ASTM

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Standard Test Method for
Determination of Relative X-ray Diffraction Intensities of Faujasite-Type Zeolite-Containing Materials[1]

1. Scope

1.1 This test method covers the determination of relative *X*-ray diffraction intensities of zeolites having the faujasite crystal structure, including synthetic *Y* and *X* zeolites, their modifications such as the various cation exchange forms, and the dealuminized, decationed, and ultrastable forms of *Y*. These zeolites have cubic symmetry with a unit cell parameter usually within the limits of 24.2 and 25.0Å (2.42 and 2.50 nm).

1.2 The samples include zeolite preparations in the various forms, and catalysts and adsorbents containing these zeolites.

1.3 The term "intensity of an *X*-ray powder diffraction (XRD) peak" is the "integral intensity," either the area of counts under the peak or the product of the peak height and the peak width.

1.4 The method provides a number that is the ratio of intensity of portions of the XRD pattern of the sample to intensity of the corresponding portion of the pattern of a reference zeolite, NaY. (Laboratories may use a modified *Y* or *X*, for example, REY as a secondary standard.) The intensity ratio, expressed as a percentage, is then labeled "% XRD intensity/NaY."

1.5 Under certain conditions such a ratio is the percent zeolite in the sample. These conditions include:

1.5.1 The zeolite in the sample is the same as the reference zeolite.

1.5.2 The absorption for the X-rays used is the same for the zeolite and the nonzeolite portions of the sample.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*
E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[2]
E 456 Terminology Relating to Quality and Statistics[2]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[2]

3. Summary of Test Method

3.1 The XRD patterns of the zeolite containing sample and the reference sample (NaY), are obtained under the same conditions. Intensities of the (533) peak (23.5° with Cu Kα radiation) are compared to provide "% XRD intensity/NaY (533)." If the XRD pattern of the zeolite is sufficiently strong, a comparison of the sums of intensities of eight peaks is used to give "% crystallinity."

4. Significance and Use

4.1 Zeolites *Y* and *X*, particularly for catalyst and adsorbent applications, are a major article of manufacture and commerce, use of which has developed since the 1960s. Catalysts and adsorbents comprising these zeolites in various forms plus binder and other components have likewise become important in this area. *Y*-based catalysts are used for fluid catalytic cracking (FCC) and hydrocracking of petroleum, while *X*-based adsorbents are used for desiccation, sulfur compound removal, and air separation.

4.2 This X-ray procedure is designed to monitor these *Y* and *X* zeolites and catalysts and adsorbents, providing a number more or less closely related to percent zeolite in the sample. This number has proven useful in technology, research, and specifications.

4.3 Drastic changes in intensity of individual peaks in the XRD patterns of *Y* and *X* can result from changes of distribution of electron density within the unit cell of the zeolite. The electron density distribution is dependent upon the extent of filling of pores in the zeolite with guest molecules, and on the nature of the guest molecules. In this XRD method, the guest molecule H_2O completely fills the pores. Intensity changes may also result if some or all of the cations in *Y* and *X* are exchanged by other cations.

4.3.1 Because of the factors mentioned in 4.3 that could vary the intensities of the XRD peaks, this XRD method will provide the best determination of relative crystallinity when the reference and sample have a similar history of preparation and composition.

4.4 Corrections are possible that can make this XRD method accurate for measuring percent zeolite in many specific situations. These corrections are well known to those skilled in

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X-ray diffraction. It is not practical to specify those corrections here.

5. Apparatus

5.1 *X-ray Diffractometer*, equipped with a strip chart recorder or with computerized data acquisition and reduction capability, using copper K-alpha radiation.

5.2 *Drying Oven*, set at 110°C.

5.3 *Hydrator (Glass Laboratory Desiccator)*, maintained at 35 % relative humidity by a saturated solution of salt, such as $CaCl_2 \cdot 6H_2O$.

5.4 *Planimeter*.

Note 1—This planimeter may not be needed if the XRD instrument is equipped with a digital integrating circuit.

6. Reagents and Materials

6.1 *NaY Powder and RE Exchanged Y Powder*, as reference standards.[3]

7. Sampling

7.1 Conduct sampling by splitting a large portion of the sample and reference material homogeneously.

7.2 Divide the sample and reference finely to permit packing of the materials into XRD sample holders.

Note 2—The best test to determine if grinding is required is to try to pack the sample in the holder. Overgrinding can lead to breaking up of fine crystals and even destruction of zeolite.

8. Procedure

8.1 Carry out the following steps, 8.2 through 8.5, in an identical manner for both the sample and the reference material, NaY.

8.2 Place about 3 to 5 g of the sample in the drying oven at 110°C for 1 h. Cool the sample in the hydrator and hold at room temperature and 35 % relative humidity for at least 16 h.

