Quantitative Analysis of Anatase-Rutile Mixtures with an X-Ray Diffractometer

ROBERT A. SPURR and HOWARD MYERS

Hughes Research Laboratories, Culver City, Calif.

▶ An analytical procedure based on x-ray diffraction intensities is presented for the determination of the relative amounts of anatase and rutile in their mixtures.

Titanium dioxide may be incorporated into a plastics molding compound to adjust the dielectric constant to a desired value. Either anatase or rutile may be used; these allotropic forms differ in dielectric behavior. Neither is available commercially in a pure state; a preparation consisting largely of one form is apt to contain, in addition to other impurities, an admixture of the other. In order to permit proper formulation of filled resins, therefore, it is desirable to establish a method for determining the relative amounts of anatase and rutile in mixtures. The application of photometry to this problem has been discussed (*2,6*). This paper develops a method using the more precise technique of diffractometry.

APPARATUS AND MATERIALS

The instrument used was a Norelco Geiger-counter x-ray diffractometer equipped with voltage and current stabilizers, counters, and a strip-chart recorder; it was operated at a voltage of 35 kv. with a filament current of 25 ma. Scanning speed was 0.25° per minute; the width of the receiving slit was 0.003°. For rapidity and convenience, most of the intensity data were obtained from the strip chart and showed a satisfactory agreement with the results obtained by direct counting. The accuracy and reproducibility of this type of instrument have been discussed by Klug and coworkers (*3, 5*). The strongest reflections for anatase and rutile are conveniently located for Cu$K\alpha$ radiation at the Bragg angles 12.68° and 13.73°, respectively.

The materials studied are two commercial products, one of which is largely anatase (A) and the other largely rutile (R). When total titanium dioxide was determined by the method of Rahm (*7*), the percentages found in three determinations were A. 98.00, 97.68, 98.08; average: 97.92. R. 98.70, 98.73, 98.62;

average: 98.68. The values for the weight fractions of anatase in anatase-rutile mixtures determined by the method described are insensitive to several per cent variations in the total titanium dioxide content.

Particle diameters smaller than 5 microns are desirable to ensure adequate reproducibility of diffraction intensity measurements (*4*). Electron micrographs taken at a magnification of 36,000 diameters indicate that particle diameters are 0.04 to 0.6 micron for anatase and 0.08 to 0.5 micron for rutile. The particle sizes are, therefore, sufficiently small for reproducibility of intensity measurements.

RESULTS AND METHOD OF CALCULATION

For a given sample, the ratio (I_A/I_R) of the intensity of the strongest anatase reflection to the intensity of the strongest rutile reflection is independent of fluctuations in diffractometer characteristics. This ratio therefore provides a useful index of sample composition. The first three columns of Table I show the weights of A and R in the samples; the average values of I_A/I_R were found from a total of 53 determinations.

The intensity data show that the A material contains a small amount of rutile and the R material a small amount of anatase. If A were pure anatase,

the value of I_A/I_R for sample 11 would be infinite; and if R were pure rutile, the value of this ratio for sample 1 would be zero. It is not difficult, however, to estimate the impurities in A and R to a sufficient degree of accuracy to establish an analytical method for anatase and rutile.
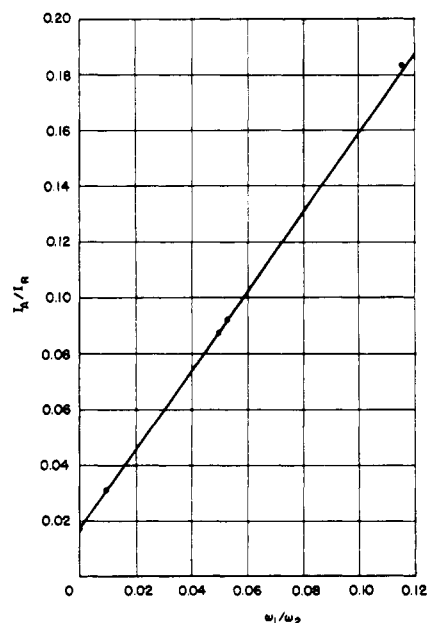

