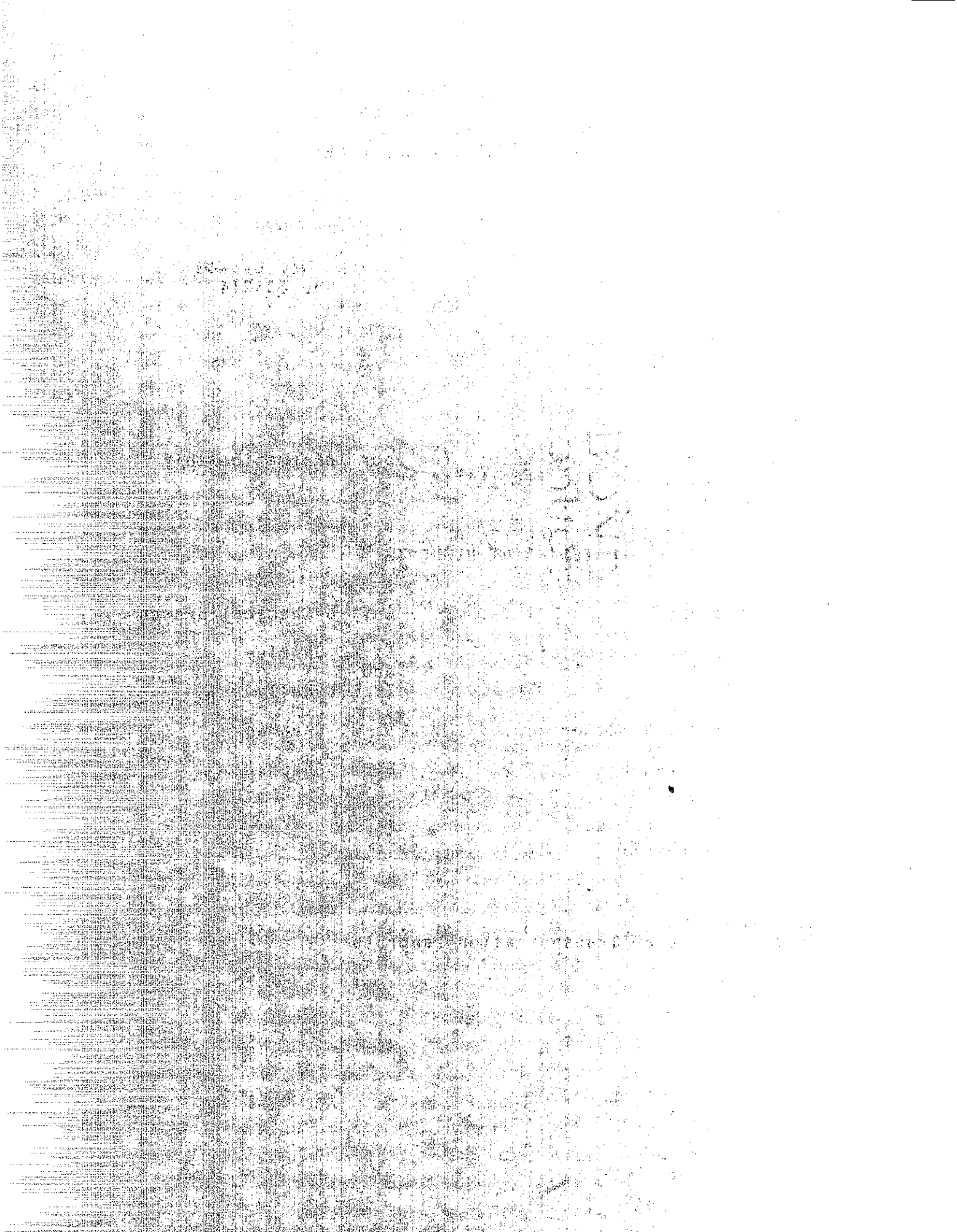

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
CONCLUSIONS	3
RECOMMENDATIONS	4
IMPLEMENTATION	5
ANALYTICAL METHOD	6
Sample Preparation	6
Diffraction Analysis	12
DATA REDUCTION	16
Dried Film Correlations	17
Packed Powder Correlations	35
Internal Standard	46
Reference Intensity	47
REFERENCES	69
APPENDIX A	71
APPENDIX B	76

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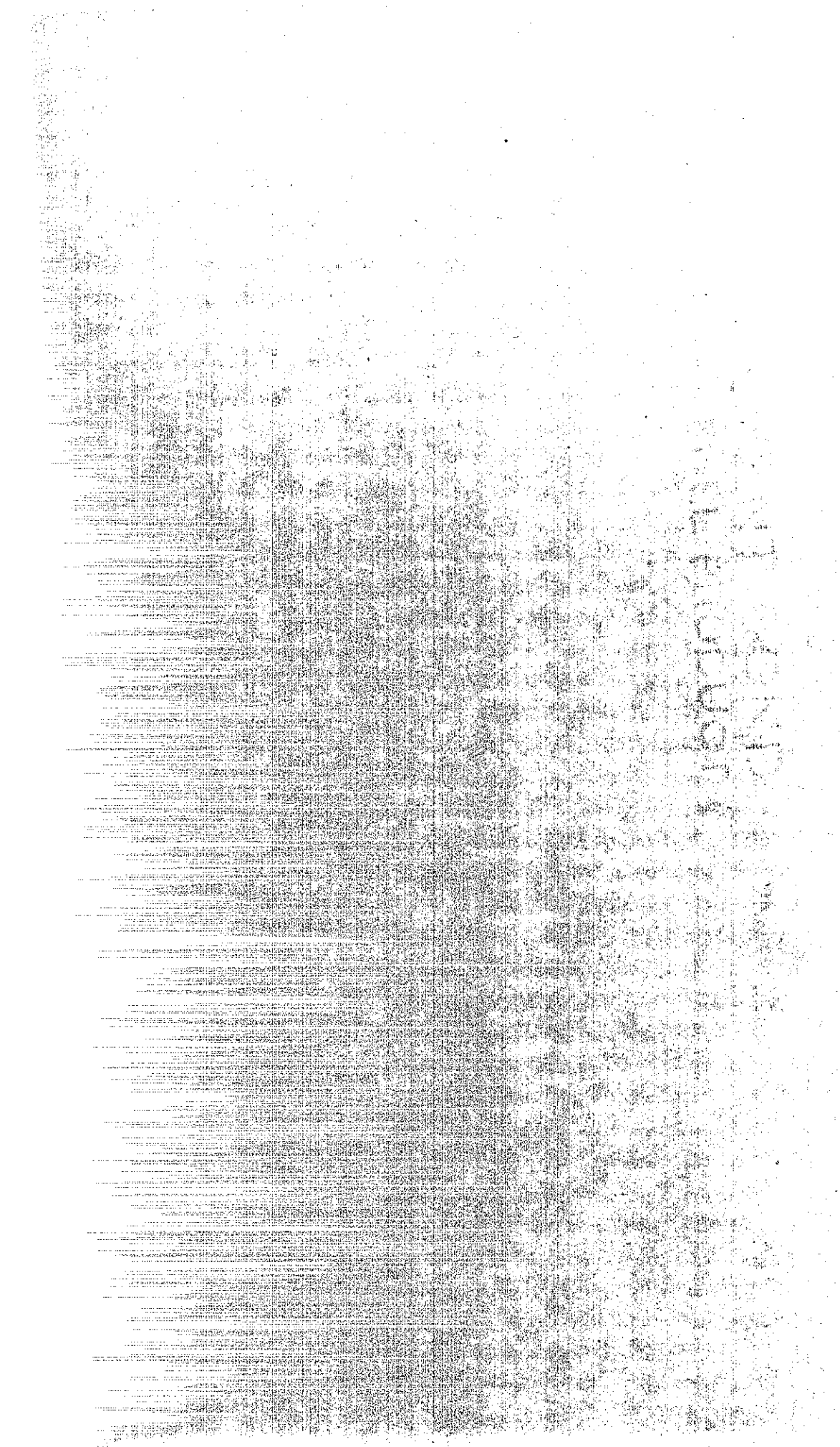

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INTRODUCTION

Since 1962, the Transportation Laboratory has used x-ray diffraction and x-ray fluorescence units to monitor highway construction materials. These materials range from expansive clay and other foundation soils, to paints, steels and other alloys, and other materials used in highway and bridge construction.

Until recently, x-ray diffraction has been used in this laboratory as a qualitative and semi-quantitative method to verify that certain components of paints and coatings, as specified in compositional specifications, were present in approximately the correct proportions in products supplied by successful bidders. This method also indicates product adulteration or substitution of the required components.

With reference to pigments and fillers used in coatings, classical bench chemistry techniques are available for the determinations of most of the "color" pigments: titanium dioxides in white paints and lead and other chromates in yellow paints being examples. These methods are well described in ASTM(1) and Federal Test Method Standards(2).

There are no such methods readily available that allow direct determination of other materials (talcs, clays or other minerals) that are used in many cases as fillers and extenders in coatings. However, many of these same materials yield specific x-ray diffraction patterns and as such lend themselves well to detection and analysis.

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While the possibilities of quantitative analysis by x-ray diffraction were suggested as early as 1919(3), more extensive development of the technique did not begin until about 1945 with the development of improved diffraction equipment(3). However, the method was most firmly established with the publishing of the work of Klug and Alexander in 1954(3), wherein was put forth theory and practice regarding the many uses of x-ray diffraction.

This research project was instituted to develop and evaluate an analytical scheme, based on techniques described by Klug and Alexander and others(4), to quantitatively determine by x-ray diffraction not only the "color" pigments but also other fillers and extenders in paints and coatings. This would enable a better characterization of these materials and make this characterization in approximately the same amount of time as regular chemical methods.

This report covers work related to the determination of pigments and extenders in white and yellow traffic paints. Traffic paint is by far the largest single type of paint in use by the Department of Transportation, with an estimated volume (fiscal year 1978-1979) of more than one-half million gallons.

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CONCLUSIONS

1. X-ray diffraction is suitable for quantitatively analyzing pigments and other components in paints and coatings.

2. Dried films of paints can be used for the analysis provided standard samples are prepared from raw materials identical to those to be used in the bulk manufacturing of the paint.

3. When the exact identity of the raw materials is in question, samples must be reduced to powders and an internal standard added for a more complete analysis.

4. X-ray diffraction can be used as one method for quality assurance testing of individual raw materials.

5. Results for determinations of titanium dioxide and lead chromate can be expected to vary by approximately one-half weight percent.

6. Determinations of talc and calcium carbonate can be expected to vary between two and five weight percent.

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RECOMMENDATIONS

1) Prepare sufficient standard specimens to fully develop the necessary regression coefficients. The minimum number of standards required should satisfy the equation $2N^2+1$, where N equals the number of independent variables to be considered. Assuming three variables, at least nineteen standards, at varying concentrations, would be required.

2) Formulate standards using the materials currently specified for the product.

3) Make at least three determinations on the prepared standards.

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IMPLEMENTATION

Findings from this project have been partially implemented. Selected samples of paints are analyzed for pigment composition, considering the limitation described in the body of the report.

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ANALYTICAL METHOD

Sample Preparation

Previous use of the x-ray diffractometer resulted in two possible methods of sample preparation that were felt to be satisfactory for use in this project:

1. Using a dried film of the whole paint.

2. Solvent extraction of the vehicle from the pigments, followed by grinding the dried powders, and packing in specimen holders for the diffractometer.

Both methods were used to prepare specimens for diffraction.

Three series (two white series and one yellow series) of "standard" traffic paints containing various amounts of pigments and extenders were prepared in the Laboratory by adding respective amounts of the dry ingredients to a previously prepared traffic paint vehicle. This vehicle is an alkyd resin-chlorinated rubber-chlorinated paraffin base material currently used in State of California traffic paints. All paints were dispersed at high speed in a Waring blender for approximately eight minutes. Two series of white paints and one series of yellow paint were prepared. The PT400 and PT401 series paints were prepared using a talc known to contain calcium carbonate, the PT800 series using a different talc that contains no carbonate. The nominal compositions of the "standard" paints comprising the series are listed in Table 1.

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Paint Number	A	B	C	D	E	F	G	H	I	J	K
White, PT-400											
Titanium Dioxide	7.96	11.95	15.93	19.91	4.04	18.25	13.71	5.92	9.88	-	-
Magnesium Silicate	48.5	37.4	38.2	33.1	52.4	48.6	28.1	41.5	46.3	-	-
Calcium Carbonate	35.9	43.0	38.2	39.3	35.9	25.5	50.6	44.9	36.2	-	-
Yellow, PT-401											
Lead Chromate	7.81	11.68	15.58	19.47	3.96	17.85	13.41	5.94	9.86	-	-
Magnesium Silicate	46.2	40.4	38.5	28.0	52.2	50.0	33.0	43.4	35.4	-	-
Calcium Carbonate	38.5	40.4	38.5	45.0	36.3	24.7	46.2	43.2	47.2	-	-
White, PT-800											
Titanium Dioxide	2.85	5.70	8.55	11.39	14.25	17.09	19.94	22.80	17.09	28.49	31.34
Magnesium Silicate	45.3	35.1	28.3	23.5	19.8	12.7	61.3	53.0	45.3	39.0	31.1
Calcium Carbonate	45.3	52.7	56.7	58.7	59.5	63.7	12.2	17.7	31.2	26.0	31.1

Raw Materials

Titanium Dioxide — PT-400 - National Lead RANC I, 93.4% TiO_2
PT-800 - National Lead 2101, 93.9% TiO_2

Lead Chromate — DuPont Y469D, Lot 16395, 89.7% $PbCrO_4$

Magnesium Silicate — PT-400, PT-401 - Johns-Manville Desertalc 54
PT-800 - Cypress Mines Beaver white 325

Calcium Carbonate — Pfizer 45-3

TABLE I. - Type and Nominal Compositions of Prepared "Standard" Paints, Expressed as Weight-percent of the Total Pigment Content.

Dried film and extracted pigment powder specimens were prepared from each of the 'standard' paints in all three series.

