Designation: C114 – 18

Standard Test Methods for Chemical Analysis of Hydraulic Cement[1]

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1. Scope*

1.1 These test methods cover the chemical analyses of hydraulic cements. Any test methods of demonstrated acceptable precision and bias may be used for analysis of hydraulic cements, including analyses for referee and certification purposes, as explained in Section 4. Specific chemical test methods are provided for ease of reference for those desiring to use them. They are grouped as Reference Test Methods and Alternative Test Methods. The reference test methods are long accepted classical chemical test methods which provide a reasonably well-integrated basic scheme of analysis for hydraulic cements. The alternative test methods generally provide individual determination of specific analytes and may be used alone or as alternates and determinations within the basic scheme at the option of the analyst and as indicated in the individual method.

1.2 *Contents:*

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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.*

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.*

[1] These test methods are under the jurisdiction of ASTM Committee C01 on Cement and are the direct responsibility of Subcommittee C01.23 on Compositional Analysis.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C25 Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime

C219 Terminology Relating to Hydraulic Cement

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

E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

E350 Test Methods for Chemical Analysis of Carbon Steel, Low-Alloy Steel, Silicon Electrical Steel, Ingot Iron, and Wrought Iron

E617 Specification for Laboratory Weights and Precision Mass Standards

E832 Specification for Laboratory Filter Papers

3. Terminology

3.1 *Definitions of Terms Specific to This Standard*—The terms used in this standard are defined in Terminology C219.

3.2 *Definitions:*

3.2.1 *analyte, n*—a substance of interest when performing a quantitative analysis.

3.2.1.1 *Discussion—For the purposes of this test method*, analytes are considered to be those items listed in column 1 of Table 1.

3.2.2 *reagent water, n*—water purified by the process of distillation, deionization, reverse osmosis, or any combination of the three processes.

3.2.2.1 *distillation, n*—the process of purification by the evaporation and vaporization of water and its subsequent condensation and collection.

3.2.2.2 *deionization, n*—the process of purification using the two-step process of converting soluble salts into acids by passing them through a hydrogen exchanger after which they are removed by an acid absorbent or synthetic resin.

3.2.2.3 *reverse osmosis, n*—water purification technology that uses a semipermeable membrane to remove ions, molecules, and larger particles from drinking water.

3.2.3 *water (potable), n*—water that is suitable for drinking.

4. Description of Referee Analyses

4.1 *Referee Analyses*—When conformance to chemical specification requirements is questioned, perform referee analyses as described in 4.1.1. The reference test methods that follow in Sections 7 – 22, or other test methods qualified according to 5.4, the *Performance Requirements for Rapid Test Methods* section, are required for referee analysis. A cement shall not be rejected for failure to conform to chemical requirements unless all determinations of constituents involved and all necessary separations prior to the determination of any

TABLE 1 Maximum Permissible Variations in Results[A]

(Column 1) Analyte	(Column 2) Maximum Difference Between Duplicates[B]	(Column 3) Maximum Difference of the Average of Duplicates from CRM Certificate Values[C,D,B]
SiO_2 (silicon dioxide)	0.16	±0.2
Al_2O_3 (aluminum oxide)	0.20	±0.2
Fe_2O_3 (ferric oxide)	0.10	±0.10
CaO (calcium oxide)	0.20	±0.3
MgO (magnesium oxide)	0.16	±0.2
SO_3 (sulfur trioxide)	0.10	±0.1
LOI (loss on ignition)	0.10	±0.10
Na_2O (sodium oxide)	0.03	±0.05
K_2O (potassium oxide)	0.03	±0.05
TiO_2 (titanium dioxide)	0.02	±0.03
P_2O_5 (phosphorus pentoxide)	0.03	±0.03
ZnO (zinc oxide)	0.03	±0.03
Mn_2O_3 (manganic oxide)	0.03	±0.03
S (sulfide sulfur)	0.01	[E]
Cl (chloride)	0.003	±0.005
IR (insoluble residue)	0.10	[E]
Cx (free calcium oxide)	0.20	[E]
CO_2 (carbon dioxide)	0.12	[E,F]
Alk_{sol} (water-soluble alkali)[G]	0.75/*w*	[E]
Chl_{sol} (chloroform-soluble organic substances)	0.004	[E]

[A] When seven CRM cements are required, as for demonstrating the performance of rapid test methods, at least six of the seven shall be within the prescribed limits and the seventh shall differ by no more than twice that value. When more than seven CRMs are used, as for demonstrating the performance of rapid test methods, at least 77 % shall be within the prescribed limits, and the remainder by no more than twice the value. When a lesser number of CRM cements are required, all of the values shall be within the prescribed limits.