Figure 1. Intensity ratio as a function of weight ratio for small w_1

Table I. Compositions and X-Ray Intensity Data for Anatase-Rutile Mixtures

Sample No.	w_1, Weight of A, G.	w_2, Weight of R, G.	I_A/I_R Intensity Ratio	x_A, Weight Fraction of Anatase	$f = \dfrac{1}{1 + 1.265\frac{I_R}{I_A}}$ Intensity Function
1	0	1.997	0.0165	0.0112	0.0115
13	0.0099	0.9898	0.0312	0.0205	0.0240
16	0.0399	0.8002	0.0869	0.0564	0.0573
14	0.0501	0.9500	0.0920	0.0588	0.0677
2	0.202	1.749	0.183	0.110	0.126
3	0.451	1.335	0.431	0.252	0.253
4	0.626	1.121	0.680	0.350	0.349
5	0.822	1.022	0.941	0.438	0.426
6	0.996	0.918	1.21	0.510	0.489
7	1.290	0.622	2.31	0.658	0.645
8	1.502	0.518	3.28	0.724	0.722
9	1.726	0.355	5.31	0.807	0.809
10	2.856	0.268	9.54	0.889	0.883
15	0.9501	0.0496	13.51	0.919	0.915
11	2.050	0	55.9	0.972	0.978

The first three columns of Table I give the weight of A (97.9% TiO₂, largely anatase), the weight of R (98.7% TiO₂, largely rutile), and the ratio of the intensity of the strongest anatase reflection to that of the strongest rutile reflection for the various sample mixtures. The last two columns give the weight fraction of anatase and a function of the intensity ratio that approximates the weight fraction of anatase.

For a given sample, the relation between the weight ratio and the intensity ratio for anatase and rutile is given by the expression

$$\frac{w_A}{w_R} = K \frac{I_A}{I_R} \qquad (1)$$

where w_A and w_R are the weights of anatase and rutile, respectively, in the sample. It is known that, for mixtures of allotropes, intensity of scattering for each component is substantially proportional to its weight fraction (1). It may be expected, therefore, that K will be approximately constant over narrow ranges of concentration.

The weight of pure anatase in the sample is given by the equation

$$w_A = a_1 w_1 + a_2 w_2 \qquad (2)$$

where w_1 is the weight of A, w_2 is the weight of R, a_1 is the weight fraction of anatase in A, and a_2 is the weight fraction of anatase in R. A similar expression gives the weight of pure rutile in the sample:

$$w_R = r_1 w_1 + r_2 w_1 \qquad (3)$$

where r_1 and r_2 are the weight fractions of rutile in A and R, respectively. Substitution of Equations 2 and 3 in 1 gives

$$\frac{a_1 w_1 + a_2 w_2}{r_1 w_1 + r_2 w_2} = K \frac{I_A}{I_R} \qquad (4)$$

r_1 is small compared with unity; therefore, for small w_1, $r_1 w_1$ may be neglected in comparison with $r_2 w_2$. The following approximate equation can thus be derived:

$$\frac{I_A}{I_R} = \frac{1}{K_1} \frac{a_2}{r_2} + \frac{1}{K_1} \frac{a_1}{r_2} \frac{w_1}{w_2} \text{ (for small } w_1)$$
$$\qquad (5)$$

Here K_1 denotes the value of K in the region where w_1 is small compared with w_2. Figure 1 is a graph of I_A/I_R vs. w_1/w_2. The fact that the points lie near a straight line is an indication that K_1 is approximately constant in this concentration range. The equation for the line is

$$\frac{I_A}{I_R} = 0.0165 + 1.425 \frac{w_1}{w_2} \qquad (6)$$

Similarly a_2 is small compared with unity and, for small w_2, the term $a_2 w_2$ may be neglected in comparison with $a_1 w_1$; the equation obtained is

$$\frac{I_R}{I_A} = K_2 \frac{r_1}{a_1} + K_2 \frac{r_2}{a_1} \frac{w_2}{w_1} \text{ (for small } w_2)$$
$$\qquad (7)$$

where K_2 is the value of K in the region where w_2 is small compared with w_1. Figure 2 is a graph of I_R/I_A vs. w_2/w_1 in this region. The straight line drawn may be represented by the equation

$$\frac{I_R}{I_A} = 0.0230 + 0.820 \frac{w_2}{w_1} \qquad (8)$$

There are now six unknown quantities—a_1, r_1, a_2, r_2, K_1, and K_2—which may be related by the following six equations. The first four are obtained by comparing coefficients in Equations 5 through 8; the last two give the total amounts of