Until this study, specimens for qualitative examination had been prepared by dipping a narrow strip of stiff paper (Opacity Chart Form 2A, Leneta Company, Ho-Ho-Kus, New Jersey) into the paint and allowing this to dry. With the development of more rapid drying paints, films prepared in this manner became unsatisfactory since the rapid drying prevented any leveling or smoothing of the films. Consequently, the preferred method now is to apply a film to the chart material using a paint applicator blade having a gap opening of 0.024 inches, followed by drying in the horizontal position for 16-24 hours. Films of traffic paints prepared in this manner have uniform smooth surfaces and are 0.2 to 0.25 millimeters in thickness. The opacity charts can contribute a diffraction pattern if the applied paint film is too thin. The use of the 24-gap blade to apply the paint results in a dry film sufficiently thick to prevent pattern interference from the chart paper.

Specimens for use in the diffractometer are cut from the charts and are approximately 25 mm by 37 mm in dimension. When placed in the diffractometer, the panels are supported from behind by a piece of fiberboard or a glass slide. Figures 1 and 2 are typical diffraction patterns obtained from the dried films.

Powdered samples are prepared by extracting the paint vehicle solution from the pigments according to ASTM D2371, using appropriate solvent mixtures.

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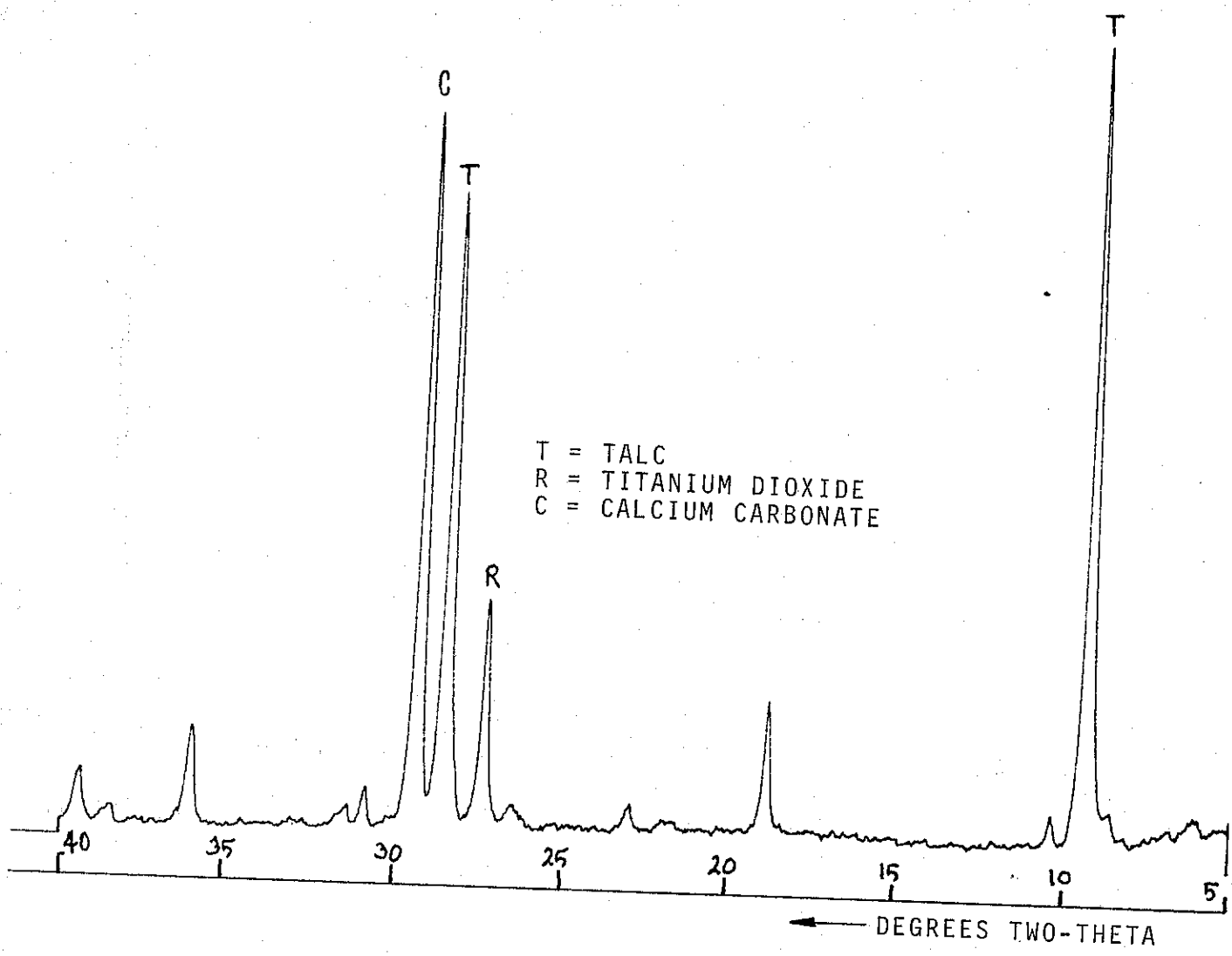

Figure 1

X-RAY DIFFRACTION PATTERN FROM
DRIED FILM OF WHITE TRAFFIC PAINT

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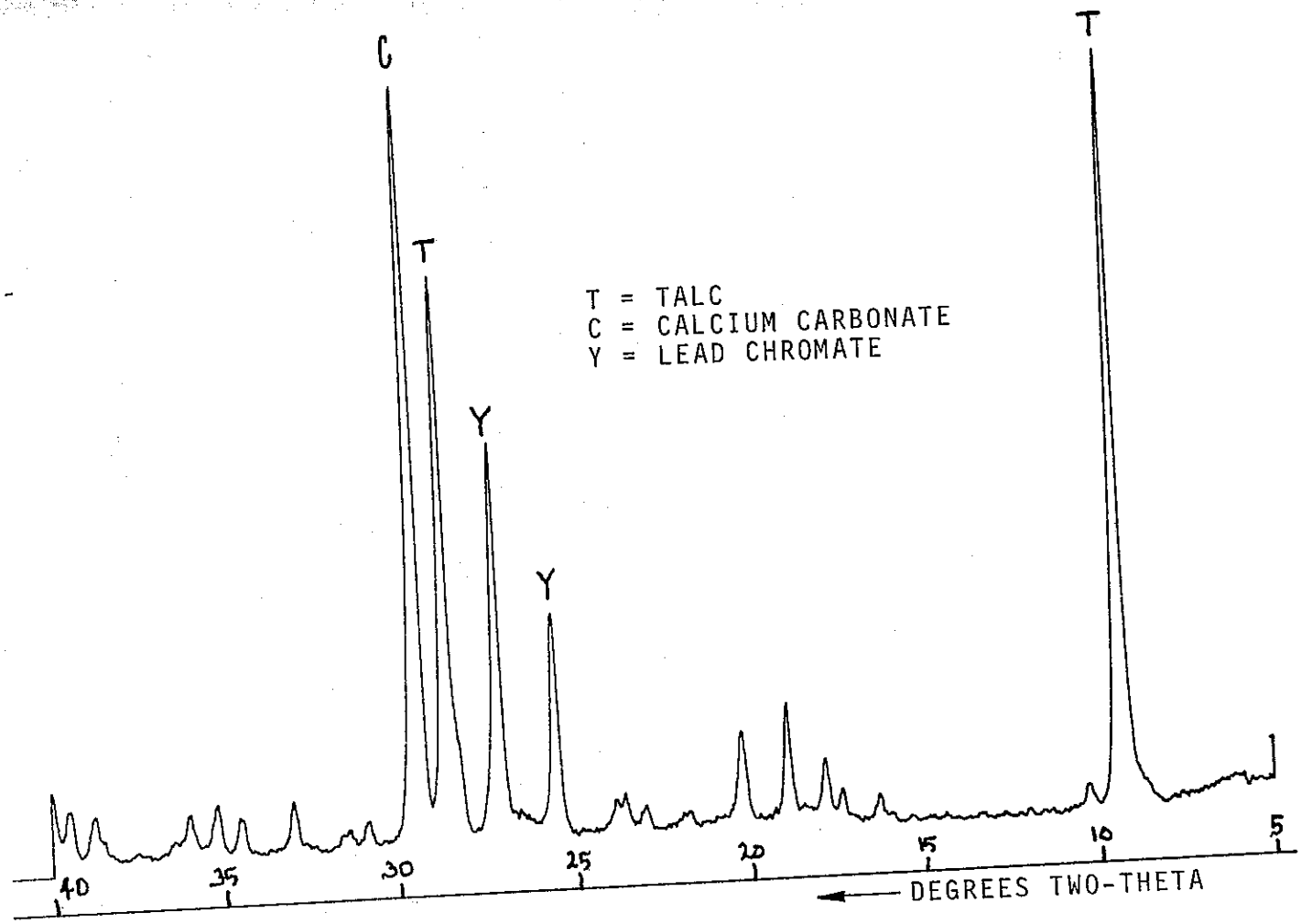

Figure 2

X-RAY DIFFRACTION PATTERN FROM
DRIED FILM OF YELLOW TRAFFIC PAINT

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The pigment portion of each of the "standard" paints was separated from the vehicle by successive washing, centrifuging, and decantation of the supernatant liquid using a 50/50, by volume, mixture of methyl ethyl ketone and toluene. A total of four washings was used to remove virtually all the vehicle, and the remaining pigment cake dried in an oven at 105°C for at least three hours.

Following drying, the respective pigments were screened to pass a 100-mesh sieve, then thoroughly remixed in plastic vials using a mixer-mill. Subsequently, a weighed amount of corundum (Linde Semiconductor Grade, Type 1.0C) was added to previously weighed amounts of pigment and Ballotini spheres (44 micron and finer, from Potters Brothers), and the mixture ground with isopropanol for 15 minutes in a micronizing mill. The corundum (alpha aluminum oxide) was added as an internal standard(4). The Ballotini spheres have been found to provide a large measure of cohesiveness to finely ground powders that might otherwise tend to fall out of the specimen holders. Being a glass, the spheres contribute no diffraction peaks to the specimens. An additional advantage of the spheres is to further dilute the samples and tend to normalize the x-ray absorptions of the specimens. Following evaporation of the alcohol, the samples were again thoroughly remixed in a mixer-mill.

Powder specimens for use in the diffractometer are prepared in fibreboard holders using the back-pack method against a ground glass plate, similar to the procedure illustrated in Klug and Alexander(3). The fibreboard holders are machined from 3 millimeter thick stock and have overall dimensions of 43 mm x 25 mm x 3 mm. A sample compartment

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is milled from the center resulting in a cavity or opening of 38 mm x 15 mm x 3 mm. This cavity, when filled with the powder mixture prepared as above, contains approximately two grams of packed material. Figures 3 and 4 are typical patterns obtained from powder specimens containing corundum as an internal standard.

Diffraction Analysis

The diffractometer used was a General Electric XRD-5 which was upgraded to Diano XRD700 specifications, allowing for minicomputer control of certain functions. The detector and associated electronics were supplied by Ortec and a graphite crystal diffracted beam monochromator was installed. A copper-target X-ray tube (Diano CA-8L) was used throughout the project.

Prior to actual analysis of the "standard" paint specimens, several representative specimens were step-scanned, using the Diano Peak-Search software(5), at 0.01° two-theta increments across the respective peaks to be used in the determinations. Information accumulated in this manner was used to select appropriate background and peak two-theta locations as well as areas for peak integrations.

Using the above information, element tables were prepared for use in the Diano QAP Quantitative Analysis Program. These element tables are used to generate quantitative analyses of specimens but were prepared in this project solely to accumulate data from the "standard" paint specimens for subsequent analysis. The tables were prepared to accumulate both peak minus background intensities and integrated peak minus background intensities.

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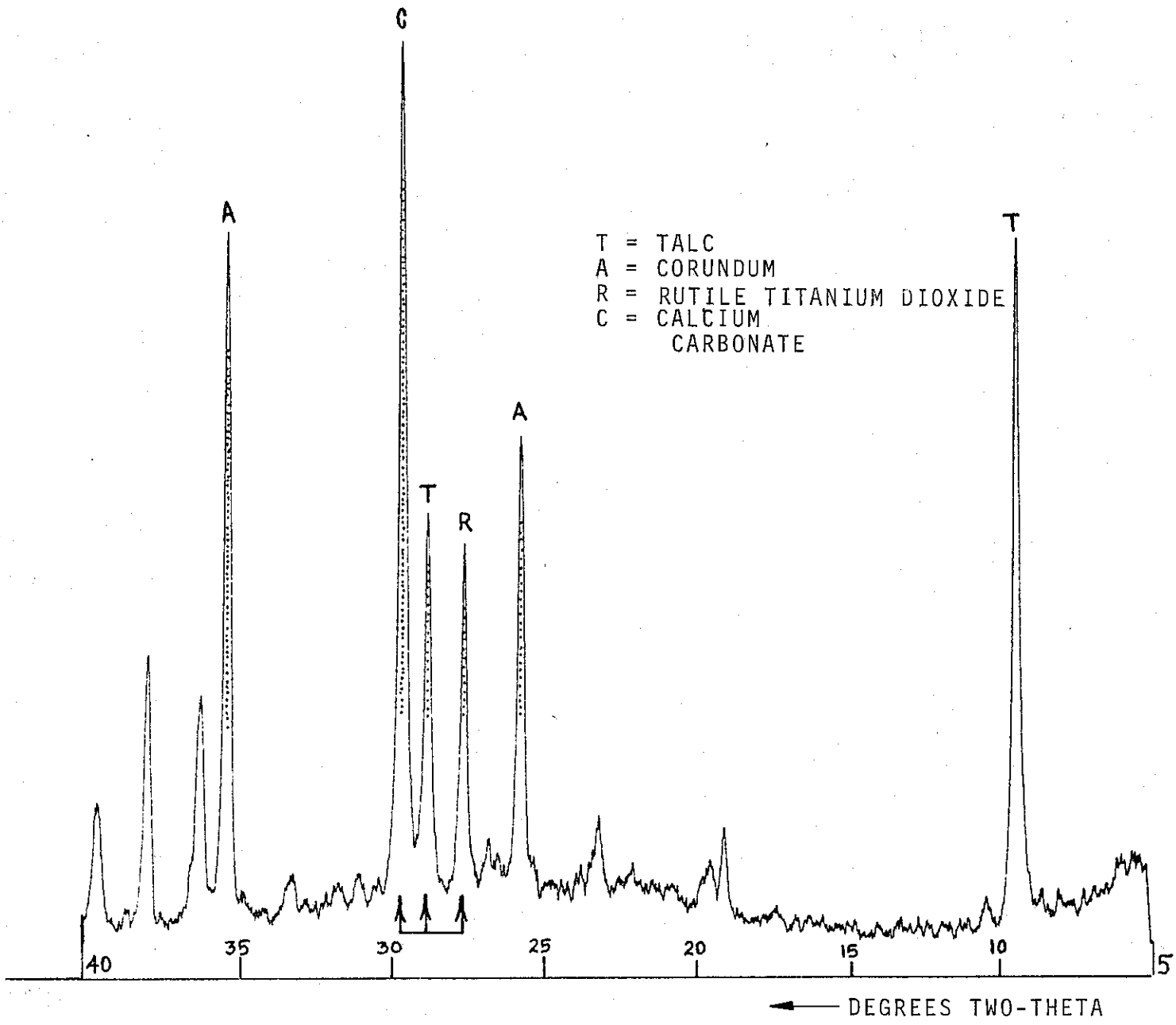

Figure 3

X-RAY DIFFRACTION PATTERN FROM PACKED-POWDER SPECIMEN OF WHITE TRAFFIC PAINT CONTAINING CORUNDUM AS INTERNAL STANDARD.