[B] Where no value appears in column 3, CRM certificate values do not exist. In such cases, only the requirement for differences between duplicates shall apply.

[C] Interelement corrections may be used for any oxide standardization provided improved accuracy can be demonstrated when the correction is applied to all seven CRM cements.

[D] Where an CRM certificate value includes a subscript number, that subscript number shall be treated as a valid significant figure.

[E] Not applicable. No certificate value given.

[F] Demonstrate performance by analysis, in duplicate, of at least one Portland cement. Prepare three standards, each in duplicate: Standard A shall be selected Portland cement; Standard B shall be Standard A containing 2.00 % Certified $CaCO_3$ (such as NIST 915a); Standard C shall be Standard A containing 5.00 % Certified $CaCO_3$. Weigh and prepare two separate specimens of each standard. Assign the CO_2 content of Standard A as the average of the two values determined, provided they agree within the required limit of column 2. Assign CO_2 values to Standards B and C as follows: Multiply the Certified $CaCO_3$ value (Y) for CO_2 (from the certificate value) by the mass fraction of Certified $CaCO_3$ added to that standard (percentage added divided by 100); multiply the value determined for Standard A by the mass fraction of Standard A in each of the other standards (that is, 0.98 and 0.95 for Standards B and C, respectively); add the two values for Standard A and for Standard B, respectively; call these values B and C.

Example:

B = 0.98A + 0.02Y.

C = 0.95A + 0.05Y.

Where for Certified $CaCO_3$, if Y = 39.9 %

B = 0.98A + 0.80 % by mass.

C = 0.95A + 2.00 % by mass.

Maximum difference between the duplicate CO_2values for Standards B and C, respectively, shall be 0.17 and 0.24 % by mass. Averages of the duplicate values for Standards B and C shall differ from their assigned values (B and C) by no more than 10 % of those respective assigned values.

[G] *w* = weight, in grams, of samples used for the test.

[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.

one constituent are made entirely by these methods. When reporting the results of referee analyses, specify which test methods were used.

4.1.1 Referee analyses shall be made in duplicate and the analyses shall be made on different days. If the two results do not agree within the permissible variation given in Table 1, the determination shall be repeated until two or three results agree within the permissible variation. When two or three results do agree within the permissible variation, their average shall be accepted as the correct value. When an average of either two or three results can be calculated, the calculation shall be based on the three results. For the purpose of comparing analyses and calculating the average of acceptable results, the percentages shall be calculated to the nearest 0.01 (or 0.001 in the case of chloroform-soluble organic substances), although some of the average values are reported to 0.1 as indicated in the test methods. When a blank determination (see Note 1) is specified, one shall be made with each individual analysis or with each group of two or more samples analyzed on the same day for a given analyte.

NOTE 1—A blank determination is a procedure which follows all steps of analysis but in the absence of a sample. It is used for detection and compensation of systematic bias.

5. Qualification for Different Analyses

5.1 *Certified Reference Materials*—A Certified Reference Material (CRM) must be used in the qualification of test methods and analysts. Acceptable reference cements are NIST CRMs, or other reference cements traceable to the NIST CRMs. The reference cement must have an assigned value for the analyte being determined. Traceability consists of documentary evidence that the assigned values of the reference cement are compatible with the certified values of NIST CRMs. To demonstrate traceability for a given analyte, perform a referee analysis (as defined in 4.1) on the proposed reference cement, using a NIST CRM for demonstration of precision and accuracy. The reference cement is acceptable if its assigned value agrees with the average referee value within the limits given in column 3 of Table 1. If the reference cement, as supplied, has no documented guarantee of homogeneity, establish its homogeneity by analyzing at least six randomly selected samples. No result shall deviate from the assigned value by more than the limits given in column 2 of Table 1. An acceptable reference cement must be accompanied by a document showing the data produced in demonstrating traceability and homogeneity.

