



# Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis<sup>1</sup>

This standard is issued under the fixed designation C 1365; 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 direct determination of the proportion by mass of individual phases in portland cement or portland-cement clinker using quantitative X-ray (QXRD) analysis. The following phases are covered by this standard: aluminate (tricalcium aluminate,<sup>2</sup> C<sub>3</sub>A), ferrite (tetracalcium aluminoferrite, C<sub>4</sub>AF), and periclase (magnesium oxide, M) (see Note 1).

NOTE 1—In the future, Subcommittee C1.23 plans to add additional phases: alite (tricalcium silicate, C<sub>3</sub>S), belite (dicalcium silicate, C<sub>2</sub>S), gypsum (C $\bar{S}$ H<sub>2</sub>), hemihydrate (C $\bar{S}$ H $\frac{1}{2}$ ), and anhydrite (C $\bar{S}$ ).

1.2 This test method specifies certain general aspects of the analytical procedure, but does not specify detailed aspects. A recommended procedure is described, but not specified. Regardless of the procedure selected, the user must demonstrate by analysis of reference materials (RM's) that the particular analytical procedure selected for this purpose qualifies (that is, provides acceptable precision and bias) (see Note 2). The recommended procedure is the one used in the round-robin analysis to determine the precision and bias levels of this test method.

NOTE 2—A similar approach was used in the performance requirements for alternative methods for chemical analysis in Test Methods C 114.

1.3 The values stated in SI units shall be regarded as the standard.

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.* For specific hazards, see Section 9.

## 2. Referenced Documents

### 2.1 ASTM Standards:

- C 114 Test Methods for Chemical Analysis of Hydraulic Cement<sup>3</sup>
- C 150 Specification for Portland Cement<sup>3</sup>
- C 183 Practice for Sampling and the Amount of Testing of Hydraulic Cement<sup>3</sup>

### C 219 Terminology Relating to Hydraulic Cement<sup>3</sup>

C 670 Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials<sup>4</sup>

E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications<sup>5</sup>

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method<sup>5</sup>

## 3. Terminology

3.1 *Definitions are in accordance with Terminology C 219.*

3.2 *Phases (1):*<sup>6</sup>

3.2.1 *alite, n*—tricalcium silicate (C<sub>3</sub>S) modified in composition and crystal structure by incorporation of foreign ions; occurs typically between 30 to 70 % (by mass) of the Portland-cement clinker; and is normally either the M<sub>1</sub> or M<sub>3</sub> crystal polymorph, each of which is monoclinic.

3.2.2 *aluminate, n*—tricalcium aluminate (C<sub>3</sub>A) modified in composition and sometimes in crystal structure by incorporation of a substantial proportion of foreign ions; occurs as 2–15 % (by mass) of the Portland-cement clinker; is normally cubic when relatively pure and orthorhombic when in solid solution with significant amounts of sodium, though tetragonal aluminate containing a substantial amount of potassium has been reported (2).

3.2.3 *belite, n*—dicalcium silicate (C<sub>2</sub>S) modified in composition and crystal structure by incorporation of foreign ions; occurs typically as 15 to 45 % (by mass) of the Portland-cement clinker as normally the β polymorph, which is monoclinic. In lesser amounts, other polymorphs can be present.

3.2.4 *ferrite, n*—tetracalcium aluminoferrite solid solution of approximate composition C<sub>2</sub>(A,F) modified in composition by variation in the Al/Fe ratio and by substantial incorporation of foreign ions as C<sub>4</sub>A<sub>x</sub>F<sub>2-x</sub> where 0 < x < 1.4; constituting 5 to 15 % (by mass) of a portland-cement clinker; and is orthorhombic.

3.2.5 *periclase, n*—free magnesium oxide (M); cubic.

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *standardization, n*—process of determining the relationship between XRD intensity and phase proportion for one or more phases.

3.3.1.1 *Discussion*—In the literature of X-ray powder diffraction analysis, this process has been commonly referred to

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<sup>2</sup> When expressing chemical formulae, C = CaO, S-SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>, M = MgO,  $\bar{S}$  = SO<sub>3</sub>, and H = H<sub>2</sub>O.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 04.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 04.02.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>6</sup> The boldface numbers in parentheses refer to the list of references at the end of this test method.

as calibration; however, we have determined that standardization is a more accurate term.

3.3.2 *diffractometer, n*—the instrument, an X-ray powder diffractometer, for determining the X-ray diffraction pattern of a crystalline powder.