Shaded peaks indicate those peaks used for quantitative determinations. Peaks marked with arrows at baseline are those used for quantitative analysis of the dried film samples.

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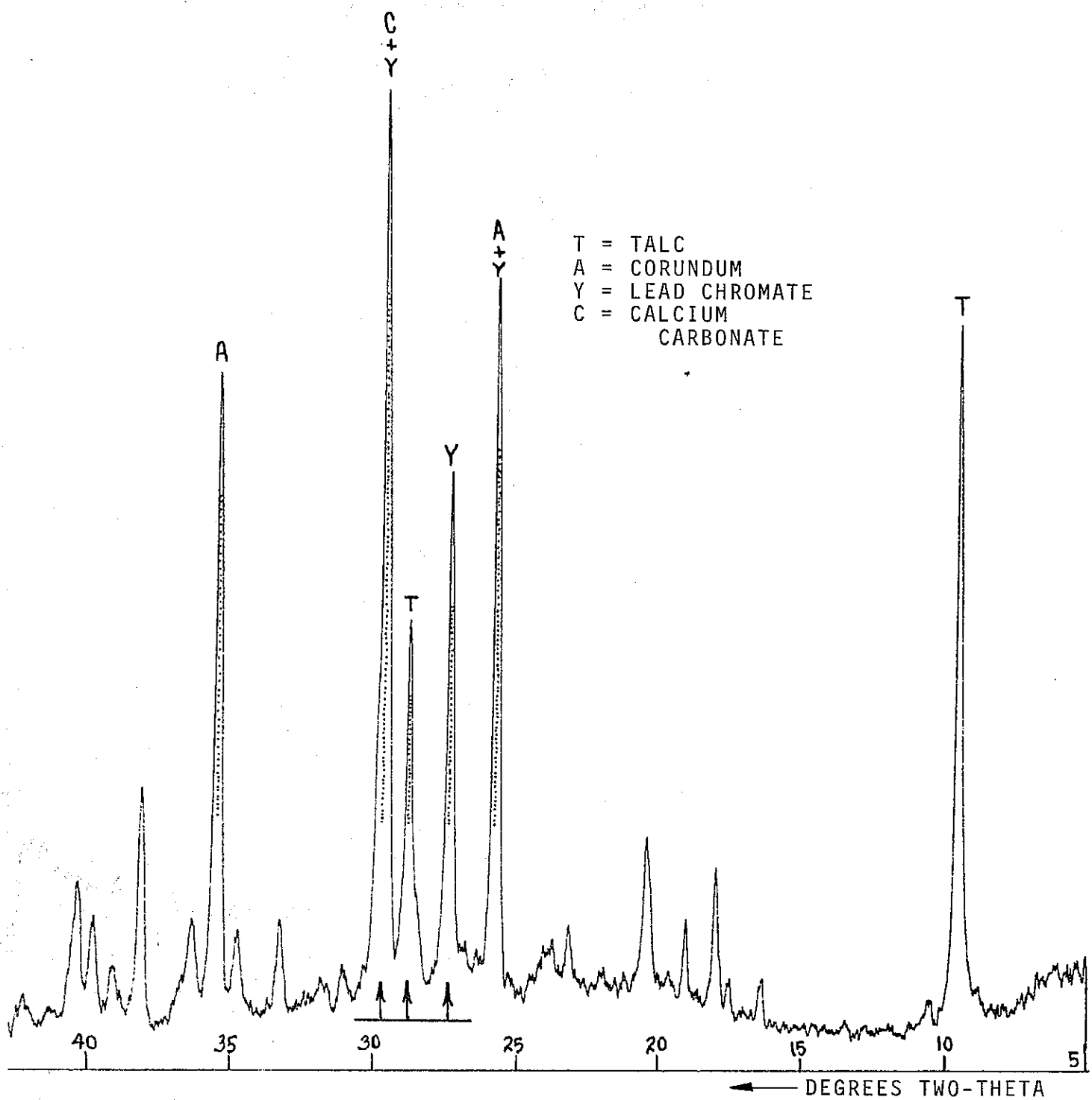

Figure 4

X-RAY DIFFRACTION PATTERN FROM PACKED-POWDER SPECIMEN OF YELLOW TRAFFIC PAINT CONTAINING CORUNDUM AS INTERNAL STANDARD.

Shaded peaks indicate those peaks used for quantitative determinations. Peaks marked with arrows at baseline are those used for quantitative analysis of the dried film samples.

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A complete explanation of the parameters entered is available from the Diano literature. Generally a table consists of an alpha-numeric identification, peak location, background location, regression coefficients for calculating concentrations, and a code designating the type of equation to be used in these calculations.

Intensity data for all peak-intensity runs were based on 180 second counting times. Time on the background is a function of peak-to-background ratio, which in this instance was entered as 5. Intensities for the integrated peak mode were accumulated at 4 seconds per 0.01° two-theta increment. Peak-to-background ratio for this mode was also fixed at 5.

A total of four modes of intensity data accumulation was used:

1) Peak intensity
2) Integrated intensity
3) Relative peak intensity
4) Relative integrated intensity

The first two modes were applied to both the dried film specimens and the powder specimens. The last two modes were applied only to the powder specimens, using the intensity of the 35.1 degree peak from the added corundum as reference. All intensities were corrected for background, measured at appropriate locations on each side of the respective peak angles.

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DATA REDUCTION

After accumulation of all intensity data from all standards, a multiple linear regression (MLR) program was used to determine correlations and standard deviations. This program is a free-standing software package included with the Diano system. For convenience, an additional 8k of memory was installated in the PDP-8 minicomputer so that the MLR program is always available for use. This program is also used for data reduction of fluorescence information from the X-ray spectrometer. The MLR program contains routines for data reduction based on any of three equations: A line interference equation, an absorption-enhancement equation, and a combination equation. The only equation of use in X-ray diffraction is the line interference type of equation.

The MLR program calculates multiple regression coefficients based on the equation:

$$\% = B_o + B_1 I_1 + B_2 I_2 + \ldots\ldots B_n I_n$$

Where:

B_o = the intercept of the calibration line

B_1 = the slope of the calibration line

B_2, B_n = correction coefficients for any line interferences from other compounds, where necessary.

I_1 = x-ray diffraction intensity of the compound of interest

I_2, I_n = x-ray diffraction intensity of affecting compounds

Each series of standard intensities was subjected to analysis using the MLR program to determine regression coefficients and standard deviations for the compounds of interest, and for any possible interferences.

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Dried Film Correlations

Examination of Figures 1 and 2 would seem to indicate that the peaks of interest appear to be free of appreciable overlap interferences. However, not shown is the direct overlap of the calcium carbonate peak by one of the lead chromate peaks in the yellow paint, and the calcium carbonate which is present in the particular talc used to prepare both the PT400 white and PT401 yellow paints.

The only reliable method of determining such interferences is by making diffraction scans of the individual materials to be used in the paint. The Powder Diffraction File(7) can be used, in some cases, to augment such scans but this will not normally disclose the presence or absence of impurities in the materials, as in the case with talc used in the PT400 white and PT401 yellow paints.

Based on information obtained as described above, the calibrations for the samples were made taking into account the following interactions:

1) The titanium dioxide and lead chromate calibrations contain a correction coefficient for a slight talc overlap.

2) The calibrations for calcium carbonate contain coefficients for the talc overlap and in addition, a correction for lead chromate overlapping in the yellow paint. The talc correction is not required for the PT800 series.

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Tables 2 through 10 list the MLR calibrations for peak intensities for the dried films. An ideal calibration "curve" would yield a coefficient of determination of 1.000. Such a fit to a least-squares line is almost never obtained in practice and other factors, such as the standard error of the estimate, absolute error, and relative error must be considered in evaluating the usefulness or validity of the calibrations. In x-ray diffraction, particularly, sample preparation is very important since variable crystalline orientation or preferred orientation can greatly influence any calibration. All of the standard paints prepared for this study contain talc and calcium carbonate. Both of these materials tend to exhibit large preferred orientation effects. This crystallite orientation can be expected to contribute to the deviations from a calibration line for these components.

Evaluation of the MLR's for the dried film specimens appears to indicate that satisfactory quantitative results can be obtained from dried films. Since such films are prepared routinely for other tests, this would appear to involve no extra procedures to prepare samples for X-ray diffraction.

Regarding the validity of the MLR calibrations, one factor of concern is the occasional extremely high intercept coefficient (Tables 4 and 7). High intercepts such as this suggest a possible error in the calibrations. Two possible causes may be incorrect background compensation or insufficient standards for the MLR to adequately reach a determination.

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ACTUAL	CALC	DIFF
7.4300	7.4316	-.0016
11.1600	11.5110	-.3510
14.8700	14.9125	-.0425
18.5900	18.1566	.4334
3.7700	3.4869	.2831
17.0400	17.1589	-.1189
12.8000	12.8057	-.0057
5.5300	5.4815	.0485
9.2200	9.4653	-.2453

NO.	COEFFICIENT
0	.5034694671630
1	.0442934036254
2	-.0013914170265

COEFFICIENT OF DETERMINATION: .997759

STANDARD ERROR OF ESTIMATE: .279791

F-TEST RATIO: 1339.671850

Table 2

CORRELATION FOR TITANIUM DIOXIDE PEAK INTENSITIES IN PT-400 WHITE TRAFFIC PAINT

DRIED FILM

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ACTUAL	CALC	DIFF
48.5000	47.9044	.5956
37.4000	36.5671	.8329
38.2000	39.3403	-1.1403
33.1000	35.6699	-2.5699
52.4000	52.2817	.1183
48.6000	49.9707	-1.3707
28.1000	29.4439	-1.3439
41.5000	36.6759	4.8241
46.3000	46.2460	.0540

NO.	COEFFICIENT
0	12.7777886390686
1	.0271878051757

COEFFICIENT OF DETERMINATION: .930771

STANDARD ERROR OF ESTIMATE: 2.265491

F-TEST RATIO: 94.127960

Table 3

CORRELATION FOR TALC PEAK INTENSITIES IN PT-400 WHITE TRAFFIC PAINT

DRIED FILM

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ACTUAL	CALC	DIFF
35.9000	36.0859	-.1860
43.0000	42.3323	.6677
38.2000	42.1338	-3.9337
39.3000	38.6533	.6467
35.9000	34.7704	1.1296
25.6000	27.3809	-1.7809
50.6000	49.6962	.9038
44.9000	45.0512	-.1512
36.2000	33.4960	2.7040

NO.	COEFFICIENT
0	30.3373861312866
1	.0279466152191
2	-.0189332256317

COEFFICIENT OF DETERMINATION: .926186

STANDARD ERROR OF ESTIMATE: 2.197420

F-TEST RATIO: 37.642946

Table 4

CORRELATION FOR CALCIUM CARBONATE PEAK INTENSITIES IN PT-400 WHITE TRAFFIC PAINT

DRIED FILM

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ACTUAL	CALC	DIFF
7.4300	7.6804	-.2504
11.1100	11.4671	-.3571
14.8200	15.0950	-.2750
18.5200	17.6667	.8533
3.7700	3.2222	.5478
16.9800	17.0772	-.0972
12.7600	13.0464	-.2864
5.6500	5.6526	-.0026
9.3800	9.5123	-.1323

NO.	COEFFICIENT
0	-.3204059600830
1	.0297817935943
2	-.0022494840621

COEFFICIENT OF DETERMINATION: .993192

STANDARD ERROR OF ESTIMATE: .483548

F-TEST RATIO: 437.626361

Table 5

CORRELATION FOR LEAD CHROMATE PEAK INTENSITIES IN PT-401 YELLOW TRAFFIC PAINT

DRIED FILM

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ACTUAL	CALC	DIFF
46.2000	45.7741	.4259
40.4000	38.9721	1.4279
38.5000	36.6648	1.8351
28.0000	29.3834	-1.3834
52.3000	53.9844	-1.6845
50.0000	48.7406	1.2594
33.0000	33.0092	-.0092
43.4000	43.8264	-.4264
35.4000	36.8447	-1.4447

NO.	COEFFICIENT
0	11.9140338897705
1	.0299646854400

COEFFICIENT OF DETERMINATION: .972279

STANDARD ERROR OF ESTIMATE: 1.423987

F-TEST RATIO: 245.546388

Table 6

CORRELATION FOR TALC PEAK INTENSITIES IN PT-401 YELLOW TRAFFIC PAINT

DRIED FILM

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ACTUAL	CALC	DIFF
38.5000	38.7213	-.2213
40.4000	41.5113	-1.1113
38.5000	39.5804	-1.0804
45.0000	44.1344	.8656
36.3000	35.5354	.7646
24.7000	24.4568	.2432
46.2000	45.6826	.5174
43.2000	43.6878	-.4878
47.2000	46.6900	.5100

