



Designation: **C1365 – 06 (Reapproved 2011) C1365 – 18**

Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis¹

This standard is issued under the fixed designation C1365; 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*~~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: alite (tricalcium silicate), belite (dicalcium silicate), aluminat (tricalcium aluminat), ferrite (tetracalcium aluminoferrite), periclase (magnesium oxide), gypsum (calcium sulfate dihydrate), bassanite (calcium sulfate hemihydrate), anhydrite (calcium sulfate), and calcite (calcium carbonate).

1.2 This test method specifies certain general aspects of the analytical procedure, but does not specify detailed aspects. Recommended procedures are described, but not specified. Regardless of the procedure selected, the user shall demonstrate by analysis of certified reference materials (CRM's) that the particular analytical procedure selected for this purpose qualifies (that is, provides acceptable precision and bias) (see **Note 1**). The recommended procedures are ones used in the round-robin analyses to determine the precision levels of this test method.

NOTE 1—A similar approach was used in the performance requirements for alternative methods for chemical analysis in Test Methods **C114**.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazards, see Section 9.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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2. Referenced Documents

2.1 *ASTM Standards:*²

C114 Test Methods for Chemical Analysis of Hydraulic Cement

~~C150~~**C150/C150M** Specification for Portland Cement

~~C183~~**C183/C183M** Practice for Sampling and the Amount of Testing of Hydraulic Cement

C219 Terminology Relating to Hydraulic Cement

C670 Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials

E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions:* Definitions are in accordance with Terminology **C219**.

3.2 *Phases (1):*³

¹ This test method is under the jurisdiction of ASTM Committee **C01** on Cement and is the direct responsibility of Subcommittee **C01.23** on Compositional Analysis. Current edition approved Dec. 1, 2011; March 1, 2018. Published May 2012/April 2018. Originally approved in 1998. Last previous edition approved in 2006/2011 as ~~C1365 – 98 (2006)~~C1365 – 06 (2011). DOI: 10.1520/C1365-06R11.10.1520/C1365-18.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The boldface numbers in parentheses refer to the list of references at the end of this standard.

*A Summary of Changes section appears at the end of this standard

3.2.1 *alite, n*—tricalcium silicate (C_3S)⁴ 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 *alkali sulfates, n*—arcanite (K_2SO_4) may accommodate Na^+ , Ca^{2+} , and CO_3 in solid solution, aphanite ($K_{4-x}Na_xSO_4$ with x usually 1 but up to 3), calcium langbeinite ($K_2Ca_2[SO_4]_3$) may occur in clinkers high in K_2O , and thenardite (Na_2SO_4) in clinkers with high Na/K ratios (1).

3.2.3 *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 to 15 % (by mass) of the portland-cement clinker; is normally cubic when relatively pure and orthorhombic or monoclinic when in solid solution with significant amounts of sodium (2).

3.2.4 *anhydrite, n*—calcium sulfate ($C\bar{S}$) and is orthorhombic (see Note 2).

NOTE 2—Calcium sulfate is added to the clinker during grinding to control setting time, strength development, and volume stability. Several phases may form as a result of dehydration of gypsum. The first 1.5 molecules of water are lost between 0 and 65°C–65°C with minor changes in structure; and, above 95°C–95°C, the remaining 0.5 molecules of water are lost transforming the structure to the metastable γ polymorph of anhydrite (sometimes referred to as ‘soluble anhydrite’) and subsequently the orthorhombic form (3).

3.2.5 *bassanite, n*—calcium sulfate hemihydrate ($C\bar{S}H_{1/2}$) and is monoclinic.

3.2.6 *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.

3.2.7 *calcite, n*—calcium carbonate is trigonal and may be present in a cement as an addition or from carbonation of free lime.

3.2.8 *ferrite, n*—tetracalcium aluminoferrite solid solution of approximate composition $C_2(A,F)$ modified in composition by variation in the Al/Fe ratio and by substantial incorporation of foreign ions as $C_4A_xF_{2-x}$ where $0 < x < 1.4$; constituting 5 to 15 % (by mass) of a portland-cement clinker; and is orthorhombic.

