Pergamon

Cement and Concrete Research 32 (2002) 1899–1906

CEMENT AND CONCRETE RESEARCH

Standard reference materials for cements

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Received 4 January 2002; accepted 3 June 2002

Abstract

The eight portland cements and two calcium aluminate cements in the Standard Reference Material (SRM) 1880 series are among the most popular SRMs in the catalog of the National Institute of Standards and Technology (NIST) Standard Reference Materials Program. Numerous laboratories rely on them for elemental analysis and qualification for ASTM C 114-00 Standard Test Methods for Chemical Analysis of Hydraulic Cement. NIST has collected new candidate materials from around the world and partnered with Construction Technology Laboratories (CTL) in their preparation and certification. This paper describes the procedures taken at NIST and CTL to prepare and test materials for certification including the homogeneity testing, the X-ray fluorescence methods and the statistical data analysis performed for value assignment.

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Keywords: Elemental analysis; Spectroscopy; X-ray fluorescence; Portland cement; Calcium aluminate cement

1. Introduction

A Standard Reference Material (SRM) from the National Institute of Standards and Technology (NIST) is a certified reference material that is well characterized, produced in quantity and certified by NIST for one or more chemical or physical properties. SRMs are used to assure the accuracy and compatibility of measurements throughout the United States and around the world. In many applications, traceability of quality control and measurement processes to the national measurement system is carried out through the use of SRMs. For many users of SRMs, it is of interest to know the details of the measurements made in arriving at the certified values.

NIST cement SRMs are primarily intended for use in the evaluation of chemical and instrumental methods for elemental analysis of commercial cements. The National Bureau of Standards produced the first portland cement certified reference material, SRM 177, in 1958 [1]. A series of five materials (SRMs 1011, 1013, 1014, 1015 and 1016) was made available in 1962. This series was replaced by seven new materials (SRMs 633–639), which became available with provisional certification in 1973 and final certification in 1977. During the 1980s, the 1880 series replaced the 633 series and included eight portland cements and two calcium aluminate cements.

The American Society for Testing and Materials (ASTM) drives much of the current demand for cement SRMs. In 1934, ASTM published the original version of C 114, Standard Test Methods for Chemical Analysis of Hydraulic Cement [2], which contains test methods intended for referee and product certification purposes. While the original version contained so-called wet chemical methods, the current version (C 114-00) allows "Any test methods of demonstrated acceptable precision and bias...." C 114 defines acceptable precision and bias through the use of SRMs run in duplicate to demonstrate a minimum level of precision and accuracy. When six or fewer SRMs are used, all results shall be within the prescribed limits in Table 1 of the method. The method encourages analysts to use as many different SRMs as are available by allowing room for error

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PII: S0008-8846(02)00896-7

Table 1
CTL test methods other than XRF spectrometry

Component	Test method
SiO_2	Gravimetry after NH_4Cl/HCl digestion
Al_2O_3	Atomic absorption spectrometry after $LiBO_2$ fusion
Fe_2O_3	Atomic absorption spectrometry after $LiBO_2$ fusion
CaO	Gravimetry by oxalate precipitation (corrected for SrO)
MgO	Atomic absorption spectrometry after $LiBO_2$ fusion
SO_3	Gravimetry after HCl digestion
SO_3	Turbidimetry after HCl digestion
Na_2O	Atomic absorption spectrometry after HCl digestion
K_2O	Atomic absorption spectrometry after HCl digestion
TiO_2	Atomic absorption spectrometry after $LiBO_2$ fusion
P_2O_5	Phosphomolybdate colorimetric analysis
Mn_2O_3	Atomic absorption spectrometry after $LiBO_2$ fusion
Cr_2O_3	Atomic absorption spectrometry after $LiBO_2$ fusion
SrO	Atomic absorption spectrometry after $LiBO_2$ fusion
ZnO	Atomic absorption spectrometry after $LiBO_2$ fusion
Loss on ignition at 950 °C	Thermogravimetry
Free lime	Franke procedure in C 114-00
F^-	Ion-specific electrode
Cl	Potentiometric titration using $AgNO_3$

only if seven or more SRMs are used. ASTM guarantees the demand for NIST SRMs by incorporating them into this standard test method for which industry laboratories must remain qualified. Requalification is required at least every 2 years. The result is that, on average, 300 units of each SRM are sold every year.