NO.	COEFFICIENT
0	79.6509361267039
1	.0026254353523
2	-.0341698312759
3	-.0279350137710

COEFFICIENT OF DETERMINATION: .987828

STANDARD ERROR OF ESTIMATE: .960223

F-TEST RATIO: 134.977722

Table 7

CORRELATION FOR CALCIUM CARBONATE PEAK INTENSITIES IN PT-401 YELLOW TRAFFIC PAINT

DRIED FILM

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
2.6800	1.6987	.9813
5.3500	5.1624	.1876
8.0300	8.0761	-.0461
10.7000	10.9825	-.2825
13.3800	13.6839	-.3039
16.0500	16.5424	-.4924
18.7300	19.3629	-.6329
21.4200	21.8919	-.4719
16.0500	16.6397	-.5897
26.7600	26.1853	.5747
29.4200	28.3441	1.0759

NO.	COEFFICIENT
0	-.4708232879638
1	.0453157424926
2	-.0026320338249

COEFFICIENT OF DETERMINATION: .994596

STANDARD ERROR OF ESTIMATE: .695847

F-TEST RATIO: 736.400699

TABLE 8

CORRELATION FOR TITANIUM DIOXIDE PEAK INTENSITIES IN PT-800 WHITE TRAFFIC PAINT

DRIED FILM

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
45.3000	44.0333	1.2666
35.1000	33.3409	1.7591
28.3000	27.1593	1.1407
23.5000	22.6484	.8516
19.8000	18.8894	.9106
12.7000	14.4620	-1.7620
61.3000	61.5757	-.2757
53.0000	53.2222	-.2222
45.3000	44.4510	.8490
39.0000	37.7682	1.2318
31.1000	36.8494	-5.7494

NO.	COEFFICIENT
0	5.0225 601196289
1	.0835349082946

COEFFICIENT OF DETERMINATION: .978631

STANDARD ERROR OF ESTIMATE: 2.262680

F-TEST RATIO: 412.218379

TABLE 9

CORRELATION FOR TALC PEAK INTENSITIES
IN PT-800 WHITE TRAFFIC PAINT

DRIED FILM

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
45.3000	51.7044	-6.4044
52.7000	53.9521	-1.2521
56.7000	60.9884	-4.2884
58.7000	59.1805	-.4805
59.5000	53.1214	6.3786
63.7000	58.3498	5.3502
12.2000	12.5162	-.3162
17.7000	19.0150	-1.3150
31.2000	29.1785	2.0215
26.0000	28.5922	-2.5922
31.1000	28.2013	2.8987

NO.	COEFFICIENT
0	-.2370376586914
1	.0488630771636

COEFFICIENT OF DETERMINATION: .954931

STANDARD ERROR OF ESTIMATE: 4.103574

F-TEST RATIO: 190.697135

TABLE 10

CORRELATION FOR CALCIUM CARBONATE PEAK INTENSITIES IN PT-800 WHITE TRAFFIC PAINT

DRIED FILM

ClibPDF - www.fastio.com

Background and peak locations were very carefully determined for several representative samples and checked on several others and found to be satisfactory. Barring any unnoticed malfunctions, the problem should not be solely resting in these areas.

The most likely source of error appears to be in the number and range of the standards. The minimum recommended number of standards for multiple regression analysis is $2n^2+1$, where n equals the number of independent variables(6). In the case of Table 7, with three variables, the minimum number of standards would be 19 and only nine were available.

The range of the standards available could be a definite factor since approximately fifty percent of the calcium carbonate intensities in the yellow paints can be directly related to the combined lead chromate and talc overlapping. Preparation of sufficient standards should involve consideration of this fact.

Regardless, the results taken as a whole indicate that analysis of traffic paint solids can be done by x-ray diffraction, thus providing a complete analysis of pigments and fillers in approximately the same amount of time as would be used in a regular wet chemical analysis for only a portion of the pigment. The only restriction is that suitable standards, using raw materials from the same sources as those to be used in the manufactured paint, must be prepared. As an example of the importance of this restriction, there are at least three, and possibly four, talcs which could conceivably be interchanged in the formulations. Figures 5 through 8 represent diffraction scans of these materials along with the intensities

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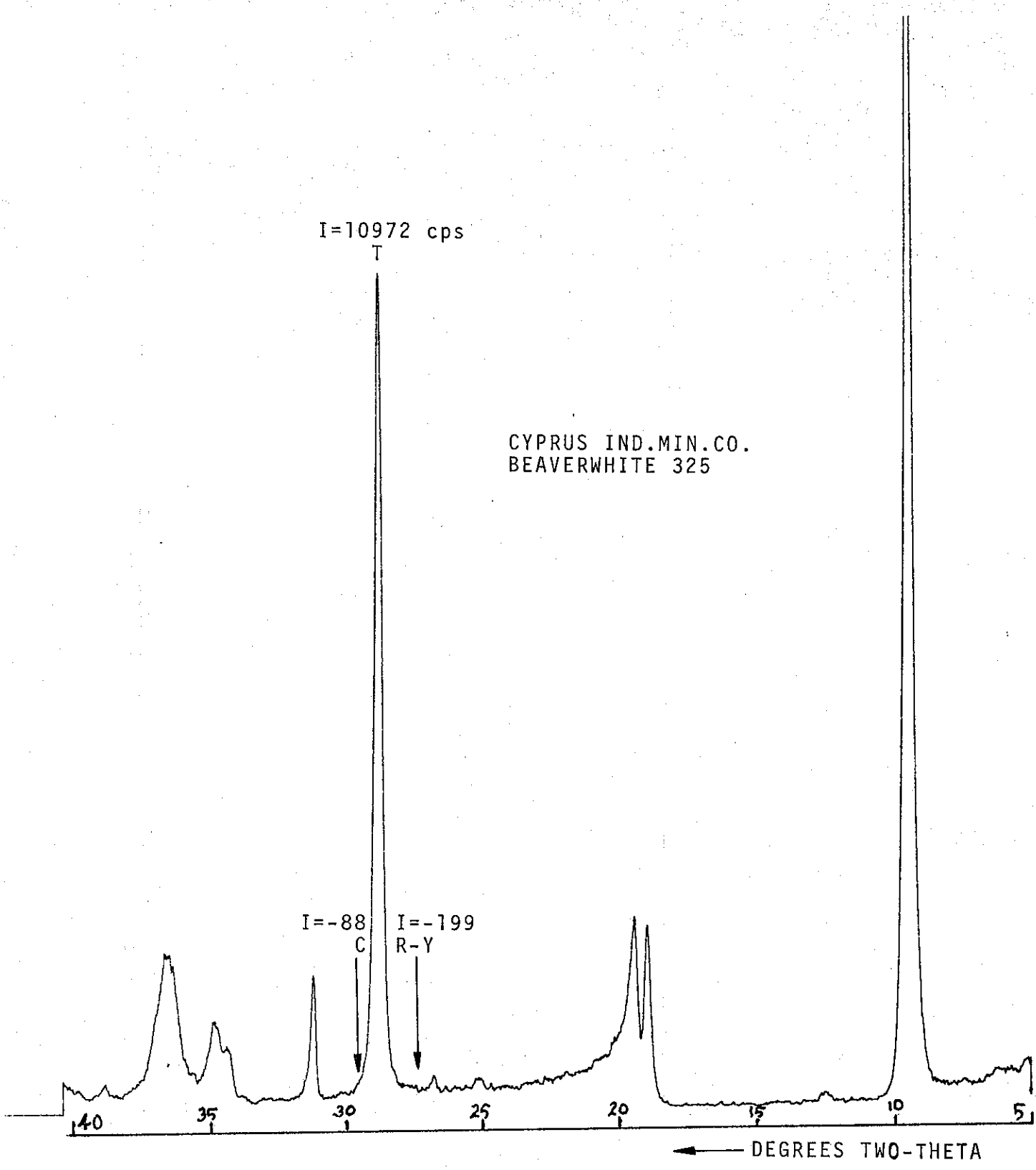