3.3.3 *phase, n*—a homogeneous, physically distinct, and mechanically separable portion of a material, identifiable by its chemical composition and crystal structure.

3.3.3.1 Phases in portland-cement clinker that are included in this test method are two major phases (aluminate and ferrite) and one minor phase (periclase).

3.3.4 *qualification, n*—process by which a QXRD procedure is shown to be valid.

3.3.5 *Reference Material (RM) Clinkers, n*—three cement clinkers with known proportions of each major phase, available as RM's, which shall be used in demonstrating qualification of a particular procedure for determination of the phases in portland cement or portland-cement clinker.<sup>7</sup>

3.3.6 *Standard Reference Material (SRM), n*—a material whose properties (in this case XRD peak position or intensity, or both) are known and certified.<sup>8</sup>

3.3.7 *X-ray diffraction (XRD), n*—the process by which X-rays are coherently scattered by electrons in a crystalline material.

## 4. Background

4.1 This test method assumes general knowledge concerning the composition of portland cement and portland-cement clinker. Necessary background information may be obtained from a number of references (1,3).

4.2 This test method also assumes general expertise in XRD and QXRD analysis. Important background information may be obtained from a number of references (4,5,6,7).

4.3 QXRD analysis is difficult and time-consuming and QXRD of portland cement and portland-cement clinker is especially difficult due to the complex and variable nature of the individual clinker phases.

## 5. Summary

5.1 A QXRD test procedure includes some or all of the following:

5.1.1 Specimen preparation,

5.1.2 Standardization,

5.1.3 Use of an internal or external standard (to correct for various effects on intensity besides phase proportion),

5.1.4 Analysis of the sample (in which the intensity of selected XRD peaks is measured), and

5.1.5 Calculation of the proportion of each phase.

5.2 This test method does not specify details of the procedure. The user must demonstrate by analysis of reference materials that the particular analytical procedure selected for this purpose provides acceptable levels of precision and bias. A recommended procedure (the procedure used to determine the

acceptable levels of precision and bias) is given in the Appendix.

## 6. Significance and Use

6.1 This test method covers direct determination of the proportion of some individual phases in portland cement or portland-cement clinker. Thus it provides an alternative to the indirect estimation of phase proportion using the equations in Specification C 150 (see Note C of Table 1 and Note B of Table 2 of C 150).

6.2 This test method assumes that the operator is qualified to operate an X-ray diffractometer and to interpret X-ray diffraction spectra.

6.3 This test method may be used as part of a quality control program in cement manufacturing.

6.4 This test method may be used in predicting properties and performance of hydrated cement and concrete, to the extent that properties and performance are a function of phase composition.

6.5 QXRD provides a bulk analysis (that is, the weighted average composition of several grams of material). Results may not agree precisely with results of microscopical methods.

## 7. Apparatus

7.1 *X-Ray Diffractometer*—The X-ray diffractometer allows measurement of the X-ray diffraction pattern from which the crystalline phases within the sample may be qualitatively identified and the proportion of each phase may be quantitatively determined. X-ray diffractometers are manufactured commercially and a number of instruments are available. The suitability of the diffractometer for this test method shall be established using the qualification procedure outlined in this test method.

## 8. Materials

8.1 *Standardization Phases*—The use of standardization phases is recommended. These phases must usually be synthesized (8).

8.2 *RM Clinkers*—The use of RM clinkers is required to qualify the QXRD procedure.

8.3 *Internal Standard*—The use of an internal standard is recommended. Suitable materials include chemical reagents (see 8.4) or SRM's (see the Appendix).

8.4 *Reagent Chemicals*—Reagent grade chemicals, if used either as an internal standard or during chemical extraction of the calcium silicate phases, shall meet the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>9</sup> Other grades may be used, provided it is first ascertained that the chemical is sufficiently pure to permit its use without lessening the accuracy of the determination.

## 9. Hazards

9.1 The need for careful and safe operation of an X-ray

<sup>7</sup> In this test method, RM clinkers refer specifically to RM 8486, RM 8487, and RM 8488. These are available from the Standard Reference Material Program, National Institute of Standards and Technology.

<sup>8</sup> SRM's are available from the Standard Reference Material Program, National Institute of Standards and Technology.