3.2.9 *free lime, n*—free calcium oxide (C); cubic (see Note 3).

NOTE 3—Free lime (CaO) may be present in clinker and cement but readily hydrates to form portlandite ($Ca(OH)_2$). Portlandite may carbonate to form calcium carbonate, generally as calcite. Heat-treating a freshly-ground sample to 600°C–600°C is useful to convert any portlandite back to free lime but will also dehydrate the hydrous calcium sulfate phases (gypsum and bassanite) to anhydrite.

3.2.10 *gypsum, n*—calcium sulfate dihydrate ($C\bar{S}H_2$) and is monoclinic.

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

3.3 Definitions of Terms Specific to This Standard:

3.3.1 *Certified Reference Material (CRM), n*—a material whose properties (in this case phase abundance, XRD peak position or intensity, or both) are known and certified (see Note 4).

NOTE 4—NIST Standard Reference Material (SRM®) Clinkers 2686, 2687, and 2688 are suitable CRMs for qualification.⁵

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 Discussion—

Phases in portland-cement clinker and cements that are included in this test method are four major phases (alite, belite, aluminate, and ferrite) and one minor phase (periclase).

3.3.3.2 Discussion—

Precision values are provided for additional phases (gypsum, bassanite, anhydrite, arcanite, and calcite). Values for these constituents may be provided using this method but are considered informational until suitable certified reference materials for qualification are available.

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

3.3.5 *Rietveld analysis, n*—process of refining crystallographic and instrument variables to minimize differences between observed and calculated X-ray powder diffraction patterns for one or more phases, estimating their relative abundance.

⁴ When expressing chemical formulae, C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, M = MgO, \bar{S} = SO₃, and H = H₂O.

⁵ Portland cement clinker SRM's® from the Standard Reference Material Program, National Institute of Standards and Technology.

3.3.6 *standardization, n*—process of determining the relationship between XRD intensity and phase proportion for one or more phases (see [Note 5](#)).

NOTE 5—In the literature of X-ray powder diffraction analysis, the standardization process has been commonly referred to as calibration; however, we have determined that standardization is a more accurate term.

3.3.6.1 *Discussion*—

Rietveld analysis uses crystal structure models to calculate powder diffraction patterns of phases that serve as the reference patterns. The pattern-fitting step seeks the best-fit combination of selected pattern intensities to the raw data. The relative pattern intensities along with the crystallographic attributes of each phase are used to calculate relative abundance. The standardization approach uses powdered samples of pure phases to assess the relationship between diffraction intensity ratios and mass fraction ratios of two or more constituents; and is referred to here as the traditional method.

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 cement and portland-cement clinker. Necessary background information may be obtained from a number of references ([1](#), [4](#)).

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 ([5-10](#)).

5. Summary

5.1 This test method covers direct determination of the proportion by mass of individual phases in cement or portland-cement clinker using quantitative X-ray powder diffraction analysis. The following phases are covered by this standard: alite (tricalcium silicate, C_3S), belite (dicalcium silicate, C_2S), aluminite (tricalcium aluminate, C_3A), ferrite (tetracalcium aluminoferrite, C_4AF), periclase (magnesium oxide, M), arcanite (potassium sulfate, $K\bar{S}$), gypsum (calcium sulfate dihydrate, $C\bar{S}H_2$), bassanite (calcium sulfate hemihydrate, $C\bar{S}H_{\frac{1}{2}}$), anhydrite (calcium sulfate, $C\bar{S}$), and calcite (calcium carbonate, $CaCO_3$).

A QXRD test procedure includes some or all of the following: (a) specimen preparation; (b) data collection and phase identification; (c) standardization (for the standardization approach); (d) collecting a set of crystal structure models for refinement (for the Rietveld approach); (e) use of an internal or external standard (to correct for various effects on intensity besides phase proportion); (f) analysis of the sample (in which the powder diffraction pattern is measured and/or the intensity of selected XRD peaks or patterns are measured); and (g) calculation of the proportion of each phase.