Figure 5

X-RAY DIFFRACTION PATTERN OF TALC
PACKED POWDER

ClibPDF - www.fastio.com

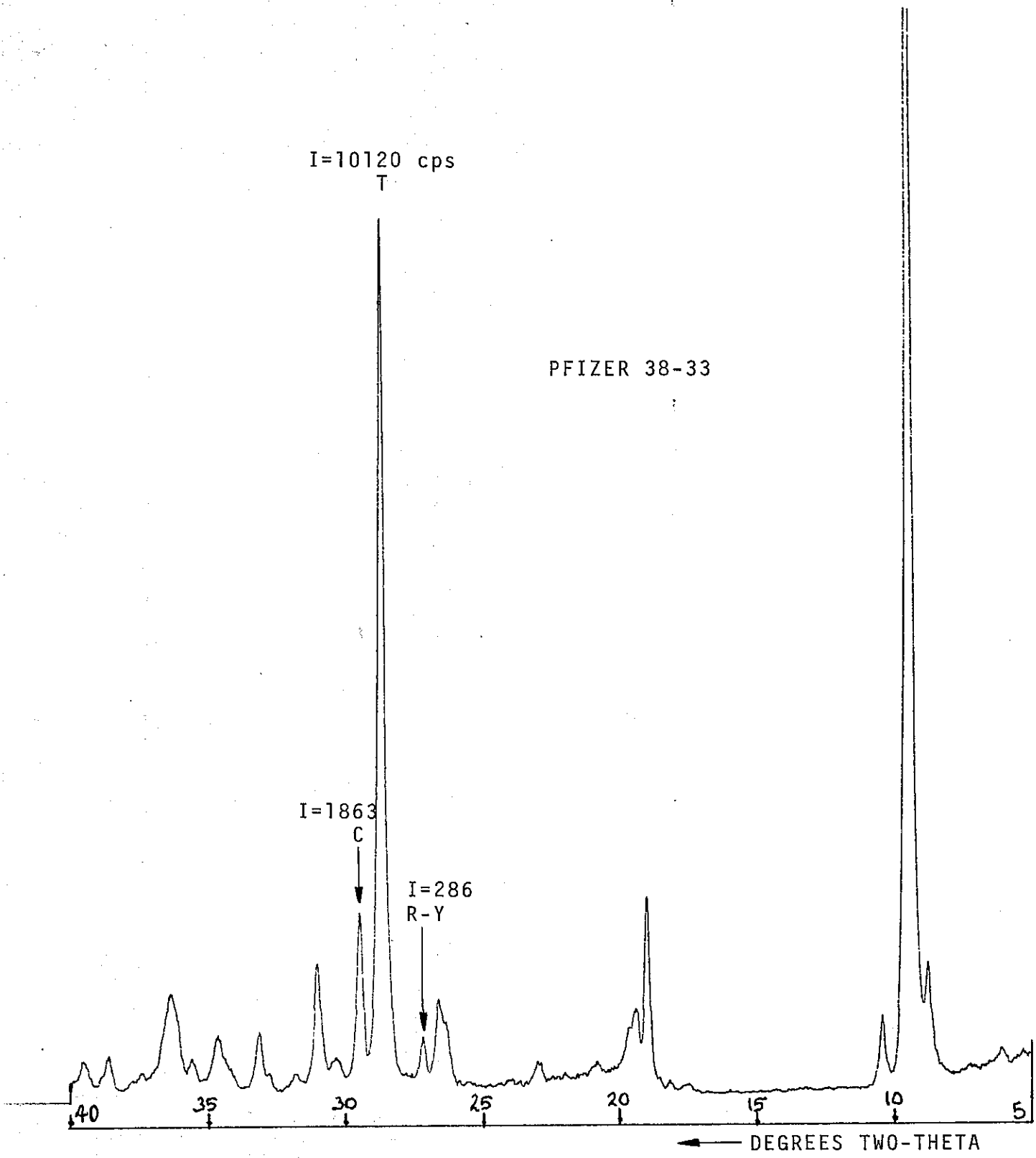

Figure 6

X-RAY DIFFRACTION PATTERN OF TALC

PACKED POWDER

ClibPDF - www.fastio.com

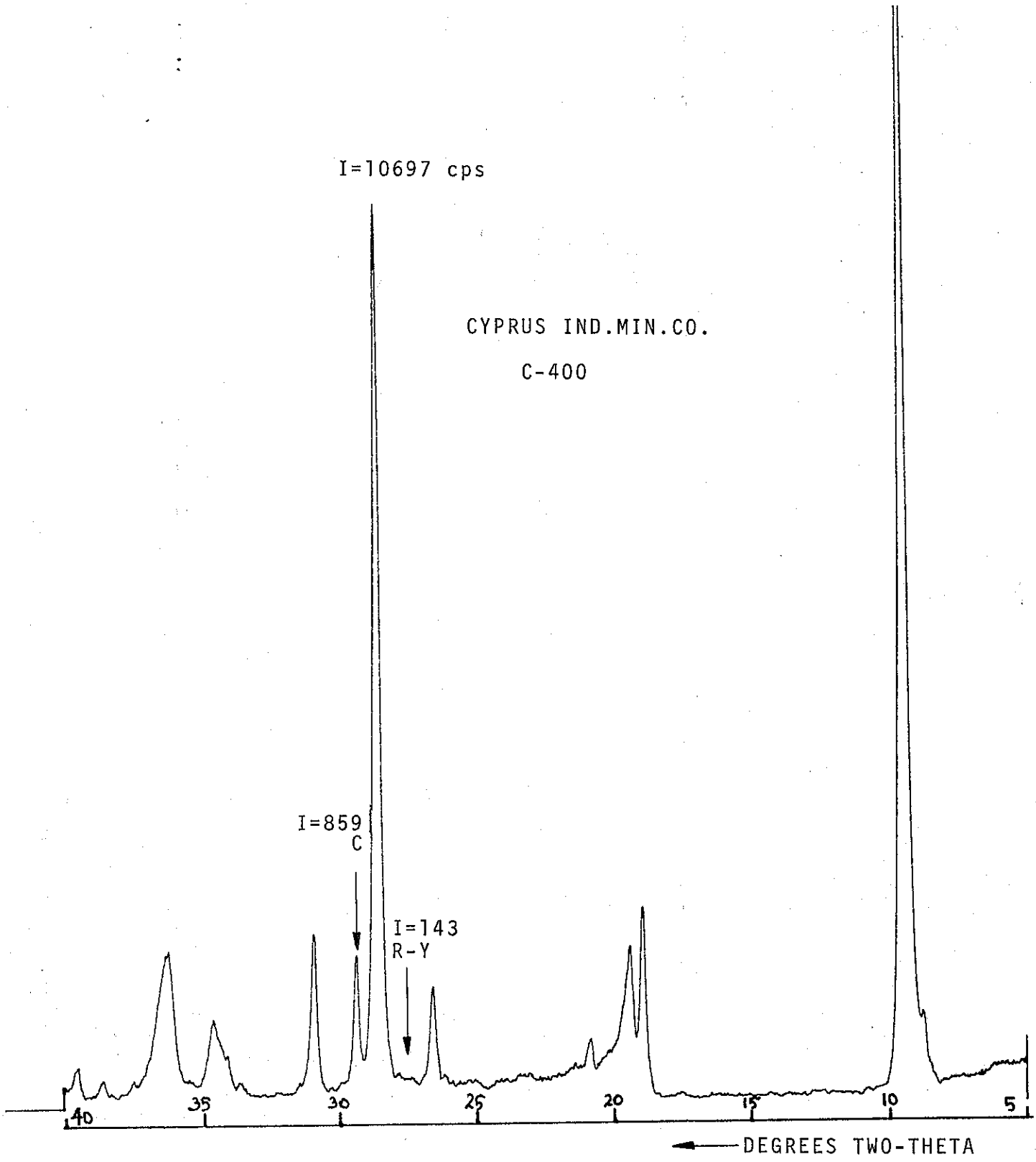

Figure 7

X-RAY DIFFRACTION PATTERN OF TALC

PACKED POWDER

ClibPDF - www.fastio.com

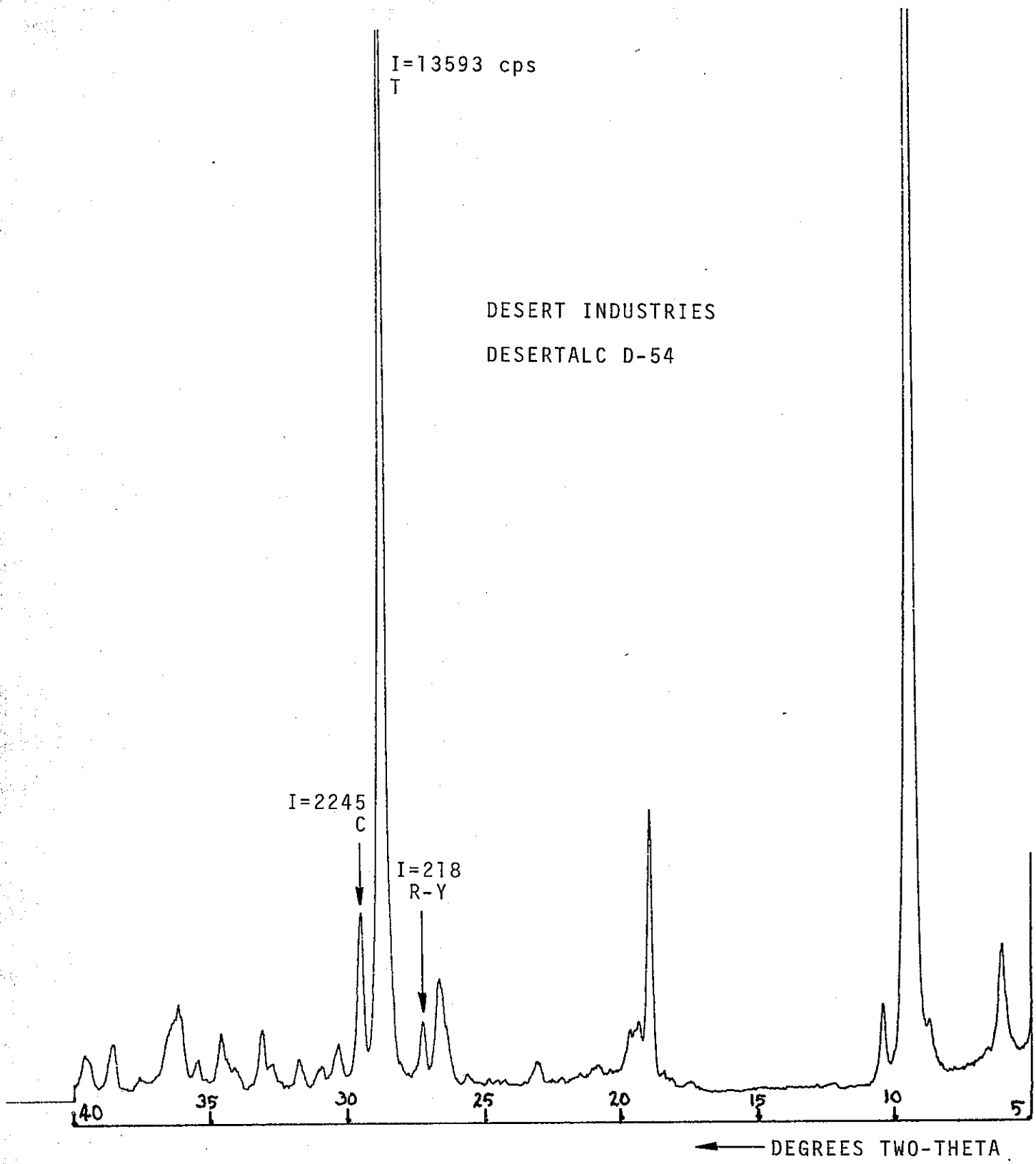

Figure 8

X-RAY DIFFRACTION PATTERN OF TALC

PACKED POWDER

ClibPDF - www.fastio.com

of the peaks used in previous calibrations. From the differences in intensities one can see that if a calibration curve is prepared from standards using, for instance, D-54 talc, and submitted samples are prepared from 38-33 talc, then the quantitative results will be seriously affected. Such changes in raw materials would, of necessity, have to be monitored very carefully in order to detect incorrect results.

One decided advantage to using dried films is that the analyst would risk less chance of exposure to dangerous materials such as lead chromate, since these materials would be significantly immobilized in the films.

A disadvantage is the necessity of preparing standards for each particular type of paint formulation. This presents no particular difficulty for some laboratories, but may be outside the capability of others.

The method and degree of dispersion of the pigments within the paints may affect any analysis. Figure 9 illustrates such an effect. Since the talc intensity enters into any computations for both lead chromate and calcium carbonate, large errors can result from a change such as shown in the figure.

There may also exist a problem of layering or segregation of the individual pigments during the drying of the films. The use of packed powder specimens of the extracted pigments should eliminate this problem.

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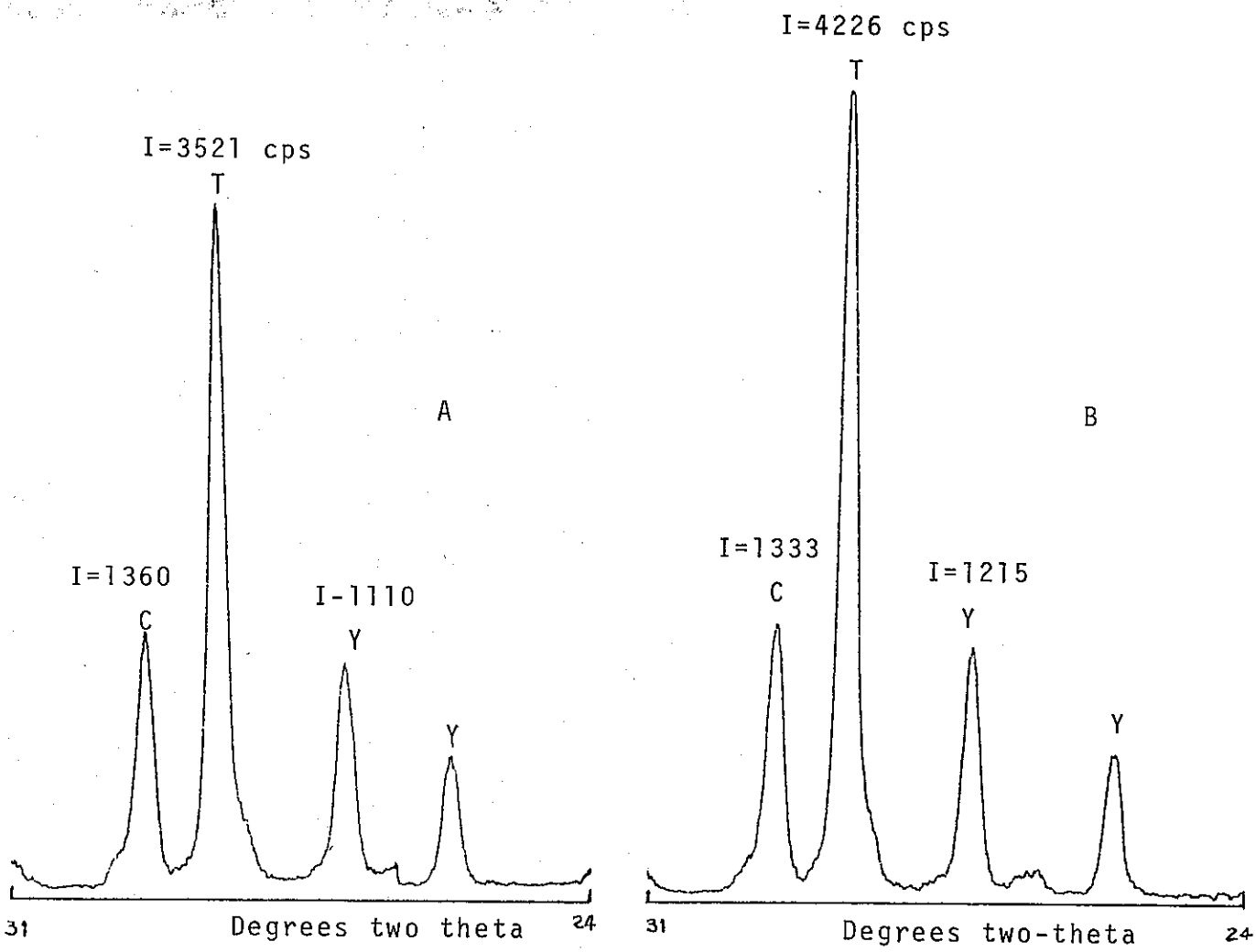

Figure 9

EFFECT OF DISPERSION ON X-RAY DIFFRACTION PEAK INTENSITIES

A. Pattern of dried film of sample as received
B. Pattern of dried film of sample redispersed in blender

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Packed Powder Correlations

The preparation of diffraction specimens using powder samples involves careful attention to technique to achieve reproducible results. The method used to pack the specimens is especially important. Recent studies(13) have supported the 'back-pack' method(3) used to prepare powder specimens for this project, although the free-falling method described in the National Bureau of Standards Monograph 25 (1971) and used by Frank Chung of the Sherwin-Williams Research Center in his work(4,8,9) is certainly applicable.

After extraction of the pigments from the standard packed powder specimens were prepared and intensities accumulated and the MLR program used as before to determine correlations and regression coefficients for the pigment components of interest. Tables 11 through 19 list these correlations using peak intensities.

It should be pointed out that the specimens had been diluted with corundum and glass which would tend to normalize the x-ray absorption effects that would be most pronounced in the yellow paints.

Table 18-A was generated after deletion of the last value from Table 18, since this value is apparently in error.

Evaluation of the MLR's for the packed powders and comparison with those for the dried films indicates no significant differences between the two techniques. There would appear to be no advantage to using one method of sample preparation as opposed to the other, in this particular instance.

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ACTUAL	CALC	DIFF
7.4300	7.5379	-.1079
11.1600	11.1169	.0431
14.8700	14.7854	.0846
18.5900	18.2749	.3151
3.7700	3.6904	.0796
17.0400	17.4697	-.4297
12.8000	12.7275	.0725
5.5300	5.5694	-.0394
9.2200	9.2379	-.0179

NO.	COEFFICIENT
0	-.8728256225585
1	.0894755363464

COEFFICIENT OF DETERMINATION: .998484

STANDARD ERROR OF ESTIMATE: .213139

F-TEST RATIO: 4620.464324

TABLE 11

CORRELATION FOR TITANIUM DIOXIDE PEAK INTENSITIES IN PT-400 WHITE TRAFFIC PAINT PIGMENT.