<sup>9</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

diffractometer cannot be overemphasized. X-rays are particularly hazardous. An X-ray diffractometer must be operated safely to avoid serious injury or death. Furthermore, the X-rays are generated by high voltages, perhaps as high as 55 kV peak, requiring care to avoid serious electric shock. Klug and Alexander (5, pp. 58–60) state, “*The responsibility for safe operation rests directly on the individual operator*” (italics are theirs).

## 10. Sampling and Sample Preparation

10.1 Take samples of portland cement in accordance with the applicable provisions of Practice C 183. Take samples of portland-cement clinker so as to be representative of the material being tested.

10.2 Prepare samples as required for the specific analytical procedure (see Appendix).

## 11. Qualification and Assessment

### 11.1 Qualification of Test Procedure:

11.1.1 When analytical data obtained in accordance with this test method are required, any QXRD test procedure that meets the requirements described in this section may be used.

11.1.2 Prior to use for analysis of portland cement or portland-cement clinker, each QXRD test procedure must be qualified for such analysis. The laboratory shall maintain records that include a description of the QXRD procedure and the qualification data (or, if applicable, requalification data). These records shall be made available to the purchaser if requested in the contract or order.

11.1.3 If more than one X-ray diffractometer is used in a specific laboratory for the same analysis, even if the instruments are substantially identical, each shall be qualified separately.

11.1.4 If more than one procedure is used to mount specimens for QXRD, the use of each procedure shall constitute a separate test procedure and each procedure shall be qualified separately.

11.1.5 Qualification shall consist of analyzing the three RM clinkers (see Note 3) for the proportions of  $C_3A$  (cubic and orthorhombic),  $C_4AF$ , and M using the desired QXRD procedure (see Note 4).

NOTE 3—Prior to qualification, it may be convenient to carry out a preliminary assessment in which one or more mixtures of synthetic phases is analyzed. Such a preliminary assessment should produce no more than the permissible variation described in 11.2.

NOTE 4—It is recommended that at least two replicate analyses be carried out.

### 11.2 Permissible Variation:

11.2.1 The values of permissible variation were computed from the within-laboratory standard deviation values obtained in the cooperative standardization and round robin analysis of mixtures of synthetic phases (see 14.2.1).

11.2.2 If replicate analyses are carried out, results should differ from each other by no more than the value shown in Table 1 for the particular number of replicates.

11.2.3 The mean result shall differ from the known value by no more than the value shown in Table 2 for the particular number of replicates.

11.2.4 *Known Values*—The known values of each phase in

**TABLE 1 Permissible Maximum Difference Between Replicate Values (percent of clinker)**

Phase	Number of Replicates	Permissible Difference <sup>A</sup>
Orthorhombic $C_3A$	2	1.06
	3	1.25
	4	1.37
	5	1.48
Cubic $C_3A$	2	1.04
	3	1.22
	4	1.33
	5	1.44
$C_4AF$	2	1.68
	3	1.98
	4	2.16
	5	2.34
M	2	0.50
	3	0.59
	4	0.65
	5	0.70

<sup>A</sup> As described in Practice C 670.

the RM clinkers provided by NIST were determined using quantitative optical microscopy and differ somewhat from those obtained using QXRD. For the purpose of this test method, the known values of the RM clinkers shall be the values in the QXRD round robin analysis (see 14.2.2). These values are listed in Table 3.

### 11.3 Partial Results:

11.3.1 QXRD procedures that provide acceptable results for some phases but not for others shall be used only for those phases for which acceptable results are obtained. However, it is not expected that a QXRD procedure would provide acceptable results for some phases and not for others, and such a result may indicate that the procedure is not, in fact, valid.

### 11.4 Assessing the Diffractometer:

11.4.1 The procedures described in the Annex shall be used to assess the diffractometer. Note that assessment is different from qualification or requalification.

11.4.2 The diffractometer shall be assessed each day that this test method is used.

11.4.3 The diffractometer shall be assessed after any substantial modification in the instrument (see Note 5).

NOTE 5—Substantial modification of the diffractometer includes changing the X-ray tube, changing slits, adding or removing a monochromator, and realigning the diffractometer.

11.4.4 QXRD procedure shall be assessed upon receipt of evidence that the test procedure is not providing data in accordance with the permissible variation.

### 11.5 Requalification of QXRD Procedure:

11.5.1 If assessment shows that the X-ray diffractometer is not properly aligned (as discussed in the Annex), it shall be realigned following the manufacturer's instructions. When subsequent assessment shows that the X-ray diffractometer is properly aligned (or was not properly aligned when the QXRD procedure was previously qualified), qualification of the QXRD procedure shall be repeated.

