Designation: C 1365 – 98

Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis[1]

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,[2] C_3A), ferrite (tetracalcium aluminoferrite, C_4AF), 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_3S), belite (dicalcium silicate, C_2S), gypsum ($C\bar{S}H_2$) , hemihydrate ($C\bar{S}H$ ln$) , and anhydrite ($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[3]
C 150 Specification for Portland Cement[3]
C 183 Practice for Sampling and the Amount of Testing of Hydraulic Cement[3]
C 219 Terminology Relating to Hydraulic Cement[3]
C 670 Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials[4]
E 29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications[5]
E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method[5]

3. Terminology

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

3.2 *Phases* (1):[6]

3.2.1 *alite*, *n*—tricalcium silicate (C_3S) 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_1 or M_3 crystal polymorph, each of which is monoclinic.

3.2.2 *aluminate*, *n*—tricalcium aluminate (C_3A) 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_2S) 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 $C_2(A,F)$ modified in composition

[1] This test method is under the jurisdiction of ASTM Committee C-1 on Cement and is the direct responsibility of Subcommittee C01.23 on Compositional Analysis.
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[2] When expressing chemical formulae, C = CaO, S-SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO, $\bar{S}$ = SO_3, and H = H_2O.

[3] *Annual Book of ASTM Standards,* Vol 04.01.
[4] *Annual Book of ASTM Standards,* Vol 04.02.
[5] *Annual Book of ASTM Standards,* Vol 14.02.
[6] The boldface numbers in parentheses refer to the list of references at the end of this test method.

by variation in the Al/Fe ratio and by substantial incorporation of foreign ions as $C_4A_XF_{2-X}$ where $O < x < 1.4$; 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 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.[7]

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.[8]

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 Appendix X1.

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 150C 150 (see Note C of Table 1 and Note B of Table 2 of C 150C 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 Appendix X1).

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

[7] 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.

[8] SRM's are available from the Standard Reference Material Program, National Institute of Standards and Technology.

Society where such specifications are available.[9] 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 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 183C 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 X1).

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 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.

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

Phase	Number of Replicates	Permissible Difference[A]
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

[A] As described in Practice C 670C 670.

[9] *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.

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

Phase	Number of Replicates	Permissible Difference[A]
Orthorhombic C_3A	1	0.74
	2	0.53
	3	0.43
	4	0.37
	5	0.33
Cubic C_3A	1	0.73
	2	0.51
	3	0.42
	4	0.36
	5	0.32
C_4AF	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

[A] 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_3A	2.63
	cubic C_3A	1.07
	C_4AF	10.61
	M	3.40
RM 8487	orthorhombic C_3A	1.18
	cubic C_3A	11.02
	C_4AF	3.11
	M	0.48
RM 8488	orthorhombic C_3A	3.21
	cubic C_3A	1.95
	C_4AF	11.46
	M	0.18

11.5 *Requalification of QXRD Procedure*:

11.5.1 If assessment shows that the X-ray diffractometer is not properly aligned (as discussed in Annex A1), 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*:

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 29E 29 or Test Methods C 114.

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

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

Phase	Repeatability Standard Deviation	Reproducibility Standard Deviation
orthorhombic C_3A	0.38	0.83
cubic C_3A	0.37	0.78
C_4AF	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_3A	0.30	1.05
cubic C_3A	0.37	0.84
C_4AF	0.59	1.61
M	0.07	0.56

14. Precision and Bias

14.1 *Analysis*—A cooperative standardization of mixtures of synthetic phases and a round-robin analysis[9] of the RM clinkers have been carried out (**8,9,10**) following the experimental procedures described in Appendix X1.

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 691E 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 691E 691 to determine precision and bias levels.

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