Note 3—Drying, followed by rehydration, results in filling the zeolite pores with water of hydration but without an excess of moisture residing on the surface of the zeolite particles.

8.3 Pack the humidity-conditioned sample into an XRD sample holder.

8.4 Obtain a first XRD pattern by scanning over the angle range from 14 to 35° 2θ at 1°/min and using other instrument parameters best suited to the diffractometer.

8.4.1 If a strip chart recorder is used, set the chart drive at 10 mm/min. Select the scale factor (amplification) for the NaY reference pattern so that the strong (533) peak at 23.6° is between 50 and 100 % of full scale. For the sample the scale factor may be reduced (amplification increased) to provide reasonable peak heights. If possible the height of the (533) peak for the sample should be at least 10 % of full scale. Fig. 1 shows such patterns for the reference NaY and for a zeolite-containing catalyst.

8.5 If this first pattern of the sample contains XRD peaks of some nonfaujasite components, it must be established whether this may cause interference in the following steps. (Fig. 2 is a complete diffractometer scan for NaY.)

[3] Available from ASTM Committee D-32.

8.6 Obtain a second XRD pattern by scanning over a small angle range at ¼ °/min.

8.6.1 If a strip chart recorder is used, set the drive at 20 mm/min. The same scale factors used in Step 8.4 are suitable. The preferred angle range is from 22.5 to 25° 2θ, the (533) peak. Fig. 3 shows such a pattern for NaY. If interference rules out this range, choose for this step (for both the sample and the reference patterns) one of the following angle ranges:

14.0 to 17.0°, (331) peak
19.0 to 22.0°, (440) peak
25.5 to 28.0°, (642) peak

Note 4—These ranges in Step 8.6 each are of such width that two or more zeolite peaks are included. Such wide ranges are specified to allow for the variation in peak position over the range of unit cell dimensions 24.2 to 25.0 Å (2.42 to 2.50 mm) and to provide a background reading on each side of the main peak. Within each range the major zeolite peak will be the desired one. See Appendix X1 of peak positions.

9. Calculation

9.1 Obtain an integral peak intensity for each of the eight peaks (measured above background) chosen from the patterns from 8.4, for both the sample and reference, in one of three ways:

9.1.1 By approximating the area under the peak as the product of peak height and peak width at half height, or

9.1.2 By measuring the area under the peak with a planimeter, or

9.1.3 From the counts recorded by a digital integrating system.

9.2 *Approximate Area Calculation*:

9.2.1 A scale factor correction, SFC, is the ratio of the scale factor used for the sample pattern, SF_X, to that used for the reference pattern, SF_R. Thus, $SFC = SF_X/SF_R$. Scale factors are usually expressed in terms of counts per second corresponding to full scale on the recorder. They are related inversely to amplification.

9.2.2 Measure the width of the (533) or alternative peaks obtained in Step 8.6. The width is measured at half the peak height, that is, half way between the background and the peak maximum. Obtain the width factor, WF, which is the ratio of the peak width of the sample, W_X, to that of the NaY reference material, W_R. Thus, $WF = W_X/W_R$.

Note 5—Peak broadening occurs for a variety of reasons. Pertinent for zeolite are the following: crystals may be of limited size, below 0.2 μm; crystals may contain disorder; crystals may exist with a range of unit cell dimensions; and diffraction may originate from varying depths below the sample surface, limited by absorption, and related to density of packing of the sample.

9.2.3 The objective of the method, a value for "% XRD intensity/NaY," is obtained in this step. This involves a comparison of the sums of peak heights (measured above background) from the patterns obtained in Step 8.4. The ratio of these sums must be corrected for difference in scale factor, by use of SFC as determined in Step 9.2.1, and for difference in peak widths, by use of WF as determined in Step 9.2.2. Eight peaks are included in the summation in Table 1:

Note 6—The 2θ value ranges tabulated in Table 1 are appropriate for zeolites with unit cell dimensions 24.2 to 25.0 Å. (2.42 to 2.50 nm).