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
48.5000	52.7005	-4.2005
37.4000	43.1572	-5.7572
38.2000	39.2420	-1.0420
33.1000	33.3692	-.2692
52.4000	47.0724	5.3276
48.6000	47.9289	.6711
28.1000	30.5552	-2.4551
41.5000	38.3855	3.1144
46.3000	41.6890	4.6110

NO.	COEFFICIENT
0	14.0378732681274
1	.122350144386 2

COEFFICIENT OF DETERMINATION: .773108

STANDARD ERROR OF ESTIMATE: 4.101748

F-TEST RATIO: 23.850779

TABLE 12

CORRELATION FOR TALC PEAK INTENSITIES
IN PT-400 WHITE TRAFFIC PAINT PIGMENT

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
35.9000	36.5978	-.6978
43.0000	39.0256	3.9744
38.2000	38.4814	-.2814
39.3000	40.4882	-1.1882
35.2000	37.7330	-1.8331
25.6000	25.6693	-.0693
50.6000	50.6814	-.0814
44.9000	45.1032	-.2032
36.2000	35.8199	.3801

NO.	COEFFICIENT
0	21.3862705230712
1	.0680243260498
2	-.0616491031646

COEFFICIENT OF DETERMINATION: .945644

STANDARD ERROR OF ESTIMATE: 1.885531

F-TEST RATIO: 52.200202

TABLE 13

CORRELATION FOR CALCIUM CARBONATE PEAK INTENSITIES IN PT-400 WHITE TRAFFIC PAINT PIGMENT

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
7.4300	7.4894	-.0594
11.1100	11.6316	-.5216
14.8200	14.9818	-.1618
18.5200	18.3321	.1879
3.7700	3.7736	-.0036
16.9800	17.1747	-.1947
12.7600	12.1189	.6411
5.6500	5.6620	-.0120
9.3800	9.2559	.1241

NO.	COEFFICIENT
0	-1.7695751190185
1	.0609142112731

COEFFICIENT OF DETERMINATION: .996103

STANDARD ERROR OF ESTIMATE: .338393

F-TEST RATIO: 1792.428684

Table 14

CORRELATION FOR LEAD CHROMATE PEAK INTENSITIES IN PT-401 YELLOW TRAFFIC PAINT PIGMENT

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
46.2000	46.5605	-.3605
40.4000	40.5398	-.1398
38.5000	37.1950	1.3050
28.0000	30.6726	-2.6726
52.3000	53.7518	-1.4518
50.0000	48.0657	1.9343
33.0000	30.6726	2.3274
43.4000	41.2088	2.1912
35.4000	38.5329	-3.1329

NO.	COEFFICIENT
0	6.7572402954101
1	.1672405433654

COEFFICIENT OF DETERMINATION: .931889

STANDARD ERROR OF ESTIMATE: 2.232182

F-TEST RATIO: 95.776672

Table 15

CORRELATION FOR TALC PEAK INTENSITIES
IN PT-401 YELLOW TRAFFIC PAINT
PIGMENT

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
38.5000	37.2386	1.2614
40.4000	42.0919	-1.6919
38.5000	37.8768	.6231
45.0000	43.9057	1.0942
36.3000	35.3197	.9803
24.7000	25.7253	-1.0253
46.2000	46.5698	-.3698
43.2000	45.1977	-1.9977
47.2000	46.0743	1.1257

NO.	COEFFICIENT
0	22.078040303344
1	.0774563121795
2	-.037503112716
3	-.0744177627563

COEFFICIENT OF DETERMINATION: .964421

STANDARD ERROR OF ESTIMATE: 1.639895

F-TEST RATIO: 45.181369

Table 16

CORRELATION FOR CALCIUM CARBONATE PEAK INTENSITIES IN PT-401 YELLOW TRAFFIC PAINT PIGMENT

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
2.6800	2.7531	-.0731
5.3500	5.2463	.1037
8.0300	7.9176	.1123
10.7000	10.5890	.1110
13.3800	12.9041	.4758
16.0500	15.2193	.8307
18.7300	19.8496	-1.1196
21.4200	22.1648	-.7448
16.0500	16.8221	-.7721
26.7600	26.8841	-.1242
29.4200	28.2198	1.2002

NO.	COEFFICIENT
0	-.0963649749755
1	.0890445899963

COEFFICIENT OF DETERMINATION: .993278

STANDARD ERROR OF ESTIMATE: .731648

F-TEST RATIO: 1330.429315

Table 17

CORRELATION FOR TITANIUM DIOXIDE PEAK INTENSITIES IN PT-800 WHITE TRAFFIC PAINT PIGMENT

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
45.3000	46.0165	-.7165
35.1000	34.9422	.1578
28.3000	27.6746	.6254
23.5000	22.4835	1.0165
19.8000	20.4071	-.6071
12.7000	12.1013	.5987
61.3000	60.8976	.4023
53.0000	50.5155	2.4845
45.3000	45.6704	-.3704
39.0000	35.9804	3.0196
31.1000	37.7108	-6.6107

NO.	COEFFICIENT
0	-1.3955 307006835
1	.346073246 0021

COEFFICIENT OF DETERMINATION: .971259

STANDARD ERROR OF ESTIMATE: 2.624280

F-TEST RATIO: 304.136753

Table 18

CORRELATION FOR TALC PEAK INTENSITIES
IN PT-800 WHITE TRAFFIC PAINT
PIGMENT

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
45.3000	46.7444	-1.4444
35.1000	35.5985	-.4985
28.3000	28.2841	.0159
23.5000	23.0595	.4405
19.8000	20.9697	-1.1697
12.7000	12.6103	.0897
61.3000	61.7216	-.4216
53.0000	51.2723	1.7277
45.3000	46.3961	-1.0961
39.0000	36.6435	2.3565

NO.	COEFFICIENT
0	-.973663330078 1
1	.3483067512512

COEFFICIENT OF DETERMINATION: .993511

STANDARD ERROR OF ESTIMATE: 1.314454

F-TEST RATIO: 1225.744009

Table 18-A

MODIFIED CORRELATION FOR TALC PEAK INTENSITIES IN PT-800 WHITE TRAFFIC PAINT PIGMENT

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
45.3000	48.3735	-3.0735
52.7000	51.1459	1.5541
56.7000	55.0913	1.6087
58.7000	58.1837	.5163
59.5000	60.3164	-.8164
63.7000	64.2617	-.5617
12.2000	12.4383	-.2383
17.7000	18.9429	-1.2429
31.2000	31.6322	-.4322
26.0000	26.3005	-.3005
31.1000	28.1133	2.9867

NO.	COEFFICIENT
0	-.5708847045898
1	.1066326379776

COEFFICIENT OF DETERMINATION: .992116

STANDARD ERROR OF ESTIMATE: 1.715841

F-TEST RATIO: 1133.196353

Table 19

CORRELATION FOR CALCIUM CARBONATE PEAK INTENSITIES IN PT-800 WHITE TRAFFIC PAINT PIGMENT

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One advantage to using powder specimens is that dispersion of the pigment can be normalized to a certain degree by additional grinding. Also, the addition of an internal standard is easier at this time than might be possible with a whole paint. As illustrated in the next section, the use of an internal standard does offer additional benefits.

Internal Standard

Klug and Alexander(3) have demonstrated that if an internal standard (a component not present in the sample) is added in a fixed proportion to a sample of N components, the concentrations of those components should be a linear function of the intensity ratios of the unknown components to the added internal standard:

$$\text{Concentration} = k \times I_{ij}/I_{ks}$$

Where:

I_{ij} = intensity of the component sought
I_{ks} = intensity of the internal standard
k = a constant which is related to the nature of the component and instrumental considerations

The determinations of the k's are normally from diffraction lines that are free from any overlapping or other interferences.

However, one method of determining these values, which are essentially the slopes of the calibration lines, in the presence of overlapping is to utilize a multiple linear regression program and sufficient standards to derive correction coefficients for the interfering

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elements. This method assumes that the measured line for the internal standard will be free of such interferences.

The choice of material to be used as the internal standard must therefore be made with some care. There are certainly other considerations(12) to be made in this selection but, for this project, corundum (alpha aluminum oxide) was chosen because the particular line to be measured appeared to be free of any apparent overlapping.

Tables 20 through 28 list the results of using the internal standard method to construct regression equations for each of the three series of 'standard' paints. Comparison with the MLR's for the two previous methods again indicates no significant differences.

As with Table 18-A, Table 27-A was prepared after deletion of the last value from Table 27.

Finally, an extension of the internal standard method has been proposed by Frank H. Chung of the Sherwin-Williams Research Center wherein the multiple standard type of calibration is replaced by using reference intensities, Ki's, which are determined essentially from binary mixtures of a standard material and the component of interest(4,8,9). Further discussion and theoretical considerations of this method were also given by Hubbard and Evans and Smith(10), Hubbard(11), and Hubbard and Smith(12).

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ACTUAL	CALC	DIFF
7.4300	7.3002	.1297
11.1600	11.0270	.1330
14.8700	14.5689	.3011
18.5900	18.7145	-.1245
3.7700	3.8107	-.0407
17.0400	17.1622	-.1222
12.8000	12.8718	-.0718
5.5300	5.6987	-.1687
9.2200	9.2560	-.0360

NO.	COEFFICIENT
0	-.2794609069824
1	30.799317359924 3

COEFFICIENT OF DETERMINATION: .999085

STANDARD ERROR OF ESTIMATE: .165702

F-TEST RATIO: 7649.264335

Table 20

CORRELATION FOR TITANIUM DIOXIDE PEAK INTENSITIES IN PT-400 WHITE TRAFFIC PAINT PIGMENT

INTERNAL STANDARD METHOD

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ACTUAL	CALC	DIFF
48.5000	51.9931	-3.4931
37.4000	43.5217	-6.1218
38.2000	39.4288	-1.2288
33.1000	34.0006	-.9006
52.4000	45.9891	6.4109
48.6000	48.9935	-.3935
28.1000	30.3189	-2.2189
41.5000	37.9242	3.5758
46.3000	41.9301	4.3699

NO.	COEFFICIENT
0	11.9732021331787
1	48.3799457550048

COEFFICIENT OF DETERMINATION: .749417

STANDARD ERROR OF ESTIMATE: 4.310436

F-TEST RATIO: 20.935420

Table 21

CORRELATION FOR TALC PEAK INTENSITIES IN PT-400 WHITE TRAFFIC PAINT PIGMENT

INTERNAL STANDARD METHOD

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
35.9000	37.1646	-1.2646
43.0000	39.3214	3.6786
38.2000	38.2467	-.0467
39.3000	40.6233	-1.3233
35.9000	37.3934	-1.4934
25.6000	25.6411	-.0411
50.6000	50.8926	-.2926
44.9000	44.7033	.1967
36.2000	35.6135	.5865

NO.	COEFFICIENT
0	15.6521558761596
1	26.9593763351440
2	-17.5060224533081

COEFFICIENT OF DETERMINATION: .950126

STANDARD ERROR OF ESTIMATE: 1.806688

F-TEST RATIO: 57.125053

Table 22

CORRELATION FOR CALCIUM CARBONATE PEAK INTENSITIES IN PT-400 WHITE TRAFFIC PAINT PIGMENT

INTERNAL STANDARD METHOD

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
7.4300	7.3356	.0944
11.1100	11.4378	-.3278
14.8200	14.9708	-.1508
18.5200	18.6624	-.1424
3.7700	3.8656	-.0956
16.9800	16.7590	.2210
12.7600	12.4895	.2705
5.6500	5.6647	-.0147
9.3800	9.2346	.1454

NO.	COEFFICIENT
0	-1.30994033 81347
1	21.72792434 69238

COEFFICIENT OF DETERMINATION: .998477

STANDARD ERROR OF ESTIMATE: .211095

F-TEST RATIO: 4617.029190

Table 23

CORRELATION FOR LEAD CHROMATE PEAK INTENSITIES IN PT-401 YELLOW TRAFFIC PAINT PIGMENT

INTERNAL STANDARD METHOD

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
46.2000	46.1258	.0742
40.4000	40.3616	.0384
38.5000	37.4351	1.0649
28.0000	30.7614	-2.7614
52.3000	53.8252	-1.5252
50.0000	48.6832	1.3168
33.0000	30.7614	2.2386
43.4000	40.8881	2.5119
35.4000	38.3582	-2.9582

NO.	COEFFICIENT
0	3.52663421630385
1	68.3775901794433

COEFFICIENT OF DETERMINATION: .935748

STANDARD ERROR OF ESTIMATE: 2.167885

F-TEST RATIO: 101.962566

Table 24

CORRELATION FOR TALC PEAK INTENSITIES
IN PT-401 YELLOW TRAFFIC PAINT
PIGMENT

INTERNAL STANDARD METHOD

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
38.5000	36.9669	1.5331
40.4000	41.9886	-1.5886
38.5000	37.6322	.8678
45.0000	44.1622	.8378
36.3000	35.7347	.5652
24.7000	25.7198	-1.0198
46.2000	46.8106	-.6106
43.2000	44.9449	-1.7449
47.2000	46.0399	1.1601

NO.	COEFFICIENT
0	14.8395538330078
1	31.3625860214233
2	-21.2113523483276
3	-13.9365100860595

COEFFICIENT OF DETERMINATION: .967083

STANDARD ERROR OF ESTIMATE: 1.578087

F-TEST RATIO: 48.924541

Table 25

CORRELATION FOR CALCIUM CARBONATE PEAK INTENSITIES IN PT-401 YELLOW TRAFFIC PAINT PIGMENT

INTERNAL STANDARD METHOD

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
2.6800	2.9178	-.2378
5.3500	5.3454	.0046
8.0300	8.0106	.0194
10.7000	10.7063	-.0063
13.3800	13.0944	.2856
16.0500	15.7169	.3331
18.7300	18.7446	-.0146
21.4200	21.5652	-.1452
16.0500	16.1220	-.0720
26.7600	27.4195	-.6595
29.4200	28.9272	.4928

NO.	COEFFICIENT
0	.3531074523925
1	30.4595756530761

COEFFICIENT OF DETERMINATION: .998672

STANDARD ERROR OF ESTIMATE: .325534

F-TEST RATIO: 6757.031440

Table 26

CORRELATION FOR TITANIUM DIOXIDE PEAK INTENSITIES IN PT-800 WHITE TRAFFIC PAINT PIGMENT

INTERNAL STANDARD METHOD

ClibPDF - www.fastio.com

ACTUAL	CALC	DIFF
45.3000	43.7550	1.5450
35.1000	34.2013	.8987
28.3000	27.4125	.8875
23.5000	22.3371	1.1629
19.8000	20.3900	-.5900
12.7000	11.8098	.8902
61.3000	59.9418	1.3582
53.0000	51.1929	1.8071
45.3000	45.0660	.2339
39.0000	38.0695	.9305
31.1000	40.2243	-9.1243

NO.	COEFFICIENT
0	-3.039947032984
1	129.80570793151 85

COEFFICIENT OF DETERMINATION: .955590

STANDARD ERRO R OF ESTIMATE: 3.261880

F-TEST RATIO: 193.682422

Table 27

CORRELATION FOR TALC PEAK INTENSITIES
IN PT-800 WHITE TRAFFIC PAINT
PIGMENT

INTERNAL STANDARD METHOD

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ACTUAL	CALC	DIFF
45.3000	44.8467	.4533
35.1000	35.0876	.0124
28.3000	28.1527	.1472
23.5000	22.9682	.5318
19.8000	20.9793	-1.1793
12.7000	12.2146	.4854
61.3000	61.3815	-.0815
53.0000	52.4445	.5555
45.3000	46.1859	-.8859
39.0000	39.0390	-.0390

NO.	COEFFICIENT
0	-2.9544677734375
1	132.5968742370605

COEFFICIENT OF DETERMINATION: .998477

STANDARD ERROR OF ESTIMATE: .636194

F-TEST RATIO: 5258.674621

Table 27-A

MODIFIED CORRELATION FOR TALC PEAK INTENSITIES
IN PT-800 WHITE TRAFFIC PAINT PIGMENT

INTERNAL STANDARD METHOD

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ACTUAL	CALC	DIFF
45.3000	45.1437	.1562
52.7000	49.5084	3.1916
56.7000	54.4615	2.2385
58.7000	58.2899	.4101
59.5000	61.0905	-1.5905
63.7000	66.5612	-2.8612
12.2000	12.4049	-.2049
17.7000	19.1419	-1.4419
31.2000	30.8059	.3941
26.0000	27.6813	-1.6813
31.1000	29.7110	1.3890

NO.	COEFFICIENT
0	.1599807739257
1	37.24131584167 48

COEFFICIENT OF DETERMINATION: .990141

STANDARD ERROR OF ESTIMATE: 1.918860

F-TEST RATIO: 904.289245

Table 28

CORRELATION FOR CALCIUM CARBONATE PEAK INTENSITIES IN PT-800 WHITE TRAFFIC PAINT PIGMENT

INTERNAL STANDARD METHOD

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The major benefit of this method is in the reduction in number of standards required; for any compound three or four should be sufficient. It is however necessary to again have diffraction lines free of interferences.

