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Standard Test Method for Major and Minor Elements in Cement by X-Ray Fluorescence^a

This standard is issued under the fixed designation X XXXX; 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 is applicable to the analysis of the major and minor elements in hydraulic cements using X-ray fluorescence spectrometry (XRF) and utilizes two different methods of sample preparation for an XRF analytical finish.

1.2 The values given in SI units are to be considered as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards^b*

C 114 Test Methods for Chemical Analysis of Hydraulic Cement

^a 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.

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^bFor 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.

C 150 Specification for Portland Cement

E 11 Specification for Wire-Cloth and Sieves for Testing Purposes

E 50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

E 883 Guide for Reflected-Light Photomicrography

3. Summary of Test Method

3.1 Part 1--Fused Disks Method

3.1.1 The cement or clinker to be analyzed is dried under standard conditions and ignited to constant weight. Previously dried materials are ignited to constant weight under standard conditions. The cement is fused with a lithium borate flux or other suitable flux and cast into a glass disk. The glass disk is then irradiated by an X-ray beam of short wavelength (high energy). The characteristic X-rays of the atom that are emitted or fluoresced upon absorption of the primary or incident X-rays are dispersed and intensities at selected wavelengths are measured by sensitive detectors. Detector output is related to concentration by calibration curves or computerized data-handling equipment.

3.1.2 The K and L spectral lines are used for most of the elements determined by this procedure.

3.2 Part 2—Pressed Powder Method

3.2.1 Cement standards and samples are ground and pelletized using the same sample preparation procedure. The pellet is then irradiated by an X-ray beam of short wavelength (high energy). The characteristic X-rays of the atom that are emitted or fluoresced upon absorption of the primary or incident X-rays are dispersed and intensities at selected wavelengths are measured

by detectors. Detector output is related to concentration by calibration curves and interelement (empirical or fundamental parameter) corrections through computerized data-handling equipment.

3.2.2 The K spectral lines are used for all of the elements determined by this procedure except barium in which the L spectral lines may be used.

3.3 *Parts 1 and 2*--All elements are determined as the element and reported as the oxide and include silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), phosphorus (P), titanium (Ti), sulfur (S), manganese (Mn), strontium (Sr), and barium (Ba). Chloride (Cl), zinc (Zn), and chromium (Cr) may be reported as the element.

4. Significance and Use

4.1 A compositional analysis of cement is used in describing the quality of the cement for its complete characterization and to assess conformance with specifications in Test Methods C 114.

4.2 This test method is in two parts.

4.2.1 Part 1 is the XRF method using the lithium borate fusion method of sample preparation for the cement and cement mixtures and can be used for analysis of all hydraulic cements and mixtures of cements with silica fume, limestone, pozzolans, fly ash, or slag. After preparing the fusion mass with the sample, the fusion mix is cast into a smooth glass disk for elemental analysis.

4.2.2 Part 2 is the XRF method using the pressed powder method of sample preparation for analysis of cement and is limited to Portland cements meeting Specification C 150. Part 2 of this method is not generally applicable to the analysis of blended cements, including those blended with silica fume, limestone, pozzolans, fly ash, slag, and any combination thereof higher than the amounts of additions found in Portland cements meeting Specification C 150. The cement

blends shall be analyzed by the fusion method described in Part 1. If the testing facility is uncertain as to the nature of the cement, or if the cement is not manufactured at the local plant, the fusion method in Part 1 shall be used for analysis.

Part 1: Fused Disks Method

5. Apparatus

5.1 *Fusion Furnace or Fluxing Device*, with an operating temperature between 975 °C and 1075°C., and capable of sustaining the temperature selected to +/- 25 ° C.

5.2 *Fusion Crucibles*, either high-purity graphite or platinum alloys of sufficient capacity.

5.3 *Casting Molds*, for casting a circular disk specimen of a diameter that can be accommodated by the spectrometer, either high-purity graphite or platinum alloys, with a smooth, flat base and minimum depth of 5 mm.

5.4 *Pulverizers*, including agate, mullite or tungsten carbide mortar, and pestle, minimum capacity 25 mL.

5.5 *Sieves*, 860-µm (No. 20) and 150-µm (No. 100 sieve) U.S. standard sieves as specified in Specification E 11.

5.6 *Compactor*, a press equipped with a gage enabling reproducible (exceeding 1.72×10^8 Pa (25,000 lb/in.²)) if pressed pellets are used.

5.7 *Excitation Source*, with a stable electric power supply (± 1 %) and a high-intensity, short-wavelength X-ray capability.

5.8 *Spectrometer*, a wavelength or energy-dispersive system equipped with a vacuum sample chamber.

5.8.1 *Analyzing Crystals (Wavelength Units)*--The choice of the analyzing crystal is made on the basis of the element to be determined. Use the crystal that yields the maximum sensitivity

with minimum interferences. The same crystal shall be used for standards and unknowns.