With such high demand, the 1880 series SRMs are going out of stock and NIST is replacing them. This task involves obtaining materials, packaging, homogeneity testing, quantitative analysis and certification. NIST is working with Construction Technology Laboratories (CTL) as was done during the 1980s. Replacements are prepared in much the same way as the older series described in Ref. [1], but the vials are now heat-sealed in foil pouches instead of glass ampoules (Fig. 1).

2. Certification work plan

NIST certification protocol requires a high level of confidence in both the materials and the quantitative determinations used to estimate the true values of the certified properties. A new material must pass homogeneity testing using the smallest quantity of material anticipated to be used in analytical procedures. A number of vials are randomly selected and samples are prepared in duplicate from each vial. An analysis of variance is performed on the measured data to test for statistically and analytically significant differences either within a vial or between vials. If the material passes this test, quantitative certification testing begins.

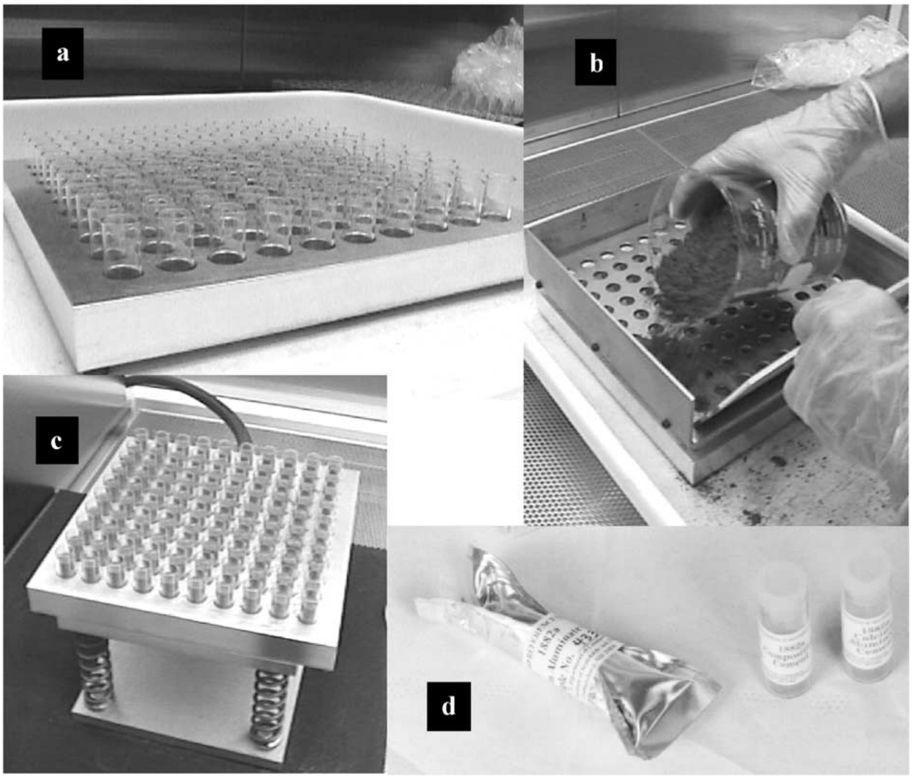

Fig. 1. Packaging of SRM 1880a series cements: (a) vials are arranged for filling in the bottom portion of the vial loading chamber; (b) cement is poured into the top portion of the vial loading chamber and into the vials inside; (c) the bottom portion of the vial loading chamber is placed on a shaker to settle the cement; (d) vials are capped and sealed in foil pouches. Four vials are included in each sales unit.

NIST Special Publication 260-136, “Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements” [3], explains the protocols available to NIST for certification of SRMs. One approach is to use two or more independent methods, i.e., different measurement techniques calibrated using different sources of standards. Another option is a combination approach where another organization contributes determinations using the same method as NIST with the work performed independently. When only one method is available, the value cannot be certified, but it may qualify as a reference or information value. All three of these modes were used in this project. The experimental design was developed in collaboration with statisticians of the NIST Statistical Engineering Division, who also contributed the statistical analyses for value assignment and uncertainty analysis.