Figure 2. Intensity ratio as a function of weight ratio for small w₂
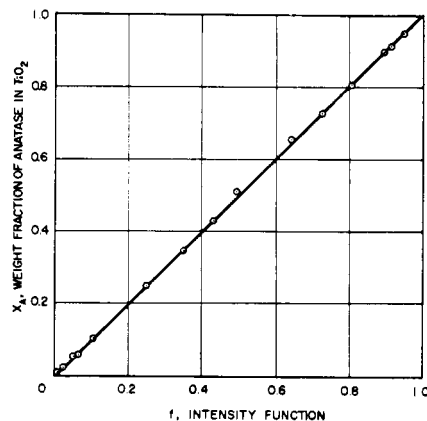
Figure 3. Weight fraction x_A as function of

$$f = \frac{1}{1 + 1.26 \frac{I_R}{I_A}}$$

titanium dioxide in A and R as determined by chemical analysis.

$$\frac{1}{K_1} \frac{a_2}{r_2} = 0.0165$$

$$\frac{1}{K_1} \frac{a_1}{r_2} = 1.425$$

$$K_2 \frac{r_1}{a_1} = 0.0230 \qquad (9)$$

$$K_2 \frac{r_2}{a_1} = 0.820$$

$$a_1 + r_1 = 0.979$$

$$a_2 + r_2 = 0.987$$

Solution of these simultaneous equations yields

$$
\begin{aligned}
a_1 &= 0.952 \\
r_1 &= 0.027 \\
a_2 &= 0.011 \\
r_2 &= 0.976 \\
K_1 &= 0.68 \\
K_2 &= 0.80
\end{aligned}
\qquad (10)
$$

It is seen that the A material contains 95.2% anatase and 2.7% rutile and that the R material contains 97.6% rutile and 1.1% anatase. It is now possible to calculate the weight fraction of anatase in the titanium dioxide for each sample; these values, given in the fourth column of Table I, may be considered reliable to within about 0.01 unit.

For the analysis of anatase-rutile mixtures, it is convenient to devise a function of the intensities that is approximately equal to the weight fraction x_A of anatase present. This weight fraction is given by

$$x_A = \frac{w_A}{w_A + w_R} \qquad (11)$$

The combining of Equations 11 and 1 yields

$$x_A = \frac{1}{1 + \frac{1}{K} \frac{I_R}{I_A}} \qquad (12)$$

If the variation of K with concentration is now neglected and if K is taken as 0.79, or $1/K$ as 1.26, an approximation to x_A is obtained that may be designated as f:

$$f = \frac{1}{1 + 1.26 \frac{I_R}{I_A}} \qquad (13)$$

This quantity f is tabulated in the last column of Table I and a graph of x_A vs. f is shown in Figure 3. It can be seen that f is, in fact, approximately equal to x_A. A better fit for $x_A \leq 0.2$ could be obtained by taking $K = 0.68$ in this region of concentration.

The weight fraction of anatase in an anatase-rutile mixture may be deter-
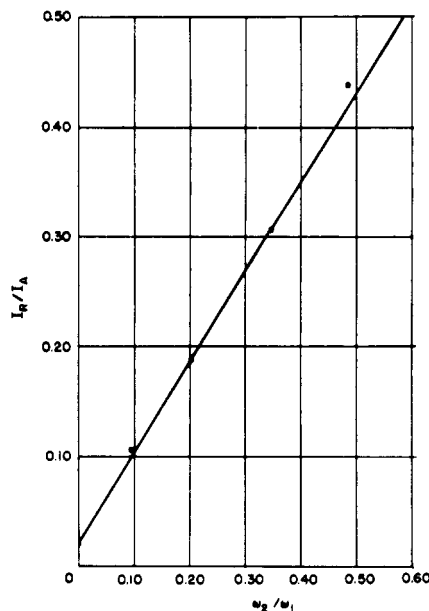
mined by calculating f from the observed x-ray intensities and by referring to Figure 3.

The most important contribution to the experimental error in f arises from the lack of reproducibility of scattering intensities recorded by the diffractometer. Optimum precision can be obtained by the use of slow scanning speed, and by averaging several values of I_A/I_R, where the ratio contains two intensity values from the same run. It was found from 18 determinations that the standard error in f due to lack of instrument reproducibility is about 2%; the inclusion of other experimental errors suggests a standard error for f

of 3 to 4%. Two experimental determinations of known mixtures led, however, to errors of only 0.9 and 0.2%.