## 12. Recommended Procedure

12.1 For required analytical data see Section 11 and a recommended QXRD procedure described in Appendix X1.

## 13. Report

13.1 *Report the Following Information:*

**TABLE 2 Permissible Maximum Difference Between Mean Value and Known Value (percent of clinker)**

Phase	Number of Replicates	Permissible Difference <sup>A</sup>
Orthorhombic C <sub>3</sub> A	1	0.74
	2	0.53
	3	0.43
	4	0.37
	5	0.33
Cubic C <sub>3</sub> A	1	0.73
	2	0.51
	3	0.42
	4	0.36
	5	0.32
C <sub>4</sub> AF	1	1.18
	2	0.83
	3	0.68
	4	0.59
	5	0.53
M	1	0.35
	2	0.25
	3	0.20
	4	0.18
	5	0.16

<sup>A</sup> Computed from within-laboratory standard deviation using 95 % confidence interval and 30 df.

**TABLE 3 Phase Proportions in RM Clinkers (determined by QXRD) (percent of clinker)**

Clinker	Phase	Proportion
RM 8486	orthorhombic C <sub>3</sub> A	2.63
	cubic C <sub>3</sub> A	1.07
	C <sub>4</sub> AF	10.61
	M	3.40
RM 8487	orthorhombic C <sub>3</sub> A	1.18
	cubic C <sub>3</sub> A	11.02
	C <sub>4</sub> AF	3.11
	M	0.48
RM 8488	orthorhombic C <sub>3</sub> A	3.21
	cubic C <sub>3</sub> A	1.95
	C <sub>4</sub> AF	11.46
	M	0.18

13.1.1 The phase and its proportion, and

13.2 Round figures to the number of significant places required in the report only after calculations are completed, in order to keep the final results substantially free of calculation errors. Follow the rounding procedure outlined in Practice E 29 or Test Methods C 114.

13.3 Note in the report that this test method was used.

## 14. Precision and Bias

14.1 *Analysis*—A cooperative standardization of mixtures of synthetic phases and a round-robin analysis<sup>9</sup> of the RM clinkers have been carried out (8,9,10) following the experimental procedures described in the Appendix.

14.1.1 A cooperative standardization and round robin analysis was undertaken to determine precision and bias levels for analysis of mixtures of synthetic phases. Results were analyzed statistically according to Practice E 691 to determine precision and bias levels.

14.1.2 A round robin was undertaken to determine precision and bias levels for analysis of portland cement or portland-cement clinker (see Note 6) using the RM clinkers. Results were analyzed statistically according to Practice E 691 to determine precision and bias levels.

**TABLE 4 Statistical Results for Mixtures of Synthetic Standardization Phases (percent of clinker)**

Phase	Repeatability Standard Deviation	Reproducibility Standard Deviation
orthorhombic C <sub>3</sub> A	0.38	0.83
cubic C <sub>3</sub> A	0.37	0.78
C <sub>4</sub> AF	0.60	0.64
M	0.18	0.19

**TABLE 5 Statistical Results for RM Clinkers (percent of clinker)**

Phase	Repeatability Standard Deviation	Reproducibility Standard Deviation
orthorhombic C <sub>3</sub> A	0.30	1.05
cubic C <sub>3</sub> A	0.37	0.84
C <sub>4</sub> AF	0.59	1.61
M	0.07	0.56

NOTE 6—Analysis of clinker is likely to include variance in addition to that found in analysis of mixtures of synthetic phases.

14.1.3 The precision and bias values are all expressed as percentage points by mass relative to the total clinker.

### 14.2 Precision:

14.2.1 *Mixtures of Synthetic Phases*—Ten laboratories participated in the cooperative standardization and round-robin analysis of mixtures of synthetic phases. The within-laboratory standard deviation for all phases averaged 0.39 percentage point, and the between-laboratory standard deviation for all phases averaged 0.61 percentage point. Values for each phase are given in Table 4.

14.2.2 *Clinkers*—Five laboratories participated in the round-robin analysis of the RM clinkers. The within-laboratory standard deviation for all phases averaged 0.33 percentage point and the between-laboratory standard deviation for all phases averaged 1.01 percentage point. Values for each phase are given in Table 5.

14.3 *Bias*—In the cooperative standardization and round-robin analysis of mixtures of synthetic phases the measured values differ from the known values by less than the reproducibility standard deviation, so there appears to be no bias in these results.