5.8.2 *Detectors*--Scintillation and gas-proportional counters are used with wavelength systems, while silicon-based solid-state detectors such as lithium-drifted diodes are used for energy-dispersive systems.

6. Reagents and Materials

6.1 *Purity of Reagents*--Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.^c Other grades are permitted, provided it is first ascertained that the reagent is sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Detector Gas*--The usual gas composition of the gas used in the flow-proportional counters is 90 % argon and 10 % methane, although other compositions may be used.

6.3 *Heavy Absorber*--Where heavy absorbers, such as lanthanum oxide or barium oxide are used, they shall be a minimum of 99.9 % purity.

6.4 *Fluxes*--Lithium borates or carbonates, or combination thereof, are often used for sample fusion. Either (1) lithium or ammonium iodide or (2) lithium or ammonium bromide are used as a nonwetting agent and lithium or ammonium nitrate is used as an oxidizing agent, provided they do not contribute to spectral interference.

NOTE 1--Prefused flux of high purity integrated with a nonwetting agent and very low water content are known to work.

6.5 *Binders*--Where pressed pellets are used for analysis, the binder used shall contribute no

^c*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.

spectral interferences during the determination.

7. Hazards

7.1 Exposure to the high energy and high voltage used in X-ray fluorescence (XRF) presents an extreme potential hazard. Obtain training before using X-ray equipment and understand completely the operation of the instrument. Follow all the instrument manufacturer's safety instructions. The equipment's safety interlocks shall be maintained in working order.

8. Preparation of Cement or Clinker

8.1 Prepare the cement from a thoroughly mixed representative analysis sample. Immediately, prepare the analysis sample or store the dry cement in a vacuum desiccator. If samples are stored and the absorption of moisture or CO₂, or both is in question, reignite the sample using the 950°C furnace. Alternatively, determine "loss on ignition" (LOI) on a separate sample weighed out at the same time as the test portion and make the necessary corrections. Thoroughly mix each sample before weighing.

8.2 Before testing, pass representative portions of each sample through a 860- μm (No. 20) sieve to mix the sample, break up lumps, and remove foreign materials. Discard the foreign materials and hardened lumps that do not break up on sieving or brushing.

8.2.1 By means of a sample splitter or by quartering, reduce the representative sample to a laboratory sample of at least 50 g.

8.3 Pass the laboratory sample through a 150- μm (No. 100) sieve. Further grind the sieved residue so that it also passes the 150- μm (No. 100) sieve. Homogenize the entire sample by passing it again through the sieve.

8.4 Transfer the sample to a clean, dry, glass container with an airtight lid and further mix the sample thoroughly.

8.5 Perform the above procedures rapidly so that the sample is exposed to the atmosphere for a minimum of time.

9. Preparation of Analytical Sample

9.1 Mix the powdered sample, weigh a portion of the sample, and mix with a suitable amount of flux (2g to 10g of flux per gram of sample) (NOTE 1). When a heavy absorber is used (NOTE 2), it is added at this point in an amount equal to the amount of sample and thoroughly blended with the mix. A portion of the flux may be used as a cap on the mix ensures washing down any of the material from the sides of the crucible during the fusion step.

NOTE 2--The amount of sample and flux used are determined by the necessity of forming a disk or pellet of 3- to 5-mm thickness to fit the sample holder of the spectrometer used. The 3- to 5-mm thickness of the disk shall be checked for infinite thickness for elements to be determined. All fluxes and other additives shall be added in an appropriate manner at the time of sample preparation.

9.1.1 Fluxing materials commonly available are not consistent and can vary in volatile losses upon fusing. To eliminate errors caused by this loss, one of four methods shall be used. First, the entire bottle of the flux may be heated to the fused state, then cooled, reground, and stored in a desiccator. Secondly, a weighed sample from each bottle is fused and a loss on fusion is determined, which is then applied as a correction for each sample prepared from that bottle. Third, the entire mass of each sample prepared (flux, sample, and heavy absorber, if used) may be weighed and an independent fusion loss calculated. Fourth, prefused fluxes with less than 0.05 % moisture are available for purchase and do not vary from batch to batch.

NOTE 3--Use of a heavy absorber has the advantage of allowing the use of a much smaller sample weight to reach infinite thickness and allows for calculation of concentrations using a

simple linear regression coefficient. It does, however, prevent determination of a number of trace elements and may be impractical for energy-dispersive systems in which its addition may cause increased detector dead time and complicated correction procedures. The use of a heavy absorber is recommended only when its absence is impractical or inconvenient.