The following work plan was developed for certification of cements:

1. Homogeneity testing using wavelength-dispersive X-ray fluorescence (XRF) spectrometry measurements of fused borate beads prepared from 0.50 g samples, the smallest quantity used in C 114.
2. Quantitative analysis using wavelength-dispersive XRF measurements of fused borate beads prepared using 2.5 g (for portland cement) or 2.0 g (for calcium aluminate) samples. Performed at both NIST and CTL with each lab using a different calibration method.
3. Quantitative analysis performed at CTL using classical and reference methods per ASTM C 114-00 or CTL standard practices (see Table 1).
4. Constituents to be certified if determined using a classical method and at least one of the two XRF methods unless there are significant, unresolved biases among the methods.
5. Physical properties testing by CTL for information values for loss on ignition at 950 °C (LOI), free lime, fly ash and slag content, and insoluble residue.

This paper briefly describes the different XRF procedures used at NIST and CTL and the statistical treatments used in Part 4 of the work plan to obtain the certified values. Classical methods are described in C 114 and will not be discussed herein. It is also important to point out that C 114 defines the convention of the cement industry to express elements as their oxides. XRF measures the elemental contents of the specimens, which are expressed as oxides in this paper to conform to the convention.

3. Experimental

3.1. Sample preparation

For XRF analysis, samples were prepared on an as-received basis by fusing with a flux consisting of a prefused mixture of two parts $Li_2B_4O_7$ and one part $LiBO_2$. For portland cement, 2.50 g of cement was weighed into a Pt/Au (95/5) crucible and was covered with 5.00 g of flux. For the calcium aluminate materials, 2.00 g of cement and 5.50 g of flux were used. NIST used an electrically heated bead preparation machine to fuse the mixture at 975 °C and cast beads of 30 mm diameter. CTL used a gas-fired machine to prepare beads of 30 mm diameter. Several drops of a nonwetting agent, LiI (aq) solution at NIST and LiBr (aq) solution at CTL, were added prior to fusion. Beads were measured as cast, with no additional preparation.

3.2. X-ray measurements

Both laboratories used sequential, wavelength-dispersive X-ray spectrometers to measure the borate beads in a vacuum environment. The elements F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Zn, Br, Sr, Zr and I were measured for homogeneity testing and quantitative analysis. The spectrometers were equipped with the necessary crystals and synthetic multilayer structures to measure the K–L series X-ray lines from the elements of interest.

4. Precision

When a laboratory attempts to qualify under ASTM C 114, they must demonstrate repeatability of duplicate determinations. The data in Table 2 illustrate the precision of NIST determinations. Six vials of each material were prepared in duplicate for a total of 12 measurements. Table 2 shows the largest differences between duplicate specimens from the same vial. Also listed is the maximum difference between duplicates allowed to qualify for C 114-00 from Table 1 of the ASTM method. As can be seen, the precision of the NIST work is more than adequate to meet ASTM

Table 2
Repeatability of duplicate determinations using XRF with borate fusion at NIST

Compound	Difference between duplicates, mass fraction (%)			
	SRM 1880a Portland cement	SRM 1881a Portland cement	SRM 1884a Portland cement	Maximum allowed by C 114-00
SiO_2	0.099	0.070	0.086	0.16
Al_2O_3	0.029	0.021	0.032	0.20
Fe_2O_3	0.010	0.010	0.012	0.10
CaO	0.21	0.13	0.17	0.20
MgO	0.011	0.015	0.033	0.16
SO_3	0.016	0.013	0.021	0.10
Na_2O	0.002	0.002	0.004	0.03
K_2O	0.009	0.004	0.006	0.03
TiO_2	0.004	0.002	0.003	0.02
P_2O_5	0.002	0.0005	0.001	0.03
ZnO	0.0005	0.0006	0.0003	0.03
Mn_2O_3	0.003	0.0004	0.0006	0.03

requirements. For SRM 1880a, where the C 114 requirement for CaO was exceeded by the NIST results (Table 2), the results exhibit excellent precision. SRM 1880a contains 63.83% CaO by mass and the largest difference between duplicate specimens is 0.21% by mass. On a relative basis, this difference between duplicates is 0.33%. It is difficult to do better with instrumental techniques and, of course, the repeatability of the other five vials is better than the C 114 requirement.