To utilize this method, binary mixtures of the individual compounds in the three series of "standard" paints were prepared and the Ki values determined for each compound. According to the equation:

$$Ki = \frac{X_c}{X_i} \times \frac{I_i}{I_c}$$

Where:

Ki = reference intensity

X_c = weight percent of corundum

X_i = weight percent of compound (corrected for purity)

I_i = intensity of the compound

I_c = intensity of the corundum

Table 29 lists the results.

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Component	Weight Ratios - Corundum/Compound		Ki
Titanium Dioxide	1/3		2.97
	2/2		3.03
	3/1		3.27
		Avg.	3.09
Calcium Carbonate	1/3		2.88
	2/2		2.87
	3/1		2.75
		Avg.	2.83
Talc (B-325)	1/3		1.15
	2/2		1.24
	3/1		1.24
		Avg.	1.21
Talc (38-33)	1/3		1.02
	2/2		1.00
	3/1		1.19
		Avg.	1.07
Talc (D-54)	1/3		1.63
	2/2		1.73
	3/1		1.77
		Avg.	1.71
Lead Chromate	1/3		1.68
	2/2		2.98
	3/1		4.26

TABLE 29

Determination of Ki (Reference Intensities) from Binary Mixtures

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With the exception of lead chromate, all other values appear to be reasonably uniform throughout the three ratios.

Using the above determined values, and the PT-800 series of standards as unknowns, the amounts of titanium dioxide, talc, and calcium carbonate were determined and are listed in Tables 30 through 32. The amounts were calculated using the following equation:

$$X_i = \frac{X_c}{Ki} \times \frac{I_i}{I_c} \times \frac{X_{sp}}{X_{sa}}$$

Where:

X_i = concentration of compound in sample
X_c = weight percent of corundum in specimen
Ki = intensity ratios
I_i = intensity of the compound
I_c = intensity of corundum
X_{sp} = total weight of specimen
X_{sa} = weight of sample in specimen

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	Percent Titanium Dioxide		
	Known	Found	Difference
A	2.68	2.72	0.04
B	5.35	5.30	0.05
C	8.03	8.14	0.11
D	10.70	11.00	0.30
E	13.38	13.54	0.16
F	16.05	16.32	0.27
G	18.73	19.54	0.81
H	21.42	22.54	1.12
I	16.05	16.75	0.70
J	26.76	28.76	2.00
K	29.42	30.36	0.94

TABLE 30

Titanium Dioxide in PT-800 White Traffic Paint Using Reference Intensity Method

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	Percent Talc		
	Known	Found	Difference
A	45.3	29.8	15.5
B	35.1	23.7	11.4
C	28.3	19.4	8.9
D	23.5	16.2	7.3
E	19.8	14.9	4.9
F	12.7	9.4	3.2
G	61.3	40.1	21.2
H	53.0	34.5	18.5
I	45.3	30.6	14.7
J	39.0	26.2	12.8
K	31.1	27.6	3.6

TABLE 31

Talc in PT-800 White Traffic Paint Using Reference Intensity Method

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	Percent Calcium Carbonate		
	Known	Found	Difference
A	45.3	42.7	2.6
B	52.7	46.8	5.9
C	56.7	51.5	5.2
D	58.7	55.2	3.5
E	59.5	57.8	1.7
F	63.7	63.0	0.7
G	12.2	11.6	0.6
H	17.7	18.0	0.3
I	31.2	29.1	2.1
J	26.0	26.1	0.1
K	31.1	28.0	3.1

TABLE 31

Calcium Carbonate in PT-800 White Traffic Paint Using Reference Intensity Method

From the above tables it is apparent that the Ki value for talc can be questioned. The results for the titanium dioxide and calcium carbonate are acceptable. There is some difference, apparently, between determining the reference intensities for talc on the pure materials as opposed to when it is incorporated into a paint. As a check, the talc content of the PT-400 series was calculated as above and the results are shown in Table 33.

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	Percent Talc		
	Known	Found	Difference
A	48.5	48.4	0.13
B	37.4	38.1	0.73
C	38.2	33.2	5.0
D	33.1	26.6	6.5
E	52.4	41.1	11.3
F	48.6	44.8	3.8
G	28.1	22.2	5.9
H	41.5	31.4	10.1
I	46.3	36.2	10.1

TABLE 33

Talc in PT-400 White Traffic Paint
Using Reference Intensity Method

This table seems to agree with the assumption that the reference intensities for talcs may not be correct when determined from the pure material. Why this happens can only be guessed at this time, although it is suspected that the grinding procedure may be the major contributor to the discrepancies. For now, the question of the correct reference intensities remains open with a possible solution as follows:

Since the term $\frac{X_c}{Ki}$ is the slope of the calibration line and passes through the origin, it should be possible to calculate in reverse and arrive at a value for Ki.

Accordingly, again using the PT-800 series as standards, Ki was calculated for talc according to the following equation:

$$Ki = \frac{\frac{X_c}{X_i}}{\left(\frac{I_i}{I_c}\right)}$$

The results are listed in Table 34.

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A	0.80	
B	0.82	
C	0.83	
D	0.83	
E	0.91	Avg. = 0.85 ±0.09
F	0.90	
G	0.79	
H	0.79	
I	0.82	
J	0.81	
K	1.07	

TABLE 34

Ki Values for Talc in PT-800
White Traffic Paint

As shown above, some phenomenon is taking place that prevents the determination of the reference intensity for talc from the pure material.

Using the same technique, the Ki's for the talc used in the PT-400 and PT-401 series, titanium dioxide in the PT-400 and PT-800 series, calcium carbonate in the PT-800, and finally, lead chromate in the PT-401 series were determined. For comparison, the Ki's obtained from pure materials are also listed again.

Talc (D-54)	Avg. = 1.40 ±0.14 (18)	Pure = 1.71
Titanium Dioxide	Avg. = 3.26 ±0.12 (20)	Pure = 3.09
Calcium Carbonate (45-3)	Avg. = 2.69 ±0.12 (11)	Pure = 2.83
Lead Chromate (Y469D)	Avg. = 5.30 ±0.45 (11)	Pure = Unknown

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The above figures seem to support the assumption made earlier that there may be a difference between grinding a sample containing several of the components and grinding pure materials, especially talcs. The problem encountered with lead chromate pigment is probably due to a strong line which overlaps the corundum reference line. In an actual sample, at the levels anticipated in a normal paint, this overlap apparently is reduced to a negligible effect.

Also, a comparison of the reference intensity values for the two talcs further illustrates the effect that could happen if one talc is substituted for another in a particular formulation.

All of the above does not mean that this method cannot be used. Until more studies regarding the assumed grinding effect have been made, the use of 'pure' materials should not be relied upon to produce the reference intensities. What can be done is to use prepared paints containing the components of interest to establish the required ratios.

Finally, a particular advantage of the Chung method is that a material balance can be used to detect the presence of amorphous materials not otherwise observed.

As a test of the foregoing methods, several randomly selected samples were analyzed. The following tables list the results obtained using each of the procedures along with the theoretical values.

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The raw materials used to manufacture these samples may or may not comply with specifications. Specifically, the talcs will not be the same as that used to prepare the standards. As a consequence, no specific decision as to whether these samples are acceptable can be made. However, these results overall do show that x-ray diffraction is capable of making a quantitative analysis of the pigments used in paints.

It should be mentioned that both the calibration standards and the manufactured paints were analyzed on the x-ray diffractometer only once. That is, no effort was made to remount, repack, or otherwise repeat any determination. Good practice would dictate running the standards at least two times, and preferably three times, each to establish average intensity values for calibration purposes.

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Sample		Theoretical Composition, Weight Percent		
		TiO_2	Talc	$CaCO_3$
Fast Dry		15.3 min.	37.4	37.4
			Found	
1.	A	15.5	30.6	40.8
	B	16.2	34.2	36.0
	C	16.2	31.1	36.4
	D	16.5	28.2	38.1
2.	A	13.7	45.9	30.4
	B	15.9	46.0	30.1
	C	15.7	41.7	32.2
	D	16.0	43.8	37.6
3.	A	16.9	38.6	42.0
	B	16.4	38.9	38.3
	C	16.2	35.4	39.7
	D	16.5	34.5	44.9

Sample		Theoretical Composition, Weight Percent		
		TiO_2	Talc	$CaCO_3$
Rapid Dry		14.5 min.	26.7	50.1
			Found	
1.	A	15.4	24.9	52.4
	B	14.9	28.5	48.7
	C	14.9	25.6	49.2
	D	15.2	20.1	53.0
2.	A	13.4	34.9	47.0
	B	14.1	33.9	43.0
	C	14.2	30.8	44.1
	D	14.5	27.7	48.6
3.	A	12.7	35.3	42.6
	B	12.7	33.6	42.7
	C	12.8	30.4	43.6
	D	13.1	27.2	47.8

TABLE 35

Analysis of Pigments and
Fillers in White Traffic Paints

A. Dried film
B. Packed powder - peak intensity
C. Packed powder - internal standard method
D. Packed powder - reference intensity method

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Sample		Theoretical Composition, Weight Percent		
		$PbCrO_4$	Talc	$CaCO_3$
Fast Dry		14.6 min	54.4	19.2
			Found	
1.	A	15.4	43.8	30.7
	B	-	-	-
	C	-	-	-
	D	-	-	-
2.	A	14.3	85.0	0
	B	16.4	54.1	19.4
	C	14.4	53.1	19.6
	D	14.4	51.8	36.5*
3.	A	13.3	30.4	47.2
	B	13.9	27.1	37.9
	C	14.3	52.6	36.8
	D	13.5	24.3	46.4*

Sample		Theoretical Composition, Weight Percent		
		$PbCrO_4$	Talc	$CaCO_3$
Rapid Dry		13.7 min	26.0	51.3
			Found	
1.	A	15.6	24.1	51.7
	B	-	-	-
	C	-	-	-
	D	-	-	-
2.	A	14.0	34.3	43.0
	B	13.7	29.0	45.1
	C	13.6	50.4	44.4
	D	12.9	25.9	55.5*

TABLE 36

Analysis of Pigments and Fillers in Yellow Traffic Paints

A. Dried film
B. Packed powder - peak intensity
C. Packed powder - internal standard method
D. Packed powder - reference intensity method
*Not corrected for overlapping lines

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APPENDIX A

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Composition	Specifications	Parts by Weight
Alkyd Resin, 60% Solids		130
Chlorinated Paraffin		50
Chlorinated Resin		25
Chlorinated Rubber, 20 Cps		60
Methyl Ethyl Ketone	TT-M-00261	100
Aliphatic Thinner		140
Toluene Substitute		60
6% Cobalt Napthenate	ASTM D-600 Class B	0.7
24% Lead Napthenate	ASTM D-600 Class B	1.5
Propylene Oxide		2.0
Anti-skinning Agent		1.0
Anti-settling Agent		8.0
95% Methanol		3.0
Soya Lecithin		4.0
Titanium Dioxide	ASTM D-476, Types II, III or IV, 90% Minimum TiO_2	100
Magnesium Silicate		220
Synthetic Hydrated Calcium Silicate		40
Calcium Carbonate		220

COMPOSITION OF
FAST DRY WHITE TRAFFIC LINE PAINT

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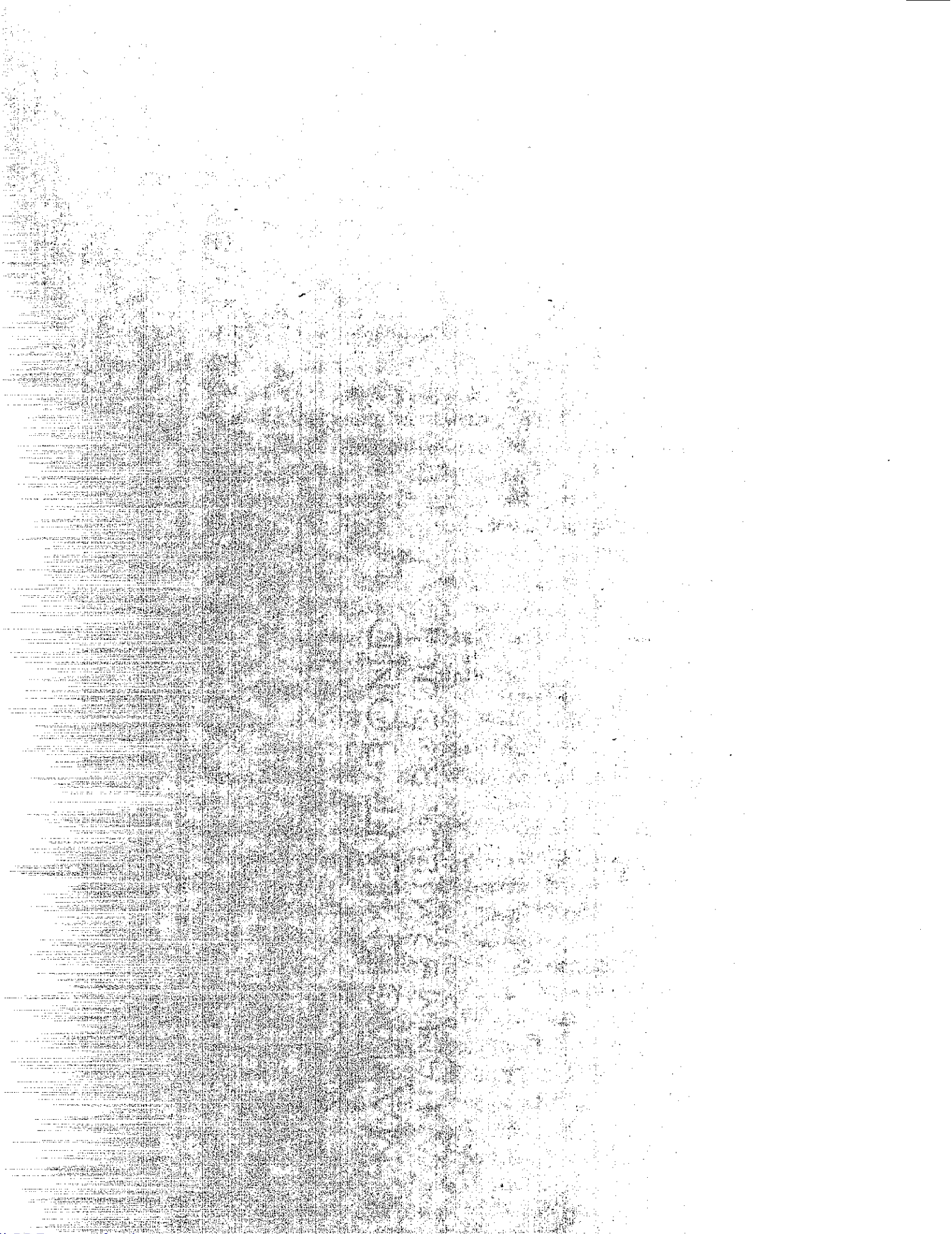