9.2 The sample mix is fused at a temperature between 975° C and 1075 ° C, depending on the flux formulation, in a fusion furnace or fluxing device maintained at the temperature selected to +/- 25 ° C for a length of time sufficient to guarantee complete dissolution of the sample. Some type of agitation of the crucible, such as swirling or shaking, shall be used to ensure a uniform melt.

9.3 The fusion melt will then be made into a suitable mount by casting the liquid into a mold and forming a glass disk. Generally, the fusion disk or pellet can be analyzed directly. If deemed necessary, allow the pellet to cool, then grind to a fine powder with 2 % of a plasticizer or binder, and press into a pellet at a minimum of 1.72×10^8 Pa (25,000-lb/in.²) pressure with a suitable backing as added support before analyzing.

9.4 The glass disk shall be cooled at a rate that is fast enough to prevent any segregation occurring and, at the same time, slowly enough to prevent stresses that will crack the glass. Cracked glass disks may be refused and recast in case of limited sample, but loss of precision and accuracy may result.

9.5 Whichever method of preparation of the analytical specimen is used, it is essential that a smooth, uniform, and flat surface is exposed to the exciting radiation.

9.6 It is essential that the entire sample preparation procedure (including sample mass, flux mass and ratio, grinding, casting, and so forth) be followed precisely for all analytical specimens and standards. Even a small change in the selected procedures will require remaking of all

standards to match the changed procedure. All calibration standards and the unknowns to be used with them shall be prepared in exactly the same manner with all the weighings made to the nearest 0.1 mg.

10. Preparation of XRF Spectrometer

10.1 Follow the manufacturer's instruction for the initial assembly, conditioning, and preparation of the XRF unit.

10.2 Follow the manufacturer's instructions with respect to control setting and operation.

11. Calibration

11.1 Standard for calibration may be prepared from standard reference materials or synthetically blended pure compounds. It is required that the range of concentrations may be accomplished by empirical fundamental parameter or linear regression in accordance with Practice E 883. A suitable drift correction procedure with stable monitor standards shall be implemented to allow the calibration to remain valid for the long term.

12. Procedure

12.1 *Excitation and Exposure*--Position the sample in the chamber provided for this purpose. Avoid touching or otherwise contaminating the sample surface. Produce and record the spectrum at the settings recommended for the instrument. Prepare and analyze supuplicate mounts for all samples with duplicate readings on each mount. For in-house laboratories, single determinations may be performed as long as the precision and bias limits are met.

13. Precision and Bias^d

13.1 *Precision*--The relative precision of this test method for the determination of major and

^d Supporting data are available from ASTM Headquarters. Request RR# C01-XXXX.

minor elements in cement was calculated from data obtained from cement with the concentration ranges shown in Table 1.

13.2 *Repeatability*--The difference in absolute value between two consecutive tests results, carried out in the same analysis sample, in the same laboratory, by the same operator, using the same apparatus, shall not exceed the repeatability interval (r) or limit more than 5 % of such paired values (95 % confidence level.) When such a difference is found to exceed the repeatability interval or limit, there is reason to question one, or both, of the test results. The repeatability intervals or limits for the elements determined by this test method are described in Table 1.

13.3 *Example*--Duplicate analysis for iron (Fe_2O_3) showed values of XXX and XXX %. The absolute difference between the two sets is 0.0X %, since this value does not exceed the 1 r value of 0.XX %; therefore, these duplicate analyses are acceptable at the 95 % confidence level.

13.4 *Reproducibility*--The difference in absolute value of replicate determinations carried out in different laboratories, on representative samples prepared from the same bulk sample after the last stage of reduction, shall not exceed the reproducibility interval (R) or limit more than 5 % of such paired values (95 % confidence level.) When such a difference is found to exceed the reproducibility interval or limit, there is reason to question one, or both, of the test results. The reproducibility intervals or limits for the elements determined by this test method are described in Table 1.

13.5 *Example*--Duplicate analysis for iron in one laboratory showed an average value of XX %, and a value of XXX.X % was obtained in a different laboratory. The difference between the different laboratory values is 0.XX %. The reproducibility interval (R) from Table 1 is given as XX %. Since the laboratory difference is less than the 1 (R), the two laboratory results are

acceptable at the 95 % confidence level.

13.6 *Bias*--Analysis of ash by XRF is empirical, and its approach to accuracy is dependent upon the accuracy of the reference materials to be used for calibration (XX.X) and compliance to this test method. No other statement on bias can be made for this test method.

Part 2: Pressed Powder Method

14. Apparatus

14.1 *Rotary Swing Mill*, with hardened steel or tungsten carbide ring and puck grinding vessel.

14.2 *Hydraulic Press*, equipped with a gage enabling reproducible results (exceeding 1.72×10^8 Pa (25,000 lb/in.²)).

14.3 *Top Loading Balance (or Equivalent)*, capable of weighing to ± 1 mg.