14.4 *Discussion*—These precision and bias levels appear reasonable. Taylor (1) concluded that the four major phases in portland-cement clinker may be determined using QXRD with an absolute accuracy of 2 to 5 percentage points (by mass) for alite and belite and 1 to 2 percentage points (by mass) for aluminate and ferrite. A bias may occur if the chemical composition or crystal structure of a phase being analyzed is different from that of the phase used for standardization. For example, a greater bias in ferrite determination may occur if the A/F ratio of that phase in the unknown is quite different from that of the standardization mixtures.

## 15. Keywords

15.1 aluminate; clinker; diffractometer; ferrite; periclase; phase analysis; portland cement; quantitative X-ray diffraction analysis; X-ray diffraction

## ANNEX

## (Mandatory Information)

## A1. ASSESSING THE X-RAY DIFFRACTOMETER

**A1.1 Introduction**—A QXRD analysis of portland cement and portland-cement clinker is made particularly difficult by the fact that individual clinker phases used for standardization are not stable over long periods of time because they hydrate easily, and are not easily synthesized. Thus it is difficult to assess standardizations directly by reanalysis of one or more standardization specimen. In addition, it is not desirable to repeat the standardization unless absolutely necessary. A more reasonable strategy is to use an external standard to assess the diffractometer and to decide when it is necessary to requalify a particular procedure. This Annex provides a procedure for assessing the diffractometer to assure the validity of the QXRD procedure over a long period of time (several years or longer).

**A1.2 Overview:**

**A1.2.1** As long as certain aspects of the procedure are not changed, the relationship between peak intensity (relative to the intensity of an internal standard peak) and proportion of the phase (relative to the proportion of the internal standard) is assumed to be universal (that is, valid over an indefinite period of time, even after changes in the diffractometer such as realignment and replacement of the X-ray tube, and transferable from one diffractometer to another).

**A1.2.2** The requirements for the QXRD standardization to be universal are: (1) specimens are free from preferred orientation, primary extinction, and microabsorption, (2) the irradiated volume of the specimen is constant and independent of scattering angle, (3) monochromator polarization effects are corrected, (4) integrated peak intensity is used, (5) when using an internal standard, standardization and analyses are carried out with an internal standard from the same lot because differences in the particle size distribution between lots of the same material can cause significant difference in peak intensity, and (6) standardization and analyses are carried out with the diffractometer in proper geometric alignment.

**A1.2.3** If analyses are carried out using only the instrument on which the standardization was carried out, then it is necessary only that preferred orientation, extinction, microabsorption, irradiated volume, and integrated peak intensity are reproducible. In that case, the standardization is valid (though not universal, in that it cannot be transferred from one diffractometer to another) as long as methods of specimen preparation, specimen mounting, and data collection are suitable and are not changed. For example, thus the use of a variable divergence slit is acceptable, because it provides reproducible irradiated volume.

**A1.3 Terminology**

**A1.3.1 extinction**—a decrease in intensity during diffraction due to interference by successive crystal planes.

**A1.3.1.1 Discussion**—Extinction is affected by the crystallite size and is negligible for specimens ground to a particle

diameter of 5 or 10  $\mu\text{m}$ .

**A1.3.2 irradiated volume**—the volume of specimen that produces XRD signal.

**A1.3.2.1 Discussion**—Irradiated volume is constant from specimen to specimen as long as the proper geometric alignment is maintained and the specimen is sufficiently thick.

**A1.3.3 microabsorption**—an increase or decrease in intensity produced by a combination of phases that differ in absorption coefficient.

**A1.3.3.1 Discussion**—Microabsorption is affected by the extent to which the absorption coefficients differ and by the crystallite size. For phases whose mass absorption coefficients differ by less than 100, microabsorption is not significant for specimens ground to a particle diameter of  $<10 \mu\text{m}$ .

**A1.3.4 peak intensity measurements**—the integrated intensity of the particular diffraction peak.

**A1.3.5 preferred orientation**—the nonrandom orientation of grains relative to the specimen surface.

**A1.3.5.1 Discussion**—Preferred orientation causes major changes in intensity of certain XRD lines, and therefore may be a source of error in QXRD analysis. Preferred orientation is not thought to be a major problem with portland-cement clinker phases because they do not typically cleave along crystallographic directions. Preferred orientation is reduced (but not prevented) by prolonged grinding. The mounting procedure must be one that reduces preferred orientation, such as the procedure as described by Klug and Alexander (5, pp. 372–374).