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Steroid X-Ray Diffraction Powder Data

JONATHAN PARSONS, WILLIAM T. BEHER, and GIZELLA D. BAKER

The Edsel B. Ford Institute for Medical Research, Henry Ford Hospital, Detroit 2, Mich.

▶ X-ray diffraction powder data and powder pattern photographs are presented for 32 steroids.

To CONTINUE the studies on the identification of steroids by x-ray powder diffraction, 32 additional compounds were investigated. Their interspacing data and powder pattern photographs are here reported. The earlier papers (1–3) in this series gave powder data for 106 steroids.

The x-ray patterns were obtained in 5 hours, using nickel-filtered copper x-radiation produced at a potential of 35 kv. and a current of 20 ma. (1,2). The methods of recrystallization used were the same as those discussed and used in the last paper of this series (3). The majority of the steroids were recrystallized from ethyl alcohol, the exceptions being noted in Table I.
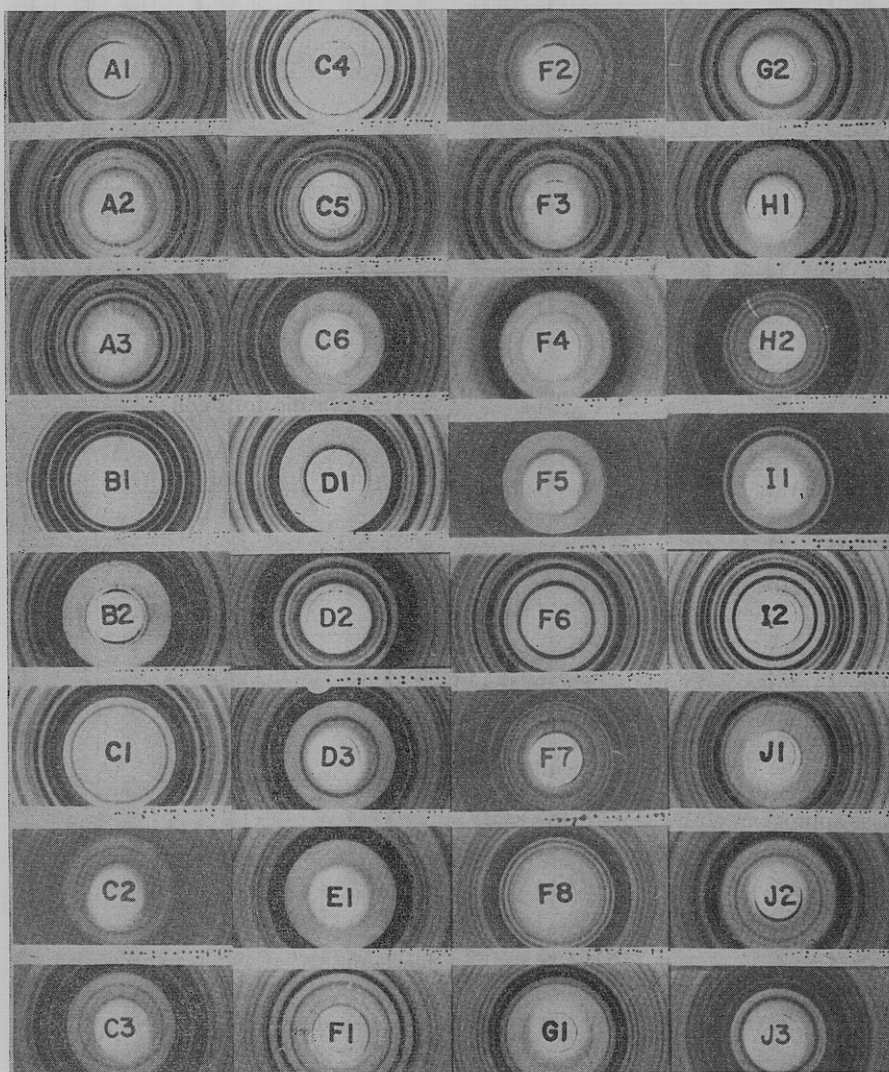

Figure 1. X-ray diffraction powder patterns of steroids

Key found in Table I