5.2 *Requirements for Qualification Testing*—Qualified test methods are required whenever testing is performed for the following reasons: (*1*) for Referee analyses; (*2*) for analyses intended for use as a basis for acceptance or rejection of a cement; or, (*3*) for manufacturer's certification. When Reference Methods are used, qualification testing of the analyst is required as described in 5.2.1. When Rapid Methods are used, qualification testing of both the analyst and the test method are required as described in 5.2.1 and 5.4. Such demonstration may be made concurrently with analysis of the cement being tested. The requirements for qualification of a test method and analyst are summarized in Table 2.

TABLE 2 Minimum Number of CRMs Required for Qualification of Chemical Testing

	Method Type	
	Reference[A]	Other[B]
Equipment Qualification	None	7
Analyst Qualification[C]	1	1

[A] Reference Methods are those outlined in Sections 7 – 22.
[B] These may be any test method as described in 5.3, the *Alternative Analyses* section, or any instrumental or rapid test method, which must be qualified in accordance with 5.4, the *Performance Requirements for Rapid Test Methods* section.
[C] Each analyst performing acceptance or reference analyses must be qualified in accordance with 5.2.1, the *Performance Requirements for Rapid Test Methods* section, at a frequency of two years. If qualification of the instrument is completed by a single analyst, the analyst has demonstrated individual qualifications per 5.2.1.

5.2.1 Qualification of the analyst shall be demonstrated by analysis of each analyte of concern using at least one CRM cement in duplicate, no matter what test method is used (Note 2). Duplicate samples shall be tested on different days. The analyst is considered qualified when the difference between the duplicate results does not vary by more than the value listed in column 2 of Table 1 and the average of the two samples agrees with the certificate value of the CRM within the limits listed in column 3 of Table 1 after correction for minor components when needed. The same test methods to be used for analysis of cement being tested shall be used for analysis of the CRM cement. If either of the two requirements listed above are not met, identify and correct any problems or errors found in the procedure. Repeat the determinations until a set of duplicate results agree within the permissible variations. Requalification of the analyst is required every two years.

NOTE 2—When qualifying a Rapid Method with seven CRMs in accordance with 5.4.2, the analyst performing the qualification of the test method may simultaneously qualify for the requirement of 5.2.1.

5.2.2 Qualification data demonstrating that the same operator or analyst making the acceptance determination obtained precise and accurate results with CRM cements in accordance with 5.2.1 shall be made available on request to all parties concerned when there is a question of acceptance of a cement. If the CRM used is not a NIST cement, the traceability documentation of the CRM used shall also be made available on request.

5.3 *Alternative Analyses*—The alternative test methods provide, in some cases, procedures that are shorter or more convenient to use for routine determination of certain constituents than are the reference test methods (Note 3). Longer, more complex procedures, in some instances, have been retained as alternative test methods to permit comparison of results by different procedures or for use when unusual materials are being examined, where unusual interferences may be suspected, or when unusual preparation for analysis is required. Test results from alternative test methods may be used as a basis for acceptance or rejection when it is clear that a cement does or does not meet the specification requirement. Any change in test method procedures from those procedures listed in Sections 7 – 30 requires method qualification in accordance with 5.4, the *Performance Requirements for Rapid Test Methods* section.

NOTE 3—It is not intended that the use of reference test methods be confined to referee analysis. A reference test method may be used in preference to an alternative test method when so desired. A reference test method must be used where an alternative test method is not provided.

5.3.1 Duplicate analyses and blank determinations are not required when using the alternative test methods. If, however, a blank determination is desired for an alternative test method, one may be used and it need not have been obtained concurrently with the analysis. The final results, when corrected for blank values, should, in either case, be so designated.

5.4 *Performance Requirements for Rapid Test Methods:*[3,4]

5.4.1 *Definition and Scope*—Where analytical data obtained in accordance with this test method are required, any test method may be used that meets the requirements of 5.4.2, the *Qualification of a Test Method* section. A test method is considered to consist of the specific procedures, reagents, supplies, equipment, instrument, and so forth, selected and used in a consistent manner by a specific laboratory. See Note 4 for examples of procedures.

NOTE 4—Examples of test methods used successfully by their authors for analysis of hydraulic cement are given in the list of references. Included are test methods using atomic absorption X-ray spectrometry and spectrophotometry-EDTA.

