Designation: D 5357 – 03

Standard Test Method for Determination of Relative Crystallinity of Zeolite Sodium A by X-ray Diffraction[1]

This standard is issued under the fixed designation D 5357; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers a procedure for determining the relative crystallinity of zeolite sodium A (zeolite NaA) using selected peaks from the X-ray diffraction pattern of the zeolite.

1.2 The term "intensity of an X-ray powder diffraction (XRD) peak" refers to the "integral intensity," either the area or counts under the peak or the product of the peak height and the peak width at half height.

1.3 This test 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 NaA. The intensity ratio, expressed as a percentage, is then labeled relative crystallinity of NaA.

1.4 *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:*

D 3906 Test Method for Determination of Relative X-ray Diffraction Intensities of Faujasite-Type Zeolite-Containing Materials[2]

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[3]

E 456 Terminology Relating to Quality and Statistics[3]

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[3]

3. Summary of Test Method

3.1 The XRD patterns of the zeolite NaA or zeolite NaA-containing sample and the reference sample (NaA) are obtained under the same conditions. A comparison of the sums of intensities of six strong peaks in the 11–32° 2θ range is made, giving relative crystallinity of NaA. This type of comparison is commonly used in zeolite technology and is often referred to as "% crystallinity."

4. Significance and Use

4.1 Zeolite NaA has been used as an active component in molecular sieves employed as desiccants for natural gas, process gas streams, sealed insulated windows, and as a builder (water softener) in household laundry detergents.

4.2 This X-ray procedure is designed to allow a reporting of the relative degree of crystallization of NaA in the manufacture of NaA. The relative crystallinity number has proven useful in technology, research, and specifications.

4.3 Drastic changes in intensity of individual peaks in the XRD pattern of NaA can result from changes in distribution of electron density within the unit cell of the NaA 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 sodium cations in NaA are exchanged by other cations.

4.4 Drastic changes in overall intensity can result from changes in X-ray absorption attributed to non-crystalline phases, if present, in a NaA sample. If non-zeolite crystalline phases are present, their diffraction peaks may overlap with some of the NaA diffraction peaks selected for this test method. If there is reason to suspect the presence of such components, then NaA peaks free of interference should be chosen for analysis.

5. Apparatus

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

5.2 *Drying Oven*, set at 100°C.

5.3 *Hydrator (Laboratory Desiccator)*, maintained at about 58 % relative humidity by a saturated solution of sodium bromide, NaBr.

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[1] This test method is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.05 on Zeolites.

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[2] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

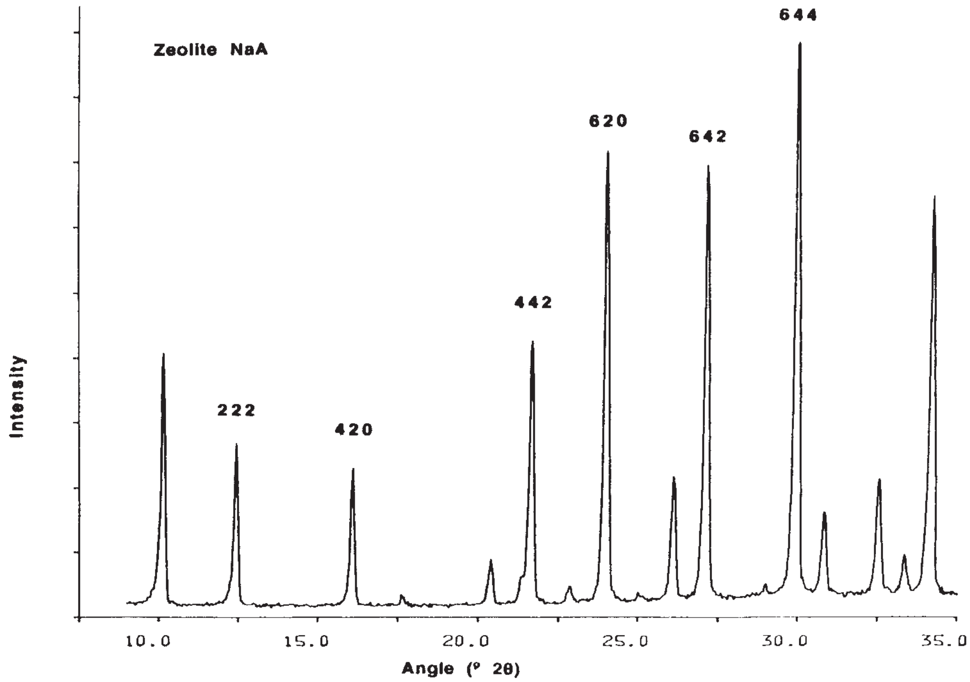

FIG. 1 X-Ray Diffraction Pattern of Zeolite NaA—ASTM Sample Z-02

5.4 *Planimeter or Appropriate Peak Profile Analysis or Digital Integration Software*, if diffractometer is not equipped with appropriate software data analysis capability.