5.2 This test method does not specify details of the QXRD test procedure. The user must demonstrate by analysis of certified reference materials that the particular analytical procedure selected for this purpose provides acceptable levels of precision and bias. Two recommended procedures (the Rietveld approach and the traditional approach used to determine the acceptable levels of precision and bias) are given in [Appendix X1X2](#) and [Appendix X2X3](#).

6. Significance and Use

6.1 This test method allows direct determination of the proportion of some individual phases in cement or portland-cement clinker. Thus it provides an alternative to the indirect estimation of phase proportion using the equations in Specification [C150C150/C150M](#) (Annex A1).

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 that are a function of phase composition.

6.5 QXRD provides a bulk analysis (that is, the weighted average composition of several grams of material). Therefore, 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 for establishing the intensity ratio/mass ratio relationships when using the traditional quantitative method. These phases must usually be synthesized (11, 12).

8.2 *CRM Clinker*—The use of three CRM clinkers is required to qualify the QXRD procedure.

8.3 *Internal Standard*—The use of an internal standard is recommended for the standardization approach. Suitable materials include chemical reagents (see 8.4) or CRM's (see Appendix X1X2).

8.4 *Reagent Chemicals*—Reagent grade chemicals, if used either as an internal standard or during chemical extraction of certain phases, shall meet the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁶ 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 importance of 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. 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 (6) (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 cement in accordance with the applicable provisions of Practice ~~C183~~C183/C183M. 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 X2X3).

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 cement or portland-cement clinker, qualify the QXRD test procedure for the analysis. Maintain records that include a description of the QXRD procedure and the qualification data (or, if applicable, re-qualification data). Make these records 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, qualify each 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 replicate determinations of the three SRM® clinkers, re-mounting the specimen for each analysis, (see Note 6) for the proportions of C₃S, C₂S, C₃A (cubic and orthorhombic), C₄AF, and M using the desired QXRD procedure (see Note 7).

NOTE 6—Prior to qualification, it may be convenient to carry out a preliminary assessment in which one or more mixtures of synthetic phases are analyzed. Such a preliminary assessment should produce no more than the permissible variation described in 11.2.

NOTE 7—It is recommended that at least two replicate analyses be carried out, but three determinations may be used for assessing permissible variation.

11.2 *Permissible Variation:*

11.2.1 The values of permissible variation were computed from the within-laboratory standard deviation values obtained in round robin analyses of mixtures of SRM® clinkers and synthetic phases (see 14.2).

11.2.1.1 *Discussion*—Qualification limits in Table 2 are prediction intervals (95 %) for a future mean and are designed to bracket values of a mean of k (=2,3,4) future measurements of the relevant phases. The intervals are based upon the performance of the 11 round robin participants.

11.2.2 Replicate analyses shall differ from each other by no more than the within-lab repeatability value shown in Table 1.

11.2.3 A test result shall be judged not equivalent if it differs from that of another laboratory by more than the between-lab reproducibility value shown in Table 1.

11.2.4 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.

11.2.4.1 *Discussion*—Qualification limits in Table 2 are prediction intervals (95 %) for a future mean and are designed to bracket values of a mean of k (=2,3,4) future measurements of the relevant phases. The intervals are based upon the performance of the eleven round robin participants.

⁶ *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 1 Permissible Maximum Difference Between Replicate Values (percent) (Percent of Clinker or Cement)^A

	Repeatability Within-Lab		Reproducibility Between-Lab	
	s-within	d2s-within	s-between	d2s-between
alite	0.74	2.04	2.27	6.30
belite	0.64	1.77	1.40	3.87
aluminat	0.47	1.31	0.79	2.19
ferrite	0.49	1.36	0.89	2.47
periclase	0.23	0.63	0.50	1.39
arcanite	0.22	0.60	0.34	0.94
gypsum	0.21	0.59	0.59	1.65
bassanite	0.39	1.08	0.58	1.60
anhydrite	0.27	0.74	0.64	1.77
calcite	0.99	2.73	0.50	1.50

^A As described in Practice C670.