14.4 *Excitation Source*, with a stable electric power supply (± 1 %) and a high-intensity, short-wavelength X-ray capability.

14.5 *Spectrometer*--A wavelength or energy-dispersive system equipped with a vacuum sample chamber.

14.6 *Analyzing Crystals (Wavelength Units)*--The choice of the analyzing crystal is made on the basis of the element to be determined. Use the crystal that yields the maximum sensitivity with minimum interferences. The same crystal shall be used for standards and unknowns.

14.7 *Detectors*--Scintillation and gas-proportional counters are used with wavelength systems, while silicon-based solid-state lithium or silicon-drifted detectors are used for energy-dispersive systems.

15. Reagents and Materials

15.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. Unless

otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.³ Other grades are permitted, provided it is first ascertained that the reagent is sufficiently high purity to permit its use without lessening the accuracy of the determination.

15.2 *Detector Gas*--The usual gas composition of the gas used in flow-proportional counters is 90 % argon and 10 % methane, although other compositions may be used.

15.3 *Grinding Aids*--The grinding aid keeps the powder from agglomerating while grinding and reduces the heat of the grinding process. It also lubricates the grinding media, keeping contamination from the grinding media to a minimum. Finally, some grinding aids can reduce dust during the removal of the ground powder from the grinding media and facilitate a contamination-free vessel after cleaning. The latter point is very important while trying to meet Test Methods C 114 (Table 2). Any grinding aid composition that can yield homogenous, sturdy pellets is acceptable.

15.4 *Binders*--The binder used shall contribute no spectral interferences during the determination. Any binder compositions that can yield homogenous, sturdy pellets are acceptable.

16. Hazards

16.1 Exposure to the high energy and high voltage used in XRF presents an extreme potential hazard. Obtain training before using X-ray equipment and understand completely the operation of the instrument. Follow all the instrument manufacturer's safety instructions. The equipment's safety interlocks must be maintained in working order.

17. Preparation of Cement or Clinker

17.1 By means of a sample splitter or quartering, reduce the representative sample (<10

mesh) to a laboratory sample if at least 50 g.

18. Preparation of Analytical Sample

18.1 The calibration standards (see Section 20) and samples are prepared identically by a method that will produce a sturdy, flat, smooth, homogenous pellet. Various binders, grinding aids, pellet cups, and sample backings have been known to produce acceptable pressed pellets and results. Method number 3 in the Bibliography is one such method that is known to work.

18.2 It is essential that the entire sample preparation procedure (including sample mass, binder mass, lubricant volume, sample cup, pressing pressure, and so forth) be followed precisely for all analytical specimens and standards. Even a small change in the selected procedures will require the remaking of all standards to match the changed procedure. All calibration standards and the unknowns to be used with them shall be prepared in exactly the same manner with all the weighings to be made to the nearest 0.1 mg.

19. Preparation of XRF Spectrometer

19.1 Follow the manufacturer's instruction for the initial assembly, conditioning, and preparation of the XRF unit.

19.2 Follow the manufacturer's instructions with respect to control setting and operation.

20. Calibration

20.1 Standards for calibration must be prepared from Certified Reference Materials (CRM) consisting of Portland cements meeting Specification C 150.

NOTE 4--NIST SRM 188X series can be used to satisfy this requirement.

20.2 Calibration over the range of concentrations is required and may be accomplished by linear regression for most elements and with empirical or fundamental parameter interelement corrections. A suitable drift correction procedure with stable monitor standards shall be

implemented to allow the calibration to remain valid for the long term.

21. Procedure

21.1 *Excitation and Exposure*--Position the sample in the chamber provided for this purpose. Avoid touching or otherwise contaminating the sample surface. Produce and record the spectrum at the settings recommended for the instrument. Prepare and analyze duplicate mounts for all samples with duplicate readings on each mount. For in-house laboratories, single determinations may be performed as long as the precision and bias limits are met.

22. Precision and Bias

22.1 Precision, bias, repeatability, reproducibility, accuracy, and other statistics used to determine the acceptability or qualification of the method may not be determined using the same CRM's used in the calibration procedure. The above suggested statistics shall be determined from a round robin or acceptable extraction of CCRL data.

23. Keywords

23.1 cement; major elements; minor elements; X-ray fluorescence

TABLE 1 Concentration Ranges and Intervals or Limits for Repeatability and Reproducibility for Major and Minor Elemental Oxides in Cements

Elemental Oxide % by Weight, of Moisture-Free Ash	Concentration Range/Repeatability/ Reproducibility
SiO ₂	
Al ₂ O ₃	
Fe ₂ O ₃	
CaO	
MgO	
Na ₂ O	
K ₂ O	
P ₂ O ₅	
TiO ₂	
MnO ₂	
SrO	
BaO	
SO ₃	
Cr	
Cl	
Zn	

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