**A1.4 Alignment**

**A1.4.1** Loss of proper alignment causes systematic variations in peak intensity with  $2\theta$  angle, thus rendering the QXRD procedure invalid.

**A1.4.2** In order to assess alignment, an external standard shall be analyzed each day that this test method is used. Measurements shall include peak position, intensity, and resolution (that is, peak width or the ratio of the peak to valley intensity of partially overlapping peaks) of two or more peaks at widely separated  $2\theta$  angles. Suitable external standards include polished specimens of novaculite quartz or silicon, or SRM 1976.<sup>8</sup>

**A1.4.3** Proper alignment is indicated by all of the following: (1) correct peak position, (2) suitable peak intensity, (3) suitable ratio of peak intensity of one or more peaks, and (4) suitable peak resolution. These must all be determined for suitably intense peaks. The correct peak position is within  $0.01^\circ 2\theta$  (Cu  $K\alpha$ ) of its nominal value; for the (101) line of novaculite quartz, this value is  $26.64^\circ 2\theta$  (Cu  $K\alpha$ ). Suitable peak intensity depends on many aspects besides alignment and therefore must be determined for a particular diffractometer based on experience; 1000 counts per second per mA is a

reasonable expected value for the (101) line of novaculite quartz. Suitable peak intensity ratio is within 5 % of the nominal value. Suitable peak resolution must likewise be determined for a particular diffractometer based on experience. A reasonable indication is provided by clear separation of the five quartz peaks [(122)  $\alpha_1$ , (122)  $\alpha_2$ , (203)  $\alpha_1$ , (203)  $\alpha_2$  plus (301)  $\alpha_1$ , and (301)  $\alpha_2$ ] that appear at about  $68^\circ 2\theta$  (Cu K $\alpha$ ) (5, p. 392–394). Another indication is provided by resolution of the (110) K $\alpha$ 1–2 doublet of tungsten that appears at about  $40.4^\circ 2\theta$  (Cu K $\alpha$ ); the valley between these peaks must be no greater than 0.5 times the intensity of the  $\alpha_2$  peak (5, p. 282–285).

A1.4.4 NIST SRM 1976 may be used for instrument sensitivity assessment (10). Certified relative intensities of diffraction peaks, by both peak height or peak area, may be used to assess and correct for instrument bias. Plotting the ratios of the observed to certificate relative intensities will allow assessment of instrument performance relative to a diffractometer deemed to be “in control.” If the plot of intensity ratios is patternless and falls within the control limits the diffractometer may be considered “in control.”

A1.4.5 When a diffractometer is found to not be properly aligned, then it must be realigned according to the manufacturer’s instructions.

## APPENDIX

### (Nonmandatory Information)

#### X1. QXRD PROCEDURES USED TO DETERMINE ACCEPTABLE LEVELS OF PRECISION AND BIAS

**X1.1 Introduction**—During development of this test method, a round-robin analysis of the RM clinkers was carried out to determine acceptable levels of precision and bias for the test method (8,9,10). Details of the QXRD procedure were specified during this analysis. Although this test method does not include detailed QXRD procedures, the procedures used in the cooperative standardization and round robin are recommended.

**X1.2 Overview**—This QXRD procedure has a number of critical features: standardization using mixtures of synthetic phases, use of an internal standard, intensity measurement of a specified peak for each phase, measurement of peak area to determine intensity, grinding samples until at least 90 % (by mass) is smaller than 10  $\mu\text{m}$  in diameter, and the use of chemical extractions in the analytical scheme (see Note X1.1).

**NOTE X1.1**—Alternative QXRD procedures may provide satisfactory precision and bias and thus be acceptable under this test method. For example, acceptable procedures need not include a standardization, but may instead involve calculating the relationships between intensity and proportion. An external standard may be used rather than an internal standard. Intensity of each phase may be measured using many peaks or even the entire pattern. Chemical extractions need not be used in the analytical scheme. The particular procedure described in this appendix simply constitutes a recommendation.

##### X1.3 Standardization Mixtures:

**X1.3.1** Three standardization mixtures were prepared using cubic  $\text{C}_3\text{A}$ , orthorhombic  $\text{C}_3\text{A}$ ,  $\text{C}_4\text{AF}$ , and M. These individual phases were obtained from the Construction Technology Laboratories, and procedures used to prepare these individual

phases and standardization mixtures were described by Struble and Kanare (8).