Note 7—If nonzeolite components give XRD peaks interfering with

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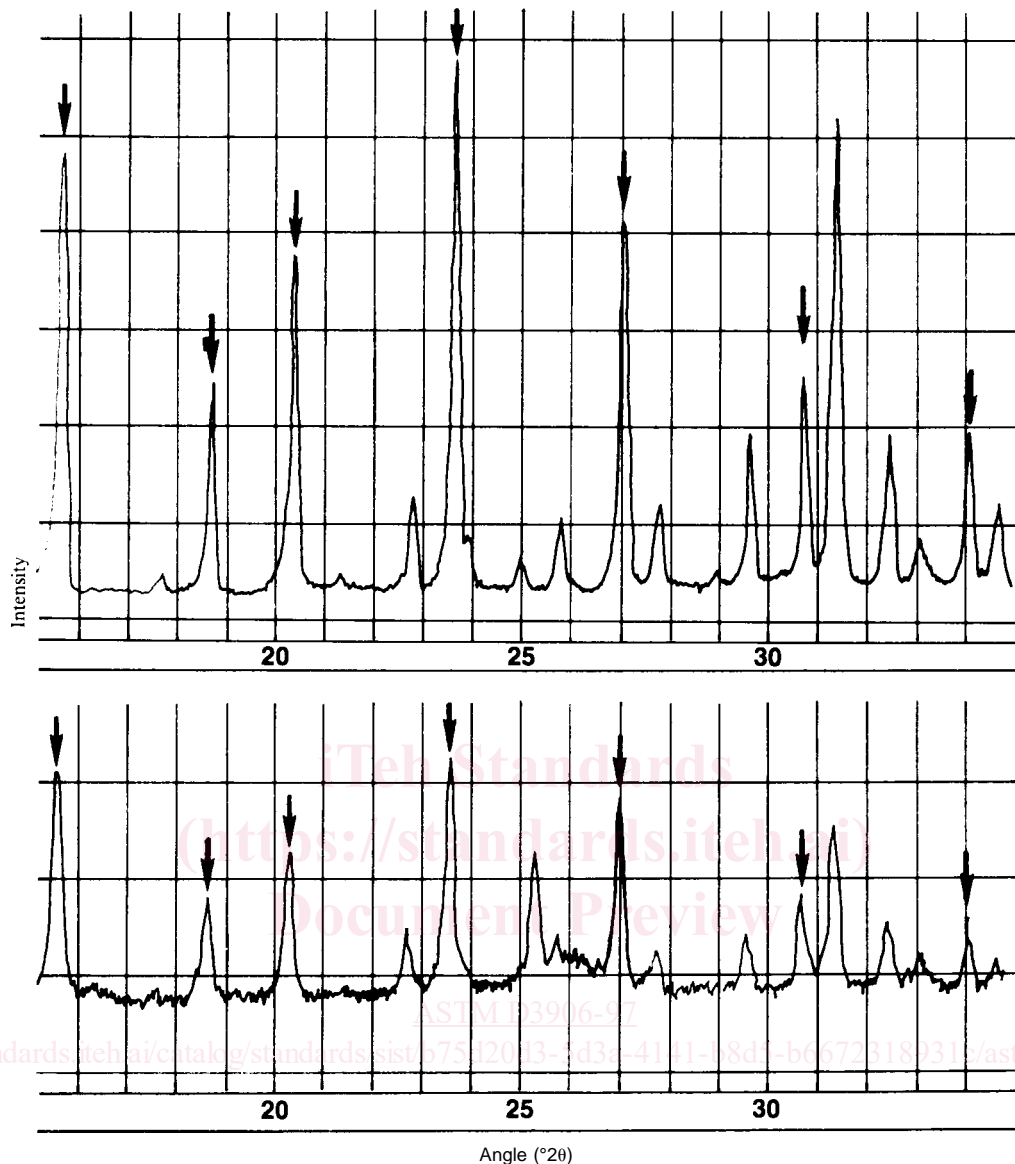
FIG. 1 X-Ray Diffraction Patterns of ASTM Zeolite Samples Upper—NaY; Lower—Cracking Catalyst Intensity

certain of the tabulated peaks, these latter peaks should be omitted from the sums, both for the sample and for the reference NaY.

9.2.4 The equation used is the following:

$$\% \text{ XRD intensity/NaY} = \text{SFX} \times \text{WF} \times (S_X/S_R) \times 100 \qquad (1)$$

where:
S_X = sum of peak heights for the sample and
S_R = sum for the reference NaY.

This test method relies on two assumptions, that the peak intensities are properly expressed as the product of peak height and peak half width, and that the ratio of half widths obtained from one peak, the (533) peak, is applicable to the other seven peaks used in the summation. The first of these two assumptions is invalid in the rare case when the peaks are doublets resulting from presence of two zeolites of distinctly different unit cell parameters. This preferred method is based on eight of the most intense diffraction peaks, not because any single peak

is more sensitive to details of crystal structure than is the sum of these eight peaks.

9.3 *Area By Planimeter*:

9.3.1 Obtain a value for "% XRD intensity/Na*Y*" by comparing the sums of integrated peak intensities (measured above background) by planimeter from the patterns obtained in 8.4 (see Note 7). Use the following equation:

$$\% \text{ XRD intensity/Na}Y = \frac{S_X}{S_R} \times 100 \qquad (2)$$

where:
S_x = sum of integral peak intensities for the sample, and
S_r = sum of the integral peak intensities for the reference NaY.

9.4 *Integrator Counts Calculation*:

9.4.1 Obtain a value for "% XRD intensity/Na*Y*" by comparing the sums of integrated peak intensities (measured above background) by counts from the patterns obtained in 8.4 (see

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