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Composition	Specifications	Parts by Weight
Alkyd Resin, 60% Solids		120
Chlorinated Paraffin		40
Chlorinated Rubber, 20 Cps		80
Methyl Ethyl Ketone	TT-M-00261	150
Aliphatic Thinner		150
6% Cobalt Napthenate	ASTM D-600 Class B	0.5
24% Lead Napthenate	ASTM D-600 Class B	1.5
Propylene Oxide		2.0
Anti-skinning Agent		1.0
Anti-settling Agent		4.0
95% Methanol		1.5
Soya Lecithin		8.0
Titanium Dioxide	ASTM D-476, Types II, III or IV 90% Minimum TiO_2	100
Magnesium Silicate		165
Synthetic Hydrated Calcium Silicate		40
Calcium Carbonate		310

COMPOSITION OF
RAPID DRY WHITE TRAFFIC LINE PAINT

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Composition	Specifications	Parts by Weight
Alkyd Resin, 60% Solids		130
Chlorinated Paraffin		50
Chlorinated Resin		25
Chlorinated Rubber, 20 Cps		60
Methyl Ethyl Ketone	TT-M-00261	100
Aliphatic Thinner		140
Toluene Substitute		60
6% Cobalt Napthenate	ASTM D-600 Class B	0.7
24% Lead Napthenate	ASTM D-600 Class B	1.5
Propylene Oxide		2.0
Anti-skinning Agent		1.0
Anti-settling Agent		8.0
95% Methanol		3.0
Soya Lecithin		4.0
Medium Chrome Yellow	ASTM D-211, Type III	100
Magnesium Silicate		325
Uncalcined Diatomaceous Silica		50
Calcium Carbonate		115

COMPOSITION OF
FAST DRY YELLOW TRAFFIC LINE PAINT

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Composition	Specifications	Parts by Weight
Alkyd Resin, 60% Solids		120
Chlorinated Paraffin		40
Chlorinated Rubber, 20 Cps		80
Methyl Ethyl Ketone	TT-M-00261	150
Aliphatic Thinner		150
6% Cobalt Napthenate	ASTM D-600 Class B	0.5
24% Lead Napthenate	ASTM D-600 Class B	1.5
Propylene Oxide		2.0
Anti-skinning Agent		1.0
Anti-settling Agent		4.0
95% Methanol		1.5
Soya Lecithin		8.0
Medium Chrome Yellow	ASTM D-211, Type III	100
Magnesium Silicate		165
Synthetic Hydrated Calcium Silicate		40
Calcium Carbonate		325

COMPOSITION OF
RAPID DRY YELLOW TRAFFIC LINE PAINT

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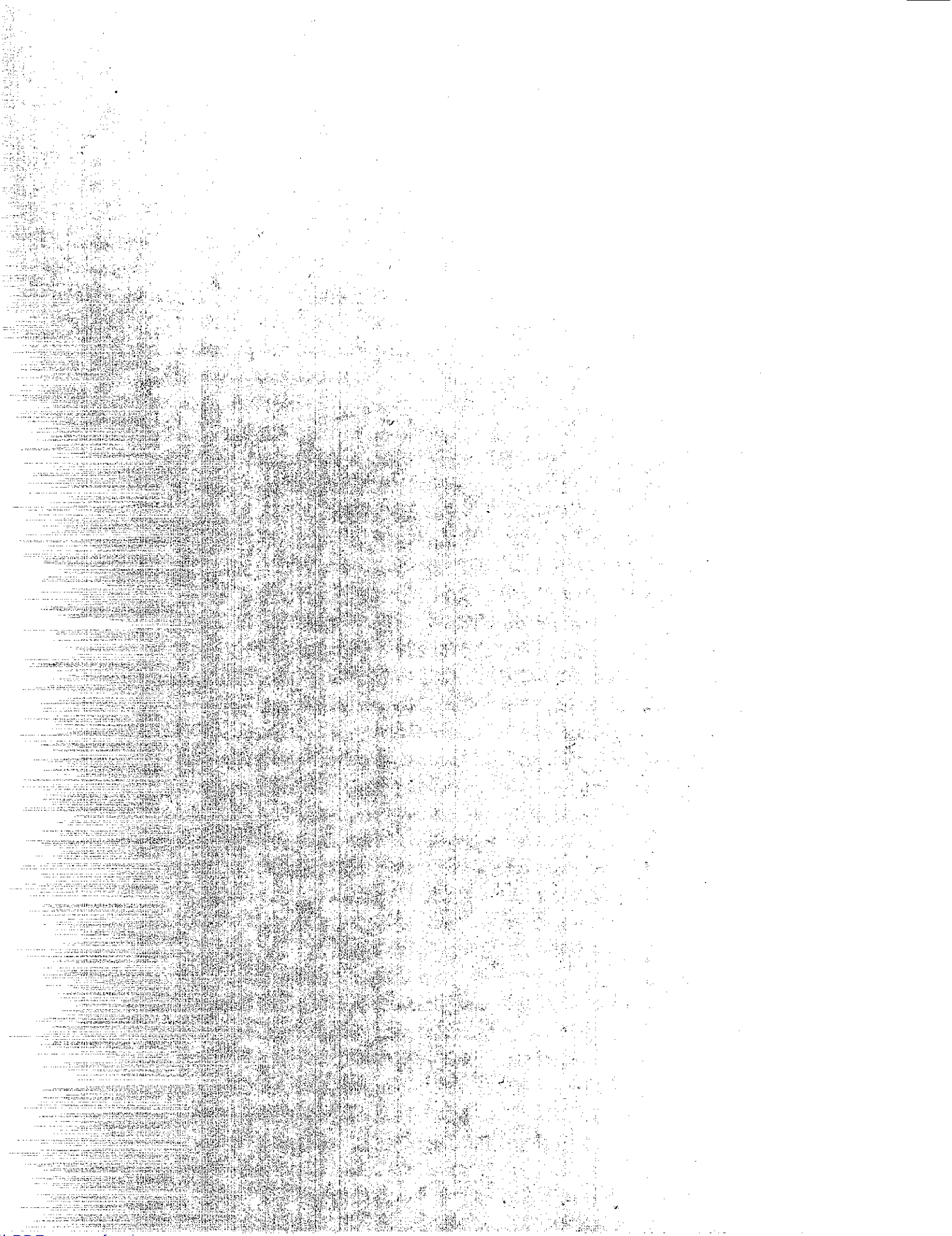

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APPENDIX B

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APPENDIX B
Statistical Information

An extended review of regression analysis is beyond the scope of this study. There are many reference books available covering the theory and practice of regression techniques. However, some general comments concerning the coefficients and other information listed in the various tables may be of value.

Regression Coefficients

A partial explanation of the regression coefficients (B_0, B_1, etc.) was given in the section on Data Reduction. In addition it should be noted that in most cases these coefficients will be valid only for the particular paints used in this study.

Regression coefficients calculated to correct for any overlapping components will usually require that these components indeed be in the sample. Corrections for overlapping are reflected, in addition to the coefficients B_2, B_3, etc., in a change in the intercept coefficient B_0. (Although where the corrections are large relative to the affected component there may also be an apparent change in the slope coefficient B_1.) Because of this the equations containing correction coefficients are not 'centered'. That is, the assumption that if all independent variables (intensities) are zero the result will be zero is not true. It can thus be seen that analysis of the affected component is dependent on the presence of the overlapping components when the calibration contains correction coefficients for these components.

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In instances where actual intensities are used to derive the regression coefficients (as opposed to relative intensities normalized to some internal standard) the sample matrix will contribute more or less to the X-ray absorption, and subsequently a change in the slope coefficient, B_1. This means, for example, that the slope coefficient for, say, Titanium dioxide in a system consisting of titanium dioxide, calcium carbonate and magnesium silicate will quite probably be different than that for a system composed of titanium dioxide, zinc oxide and lead carbonate.

The correction coefficients for overlapping, B_2, B_3, etc., are derived for specific materials contributing a specific amount of overlap interference. They are based on the assumption that this interference will be directly proportional to the amount of affecting component in the sample and that this proportionality will be a constant that can be determined indirectly by measuring the intensity from some diffracted line from the affecting component. It is therefore mandatory that the components used to determine the regression coefficients be identical to those anticipated to be in any subsequent samples. As illustrated in Figures 5 through 8, not only would the regression coefficients for determining these components be different, it is also apparent that their contributions to any overlapping of other components will also be different. Tables 35 and 36 tabulate the magnitude of error that might be expected from using coefficients that have been determined from 'same but different' materials.

The effect of changes in X-ray absorptions for the same component in different matrices can be overcome by the use of some added material as an internal standard and

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normalizing the intenities relative to this material. Such an internal standard does not, however, compensate for any overlapping effects from other components nor the requirement that these components be the same materials in the standards as in the samples.

Statistical Information

In addition to the regression coefficients the various tables also contain statistical information regarding the 'goodness of fit' and the validity of the coefficients.

The Coefficient of Determination is a measure of how well the 'calculated' values agree with the 'actual' values. It will approach 1.0 as the differences between these two values approach o.O. It is an indication of how well the regression model (equation) and the variables entered can account for the variations between 'actual' and 'calculated' values.

The Standard Error of Estimate is a measure of the precision of a determination and is commonly referred to as the standard deviation. Since it is a numerical expression of the error in a determination, the goal of any calibration is to reduce this value as much as possible.

The F-Test Ratio provides a measure of the validity of correctness of the determined regression coefficients. The number of variables and the number of observations (standards) containing these variables directly effect the magnitude of the F-Test Ratio. Where a limited number of standards is available the F-Test Ratio may actually decrease in value, that is the certainty that

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the coefficients are correct becomes less, with the introduction of further variables even though the coefficients may be valid. The best method of verifying the acceptability of the coefficients is by testing unknown samples (samples whose composition is known and different from that used to derive the initial coefficients).

As mentioned, the number of variables and number of standards have an effect on the resultant F-Test Ratio. This is also true of the Coefficient of Determination and the Standard Error of Estimate, both of which can be made to approach optimum values by the introduction of enough variables. The analyst must therefore use caution in adding variables simply because the regression analysis 'looks better'.

Test Method Precision and Detection Limits

In order to get an overall indication of the precision of the test method, it is frequently convenient to convert the Standard Error of Estimate, or standard deviation, to a relative value by dividing the outputted Standard Error by the average composition and expressing the results as a percentage. Table 37 lists the resultant values for three of the procedures used in this study. As indicated, The overall relative precision of the method is around 4%.

Compound	Average Composition Percent	Relative Standard Deviation, Percent Dried Film	Pigment	Internal Standard	Average RSD
Titanium Dioxide	13.25	3.5	3.4	1.8	2.9
Magnesium Silicate	39.4	5.1	6.4	5.8	5.8
Calcium Carbonate	40.1	6.0	4.4	4.4	4.9
Lead Chromate	11.2	4.3	3.0	1.9	3.1
Average RSD, Procedure		4.7	4.3	3.5	Average RSD, Method 4.2

TABLE 37

RELATIVE STANDARD DEVIATIONS FOR THREE PROCEDURES AND METHOD OVERALL

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The detection limits for the materials used in this study can be calculated according to the formula:

$$\frac{3}{M}\ \frac{R_b}{T_b}$$

Where: M = slope in counts per second per percent
R_b = Countrate of background
T_b = Counting time in seconds of background

As mentioned in the study, counting time on the background is a function of the peak-to-background ratio and varies inversely to this ratio. Unfortunately, it was not possible to measure this time during the analysis of the standard samples. However, by arbitrarily using 60 seconds as a nominal figure, and a background rate of 30 cps, tentative detection limits may be calculated. Table 38 lists the detection limits for the various pigments used in this study. It is worth noting that these are theoretical limits, a more realistic value will be about three times the listed limits. Note also the very large differences in detection limits for the magnesium silicates between the dried film method and the packed powder. This is further indication that the procedure used to prepare the powder specimens is contributing some effect on the silicates. These materials are relatively soft and plate-like in shape: there is the possibility that the method of grinding is disrupting the crystalline lattice or that the crystalline size is being reduced such that a more random orientation is achieved, or perhaps a combination of both.

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Compound	Detection Limits	
	Dried Film	Packed Powder
Titanium Dioxide	0.18%	0.34%
Magnesium Silicate(1)	0.12%	0.76%
Magnesium Silicate(2)	0.34%	1.54%
Calcium Carbonate	0.28%	0.45%
Lead Chromate	0.15%	0.26%

(1) Desertale D-54
(2) Beaverwhite 325

TABLE 38

MINIMUM DETECTION LIMITS
FOR PIGMENTS IN THIS STUDY

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