5.4.1.1 If more than one instrument, even though substantially identical, is used in a specific laboratory for the same analyses, use of each instrument shall constitute a separate test method and each must be qualified separately.

5.4.2 *Qualification of a Test Method*—Prior to use for analysis of hydraulic cement, each test method (see 5.4.1) must be qualified individually for such analysis. Qualification data, or if applicable, requalification data, shall be made available pursuant to the Manufacturer's Certification section of the appropriate hydraulic cement specification.

5.4.2.1 Using the test method chosen, make single determinations for each analyte under consideration on at least seven CRM samples. Requirements for a CRM are listed in 5.1, the *Certified Reference Material* section. Complete two rounds of tests on different days repeating all steps of sample preparations. Calculate the differences between values and averages of the values from the two rounds of tests.

5.4.2.2 When seven CRMs are used in the qualification procedure, at least six of the seven differences between duplicates obtained of any single analyte shall not exceed the limits shown in column 2 of Table 1 and the remaining differences by no more than twice that value. When more than seven CRMs are used, the values for at least 77 % of the samples shall be within the prescribed limits, while the values for the remainder shall differ by no more than twice that value.

5.4.2.3 For each analyte and each CRM, the average obtained shall be compared to the certified concentrations. Where a certificate value includes a subscript number, that subscript shall be assumed to be a significant number. When seven CRMs are used in the qualification procedure, at least six of the seven averages for each analyte shall not differ from the certified concentrations by more than the value shown in column 3 of Table 1, and the remaining average by more than twice that value. When more than seven CRMs are used in the qualification procedure, at least 77 % of the averages for each analyte shall not differ from the certified concentrations by more than the value shown in column 3 of Table 1, and the remaining average(s) by more than twice that value.

5.4.2.4 The standardization, if needed, used for qualification and for analysis of each constituent shall be determined by valid curve-fitting procedures. A point-to-point, saw-tooth curve that is artificially made to fit a set of data points does not constitute a valid curve-fitting procedure. A complex polynomial drawn through the points is similarly not valid. For the same reason, empirical inter-element corrections may be used, only if $\leq (N - 3)/2$ are employed, where N is the number of different standards used. The qualification testing shall be conducted with specimens newly prepared from scratch, including all the preparation stages applicable for analysis of an unknown sample, and employing the reagents currently in use for unknown analyses.

5.4.3 *Partial Results*—Test Methods that provide acceptable results for some analytes but not for others may be used only for those analytes for which acceptable results are obtained.

5.4.4 *Report of Results*—When performing chemical analysis and reporting results for Manufacturer's Certification, the type of method (Reference or Rapid) and the test method used along with any supporting qualification testing shall be available on request.

5.4.5 *Rejection of Material*—See 4.1, the *Referee Analyses* section, and 5.3, the *Alternative Analyses* section.

5.4.6 *Requalification of a Test Method:*

5.4.6.1 Requalification of a test method shall be required upon receipt of substantial evidence that the test method may not be providing data in accordance with Table 1 for one or more constituents. Such requalification may be limited to those constituents indicated to be in error and shall be carried out prior to further use of the method for analysis of those constituents.

5.4.6.2 Substantial evidence that a test method may not be providing data in accordance with Table 1 shall be considered to have been received when a laboratory is informed that analysis of the same material by Reference Test Methods run in accordance with 4.1.1, the final average of a CCRL sample, a certificate value of an NIST CRM, the assigned value of an alternate CRM, or an accepted value of a known secondary standard differs from the value obtained by the test method in question by more than twice the value shown in column 2 of Table 1 for one or more constituents. When indirect test methods are involved, as when a value is obtained by difference, corrections shall be made for minor constituents in order to put analyses on a comparable basis prior to determining the differences. For any constituents affected, a test method also shall be requalified after any substantial repair or replacement of one or more critical components of an instrument essential to the test method.

[3] Gebhardt, R. F., "Rapid Methods for Chemical Analysis of Hydraulic Cement," ASTM STP 985, 1988.

[4] Barger, G. S., "A Fusion Method for the X-Ray Fluorescence Analysis of Portland Cements, Clinker and Raw Materials Utilizing Cerium (IV) Oxide in Lithium Borate Fluxes," Proceedings of the Thirty Fourth Annual Conference on Applications of X-Ray Analysis, Denver Conference, Volume 29 pp. 581–585, August 5, 1985.