**X1.3.2** The proportions in each mixture are listed in Table X1.1. The phases in this standardization are the principal phases in a clinker that has been chemically extracted using maleic acid or salicylic acid (see X1.3.3).

**X1.3.3** Standardization phases were ground such that at least 95 % (by mass) was finer than 10  $\mu\text{m}$  and not more than 5 % were finer than 1  $\mu\text{m}$  in diameter. This particle size was selected to minimize microabsorption preferred orientation and to avoid loss of X-ray intensity due to grinding to particle sizes <1  $\mu\text{m}$ .

##### X1.4 Internal Standard:

**X1.4.1** Participants were required to use an internal standard—a pure, stable material, 95 % of which is finer than 10  $\mu\text{m}$ . One recommended material was SRM 640a (silicon).<sup>8</sup> However, it should be noted that silicon intensity may be affected by particle size distribution. Also recommended were any one of the materials in SRM 674.<sup>8</sup> Another suitable material is SRM 676.<sup>8</sup>

**X1.4.2** Standardization mixtures were mixed with the internal standard material in recommended proportions of 0.1200 g internal standard per 1.0000 g standardization or unknown mixture, corresponding to 0.0200 g internal standard per 1.0000 g clinker. These proportions assume that the standardization mixture and unknown mixtures represent 17 % (by mass) of a clinker.

**X1.5 Blending**—Components must be blended to provide homogeneous specimens. The recommended procedure was to blend each standardization mixture for approximately 10 minutes using a vibratory-type mill with approximately 5 mL of a nonaqueous solvent (see Note 14) for each gram of powder and with appropriate grinding media.

**NOTE 14**—Suitable solvents include cyclohexane or alcohol (ethanol, methanol, or 2-propanol). Alcohol often contains sufficient water to cause hydration, so this water must be removed (9).

**X1.6 Diffraction Procedures**—Participants were instructed to use their normal procedures for preparing specimens and for

**TABLE X1.1 Proportion of Phases in Standardization Mixtures**

Phase	Percent of Mixture			Percent of Clinker		
	A	B	C	A	B	C
Orthorhombic $\text{C}_3\text{A}$	0	51	7	0.00	8.67	1.19
Cubic $\text{C}_3\text{A}$	65	11	29	11.05	1.87	4.93
$\text{C}_4\text{AF}$	35	11	60	5.95	1.87	10.20
M	0	27	4	0.00	4.59	0.68

collecting diffraction patterns. Specimen preparation procedures should minimize preferred orientation. Procedures to collect diffraction patterns should provide reproducible peak intensity measurements (for example, slow scanning speeds and moderately large receiving-slit widths).

**X1.7 Peak Selection**—Participants were required to measure intensity of the peaks specified in Table X1.2 plus one or more peaks for the internal standard, though they were encouraged to measure additional peaks, as many as possible for each phase. Analysis using a manual diffractometer is probably limited to the few peaks in Table X1.2, whereas analysis using a computer-controlled diffractometer can utilize many peaks for each phase.

**X1.8  $C_3A$  Correction**—The intensity of the (113) peak of orthorhombic  $C_3A$  must be corrected for any contribution from the (023) peak of cubic  $C_3A$ . This (023) intensity contribution is calculated by multiplying the (213) peak by a correction factor, which is the intensity ratio of the (023) peak to the (213) peak for cubic  $C_3A$  using Sample A (which contains no orthorhombic  $C_3A$ ).

**X1.9 Intensity Measurement**—Integrated intensity above the background must be measured for each peak. There are a number of procedures for measuring integrated intensity, and no specific procedure is required for this standardization.

**X1.10 Standardization Curve**—Once the standardization mixtures have been analyzed, standardization curves relating the measured intensity of each peak, relative to the intensity of the internal standard peak, to the known proportion of the phase must be developed. These curves may be prepared graphically or using accepted statistical procedures to determine the best-fitting curve. When an internal standard is used, it is assumed that the peak intensity is linearly related to the phase proportion. However under certain circumstances it may be found that the relationship is not linear, but is better described by some other mathematical function.

**X1.11 Analysis of Unknown Mixtures**—Two additional mixtures of the standardization phases were analyzed using the same QXRD procedures to provide a preliminary assessment of the standardization.

**X1.12 Analysis of Cement or Clinker**—The following procedures were followed during analysis of the RM clinkers and are recommended for analysis of any portland cement or portland-cement clinker.