6. Reagents and Materials

6.1 *NaA Powder* [4], as reference standard, preferably with a mean particle diameter of 3 to 5 microns (mean crystal size 1 to 2 microns).

7. Procedure

7.1 Carry out the steps (described in 7.1.1-7.1.3) in an identical manner for both the sample and the NaA reference.

7.1.1 Place about 1.5 g of finely divided sample in the drying oven at 100°C for 2 h. Cool the sample in the hydrator and hold there at room temperature and about 58 % relative humidity for at least 16 h.

NOTE 1—Grinding of course-textured samples should be done gently. Over-grinding can lead to breaking up of fine crystals and destruction of the zeolite.

NOTE 2—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.

7.1.2 Pack the sample into an XRD sample holder.

7.1.3 Obtain an XRD pattern of the NaA reference by scanning over the angle range from 11 to 32° 2θ at 0.25°/min. In the step mode, a 0.02° 2θ step for 2 s may be acceptable for pure NaA, while 10 to 20 s may be necessary for lower NaA content samples. This scan range includes the six strong diffraction peaks that are to be used in the calculation for "% crystallinity":

hkl index	d (Angstrom)	°2θ (Cu K-α radiation)
222	7.104	12.46
420	5.503	16.11
442	4.102	21.67
620	3.710	23.99
642	3.289	27.12
644	2.984	29.94

Fig. 1 shows a pattern for the reference zeolite NaA used in testing of this method.

NOTE 3—1 nanometer (nm) = 10 Angstroms.

7.1.3.1 If a strip chart recorder is used, set the chart drive at 20 mm/min. Select the scale factor (amplification) for the NaA reference pattern so that the strong (644) peak at 29.94° is between 50 and 100 % of full scale. The same scale factor should be used for the sample pattern. However, if the sample gives considerable lower peak intensity, the scale factor may be reduced (amplification increased) to provide reasonable peak heights.

NOTE 4—If a shortened scan program covering just the six NaA peaks is used, a range for each peak should be chosen so that a suitable background reading can be determined. This range, covering each peak, is typically about 1°2θ.

8. Calculation

8.1 Determine the integral peak intensity for each of the six peaks of 7.1.3 for both the sample and the reference NaA in one of three ways:

8.1.1 From the counts recorded by a digital integrating system used while obtaining the pattern of 7.1.3,

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

8.1.3 By approximating the area under the peak as the product of peak height and peak width at half height.

[4] Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 3460, Gaithersburg, MD 20899-3460.

8.2 In all cases the integral peak intensity values are measured above background.

NOTE 5—Peak areas determined by the techniques described in 8.1.2 or 8.1.3 must have a correction factor applied if the scale factors used for the NaA reference and sample patterns are different; see Test Method D 3906.

8.3 Obtain a value for NaA by comparing the sums of integrated peak intensities (measured above background) from the patterns obtained in 7.1.3. Use the following equation:

$$\text{relative crystallinity of NaA} = \frac{S_x}{S_r} \times 100\ \% \qquad (1)$$

where:

S_x = sum of integral peak intensities for the sample, and
S_r = sum of the integral peak intensities for the reference NaA.

NOTE 6—This test method is based on six of the most intense diffraction peaks, not because a single peak cannot be measured accurately, but because any single peak is more sensitive to details of crystal structure than is the sum of these peaks.

NOTE 7—Peak broadening can occur 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; and diffraction may originate from varying depths below the sample surface, limited by absorption, and related to density of packing of the sample.

NOTE 8—If non-zeolite components give XRD peaks that interfere with certain of the tabulated peaks, these latter peaks should be omitted from the sums, both for the sample and for the reference NaA.

NOTE 9—Some samples of zeolite may be slightly more crystalline than a chosen reference material; see, for example, 10.2.

9. Report

9.1 Report the following information:

9.1.1 Relative crystallinity of NaA, and

9.1.2 Non-NaA impurity peaks, if present (impurity identification, if possible) and any interferences with NaA peaks.

10. Precision and Bias

10.1 *Test Program*—An inter-laboratory study was conducted in which the named property was measured in one separate test material in eight separate laboratories. Practice E 691, modified for non-uniform data sets, was followed for the data reduction. Analysis details are in the research report.[5]

10.2 *Precision*—Pairs of test results obtained by a procedure similar to that described in the study are expected to differ in absolute value by less than 2.772*S, where 2.772*S is the 95 % probability interval limit on the difference between two test results, and S is the appropriate estimate of standard deviation. Definitions and usage are given in Practices E 456 and E 177, respectively.

Test Result (consensus mean)	95 % Repeatability Interval (within laboratory)	95 % Reproducibility Interval (between laboratories)
1.0448 S(sample)/S(ref)	0.0223 (2.14 percent of mean)	0.0276 (2.64 percent of mean)

10.3 *Bias*—The test method is without known bias.

11. Keywords

11.1 crystallinity; X-ray diffraction; zeolite sodium A

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D32-1036.