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

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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 0.0003°. 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 King and co-workers (2, 6). The strongest reflections for anatase and rutile are conveniently located for CuKα 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: 98.02. 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 achieve adequate reproducibility of diffraction intensity measurements (4). Electron micrographs taken at a magnification of 30,000 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 \( w_A \).](image)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>( w_A ), Weight of A, G.</th>
<th>( w_R ), Weight of R, G.</th>
<th>( I_A/I_R ), Intensity Ratio</th>
<th>( f ) = ( \frac{1}{1 + 1.265 \frac{I_A}{I_R}} )</th>
<th>( x_A ), Weight Fraction of Anatase</th>
<th>Intensity Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>9.07</td>
<td>0.0168</td>
<td>0.112</td>
<td>0.0115</td>
<td>0.0240</td>
</tr>
<tr>
<td>2</td>
<td>0.0009</td>
<td>0.0009</td>
<td>0.0162</td>
<td>0.0205</td>
<td>0.0240</td>
<td>0.0240</td>
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<tr>
<td>3</td>
<td>0.451</td>
<td>1.335</td>
<td>0.431</td>
<td>0.252</td>
<td>0.255</td>
<td>0.255</td>
</tr>
<tr>
<td>4</td>
<td>0.626</td>
<td>1.212</td>
<td>0.680</td>
<td>0.350</td>
<td>0.349</td>
<td>0.349</td>
</tr>
<tr>
<td>5</td>
<td>0.822</td>
<td>1.022</td>
<td>0.941</td>
<td>0.438</td>
<td>0.428</td>
<td>0.428</td>
</tr>
<tr>
<td>6</td>
<td>0.996</td>
<td>0.918</td>
<td>1.21</td>
<td>0.510</td>
<td>0.489</td>
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</tr>
<tr>
<td>7</td>
<td>1.290</td>
<td>0.622</td>
<td>2.31</td>
<td>0.658</td>
<td>0.645</td>
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<tr>
<td>8</td>
<td>1.502</td>
<td>0.515</td>
<td>3.28</td>
<td>0.724</td>
<td>0.722</td>
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</tr>
<tr>
<td>9</td>
<td>1.720</td>
<td>0.355</td>
<td>5.31</td>
<td>0.807</td>
<td>0.800</td>
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<tr>
<td>10</td>
<td>2.586</td>
<td>0.268</td>
<td>9.54</td>
<td>0.889</td>
<td>0.883</td>
<td>0.883</td>
</tr>
<tr>
<td>11</td>
<td>2.991</td>
<td>0.0496</td>
<td>13.51</td>
<td>0.919</td>
<td>0.915</td>
<td>0.915</td>
</tr>
</tbody>
</table>

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

\[ w_A = K \frac{I_A}{I_R} \]  

(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 (2).

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

\[ w_A = a_1 w_1 + a_2 w_2 \]  

(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:

\[ w_R = r_1 w_1 + r_2 w_2 \]  

(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

\[ a_1 w_1 + a_2 w_2 = K \frac{I_A}{I_R} \]  

(4)

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

\[ \frac{I_A}{I_R} = 1 + \frac{a_1}{K_1 r_1} w_2/ w_1 \]  

(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. \( w_2/w_1 \). 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

\[ \frac{I_A}{I_R} = 0.0165 + 1.425 \frac{w_2}{w_1} \]  

(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

\[ I_A = K_2 \frac{r_2}{a_1} + K_3 \frac{r_2}{a_1} \frac{w_2}{w_1} \]  

(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 \( I_A/I_R \) vs. \( w_2/w_1 \) in this region. The straight line drawn may be represented by the equation

\[ \frac{I_A}{I_R} = 0.0230 + 0.820 \frac{w_2}{w_1} \]  

(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 anatase and rutile in A and R respectively, as determined by chemical analysis.

\[ 1 = a_1/ K_1 r_1 \]  

(9)

\[ 1 = a_2/ K_2 r_2 \]  

(10)

\[ a_1 + r_1 = 0.979 \]  

(11)

\[ a_2 + r_2 = 0.987 \]  

(12)

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

\[ x_A = \frac{w_A}{w_A + w_R} \]  

(13)

The combining of Equations 11 and 1 yields

\[ x_A = \frac{1}{1 + \frac{I_A}{I_R} K_1} \]  

(14)

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 \( f \):

\[ f = \frac{1}{1 + 1.26} \frac{I_R}{I_A} \]  

(15)

This quantity \( f \) is tabulated in the last column of Table I and a graph of \( f \) 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-
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 \( I_2/I_1 \), 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%.

**ACKNOWLEDGMENT**

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**LITERATURE CITED**


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**Steroid X-Ray Diffraction Powder Data**

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> 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 inter-spacing 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