**TABLE X1.2 Peaks Recommended for QXRD Analysis**

Phase	hkl	d-spacing (nm)	Position ( $2\theta$ ) using Cu $K\alpha$
Orthorhombic $C_3A^A$	(113)	0.4210	21.1
	(023)	0.4236	21.0
Cubic $C_3A$	(213)	0.4083	21.8
	(130)	0.3654	24.3
$C_4AF$	(200)	0.2106	42.9

<sup>A</sup> Note that the intensity of the (113) peak of orthorhombic  $C_3A$  must be corrected for any contribution from the (023) peak of cubic  $C_3A$ . The intensity of the (023) peak is calculated by multiplying the (213) peak by a correction factor. The correction factor is determined by measuring the intensity ratio of the (023) peak to the (213) peak in a sample containing cubic  $C_3A$  and no orthorhombic  $C_3A$ .

**X1.12.1 Grinding**—The clinker samples were ground such that at least 95 % was finer than 10  $\mu m$  and not more than 5 % was finer than 1  $\mu m$ . The following procedure has been found to be suitable: grind using a tungsten carbide ring and puck mill, with approximately 5 drops ethylene glycol as a grinding aid, for 4 to 6 min. It is necessary to start with enough sample to provide sufficient powder for the specimen mount, considering that extraction of the calcium silicates will leave ca. 15 % to 20 % (by mass) for XRD analysis.

**X1.12.2 Ignition**—In the case of portland cement, gypsum ( $CSH_2$ ) and hemihydrate ( $CSH_{1/2}$ ) must be converted to anhydrite ( $C\bar{S}$ ) before QXRD analysis to eliminate interfering XRD peaks. This conversion can be carried out by igniting the cement for 30 min at 500°C.

**X1.12.3 Blending with Internal Standard**—The ground sample was blended with the internal standard using the same procedure as used during the standardization. The recommended proportion was 0.0200 g internal standard per gram of clinker to approximate the 12 % (by mass) recommended for the standardization mixtures.

**X1.12.4 Extraction**—The calcium silicates were extracted chemically using salicylic acid or maleic acid and methanol using procedures described by Struble (11). This extraction was not quantitative; because the internal standard was added relative to unextracted clinker, the phase contents were determined relative to the unextracted clinker.

**X1.12.5 XRD Analysis**—The clinkers were analyzed using the same procedures (for example, collection of the diffraction pattern, measurement of peak intensities, and calculation of phase proportions) that were used in the standardization.



## REFERENCES

- (1) Taylor, H. F. W., *Cement Chemistry*, Academic Press, San Diego, CA, 1990.
- (2) Gebhardt, R. F., "KC<sub>8</sub>A<sub>3</sub>: X-Ray Diffraction Characterization of the Compound and Comparison with NC<sub>8</sub>A<sub>3</sub> and C<sub>3</sub>A," *Cement, Concrete and Aggregates*, Vol 9, No. 2, 1987, pp. 117-128.
- (3) Lea, F. M., *The Chemistry of Cement and Concrete*, 3rd ed., Arnold, London, 1970, 727 pp.
- (4) Cullity, B. D., *Elements of X-Ray Diffraction*, Addison-Wesley Publishing Company, Inc., Reading, MA, 1978.
- (5) Klug, H. P., and Alexander, L. E., *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed, John Wiley & Sons, New York, NY, 1974.
- (6) Bish, D. L., and Post, J. E., eds, *Modern Powder Diffraction, Reviews in Mineralogy*, Vol 20, Mineralogical Society of America, Washington, DC, 1989.
- (7) *Methods and Practices in X-Ray Powder Diffraction*, 3rd ed, International Centre for Diffraction Data, Swarthmore, PA, 1989.
- (8) Struble, L., and Kanare, H., "Cooperative Calibration and Phases, Report 2," *Structural Research Series No. 556*, University of Illinois at Urbana-Champaign, 1990.
- (9) Struble, L., "Quantitative Phase Analysis of Clinker Using X-Ray Diffraction," *Cement, Concrete and Aggregates*, Vol 13, No. 2, 1991, pp. 97-102.
- (10) Certificate of Analysis, "Standard Reference Material 1976, Instrument Sensitivity Standard for X-ray Powder Diffraction," *Standard Materials Reference Program*, National Institute of Standards and Technology, Gaithersburg, MD.
- (11) Struble, L., "The Effect Of Water On Maleic Acid And Salicylic Acid Extractions," *Cement and Concrete Research*, Vol 15, 1985, pp. 631-636.

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