TABLE 2 Permissible Maximum Difference Between Mean Value and Known Value (Mass percent) Expressed at a 95 % Confidence Level for the Mean of a Selected Number of Replicates (k) = 2, 3, 4^A

Phase	2 replicates	3 replicates	4 replicates
alite	5.93	4.91	4.31
belite	3.70	3.06	2.69
aluminat	2.14	1.77	1.55
ferrite	2.46	2.04	1.79
periclase	0.77	0.64	0.56
arcanite	0.85	0.70	0.61
gypsum	1.55	1.28	1.12
bassanite	1.52	1.26	1.11
anhydrite	1.67	1.38	1.21
calcite	0.68	0.56	0.49

^A Computed from within-laboratory standard deviation using 95 % confidence interval and 30 df.

11.2.5 *Known Values*—The known values of each phase in the SRM® clinkers provided by NIST was determined using quantitative X-ray powder diffraction and optical microscopy (13).

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 re-qualification.

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

11.4.3 The diffractometer shall be assessed after any substantial modification in the instrument (see Note 8).

NOTE 8—Substantial modification of the diffractometer includes changing the X-ray tube, changing a detector, adding or removing a monochromator, and realignment.

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 Re-qualification 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 the recommended QXRD procedures described in Appendix X1X2.

13. Report

13.1 Report the following information:

13.1.1 The phase and its proportion, and which method (Rietveld or standardization) was used. 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 E29.

14. Precision and Bias

14.1 *Analysis*—A round-robin analysis by Rietveld refinement of the SRM® clinkers with calcium sulfate and calcium carbonate additions has been carried out following experimental procedures described in Appendix X1X2. An earlier cooperative standardization of mixtures of synthetic phases and a round-robin analysis⁷ of the RM clinkers have been carried out (11, 12) following the experimental procedures described in Appendix X2X3 (see Note 9). Results were analyzed statistically according to Practices E691 and C670 to determine precision levels.

NOTE 9—Analysis of clinker is likely to include variance in addition to that found in analysis of mixtures of synthetic phases.

14.1.1 The precision values are all expressed as percentage points by mass relative to the total clinker or cement.

14.2 *Precision*—The within-laboratory standard deviation and the between-laboratory standard deviation for all phases are given in Table 1, representing pooled results from the four test mixtures. The within-laboratory standard deviation for each phase is reported as ‘s-within.’ Results of two properly conducted tests by the same operator should not vary more than d2s-within in 95 % of comparisons, where $d2s\text{-within} = 1.96 \cdot \sqrt{2} \cdot s_{\text{within}}$. The multi-laboratory standard deviation for each phase is reported as ‘s-between.’ Results of two properly conducted tests on the same clinker or cement by two different laboratories should not differ from each other by more than d2s-between in 95 % of comparisons, where $d2s\text{-between} = 1.96 \cdot \sqrt{2} \cdot s_{\text{between}}$.

14.3 *Bias*—The difference between the estimate of true mean phase concentration and the accepted reference values.

14.4 *Discussion*—Eleven laboratories participated in a cooperative round-robin analysis of mixtures of four separate reference materials. Reference values were that of the SRM® clinkers adjusted for the known amounts of added calcium sulfates and calcite. 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. The SRM® clinkers do not contain gypsum, bassanite, anhydrite or calcite so these data are provided for informational purposes. The qualification requires assessment of certified phases in the clinker SRMs® only. As new SRMs® become available, additional phase qualifications will be added to the test method. There is insufficient data to estimate method bias at this time.

15. Keywords

15.1 alite; alkali sulfate; aluminate; belite; cement; clinker; diffractometer; ferrite; periclase; phase analysis; quantitative X-ray powder diffraction analysis; QXRD; Rietveld analysis; X-ray powder diffraction; XRD

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ANNEX

(Mandatory Information)

A1. ASSESSING THE X-RAY DIFFRACTOMETER

A1.1 *Introduction*—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). 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 specimens. 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 re-qualify 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 ratio and mass ratio 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).

⁷ SRM's from the Standard Reference Material Program, National Institute of Standards and Technology are Certified Reference Materials.