4.1. Homogeneity testing

Another illustration of precision may be seen in the results of homogeneity testing. The goal of homogeneity testing is to demonstrate that the material is characterized by sufficiently low heterogeneity to be useful as a reference material. For each cement, NIST tested the uniformity of the material throughout the batch by looking for variability between containers and within containers. This was done after all grinding, sieving and packaging were finished and the vials were sealed in airtight, foil pouches. Twenty-five vials, randomly selected, were sampled in duplicate and specimens were prepared using borate fusion.

It is important to carefully consider the question of what quantity of material to take from a vial for each replicate specimen. Consideration was given to the intended and unintended uses of the material. In the cement industry, it is expected that the SRM will be sampled in accordance with ASTM C 114. It is also conceivable that other analysts, such as geologists and environmental scientists, will use the SRM. In the case of cement, a quantity of 0.5 g was chosen and listed on the certificate of analysis as the recommended minimum quantity of material that could be taken as representative of the entire batch of cement. In other words, the analyst is advised to take samples of no less than 0.5 g in order to correctly compare his/her results to the certified values within the stated uncertainty given by NIST.

Homogeneity test data from a total of 50 specimens were subjected to an analysis of variance (ANOVA). Table 3 shows test results for Fe in SRM 1885a, including the average count rate for duplicate samples from each vial, the sample variance for two measurements (i.e., the square of the difference between two measurements divided by 2), and summary statistics describing variability of within- and between-vial measurements. The F value is less than F_{critical} (F_{crit}), indicating that variability among vials is not significantly different from variability between duplicates from any single vial. The two columns marked by the *Significant Difference* heading are flags from a set of control chart tests [4] used to indicate whether any single vial exhibits a statistically significant difference from the rest of the vials or a significantly greater difference between duplicate specimens than the remainder of the vials. It was expected that at least one vial out of 25 would be flagged for one or both *Significant Difference* columns, as was the case for vial number 171 for Fe in Table 3 because ANOVA and control chart tests were applied at the 95% confidence level.

Table 3
ANOVA for iron in proposed SRM 1885a

Vial numbers[a]	Count	Average (kcps)	Variance (kcps^2)	Significant difference	
				Between duplicates	From set of vials
1.0	2	22.119	0.00844		
1.1	2	21.943	0.01086		
3.2	2	22.065	0.00998		
4.2	2	22.036	0.00344		
5.5	2	22.013	0.00008		
8.1	2	21.974	0.00325		
10.0	2	21.979	0.00043		
10.1	2	22.082	0.00820		
12.2	2	21.963	0.00150		
15.3	2	21.980	0.00055		
16.2	2	22.012	0.00570		
17.1	2	21.959	0.02307	YES	
19.0	2	22.022	0.00000		
20.2	2	22.012	0.01079		
20.4	2	21.965	0.00402		
21.3	2	21.967	0.00068		
24.5	2	22.119	0.00314		
25.0	2	22.021	0.00018		
27.1	2	22.021	0.01348		
Average		22.013			
Standard deviation		0.052			

Source of variation	SS	df	MS	F	F_{crit}
Between vials	0.098	18	0.0055	0.96	2.18
Within vials	0.108	19	0.0057		
Total	0.206	37			

kcps = the measured X-ray count rate expressed as kilo-counts per second; SS = sum of squares; df = degrees of freedom; MS = mean square; F is the calculated MS ratio; F_{crit} is the 5% significance level critical value for the corresponding F distribution.

[a] The vial numbers represent 27 boxes of vials each containing

5. Accuracy

5.1. Bias

For certification of a material as an SRM, each contributing analytical method must be evaluated for sources of bias. In the case of XRF spectrometry, important sources of bias result from spectral line overlaps and physical interference including absorption and enhancement. The reader is referred to texts such as Bertin [5] for explanations of these effects. For cements, the following effects must be controlled or eliminated:

(a) the characteristic X-rays of each element are absorbed by the elements in the sample,

(b) the thickness of the borate bead is less than the infinite thickness for the characteristic X-rays of certain elements,
(c) the L-series X-ray lines of iodine (antiwetting agent at NIST) overlap the Ti $K-L_{2,3}$ lines used to determine the Ti contents of the cements, and
(d) the second-order diffraction of the $K-L_{2,3}$ lines of bromine (antiwetting agent at CTL) overlaps the Mn $K-L_{2,3}$ lines used to determine the Mn contents of the cements.

X-ray absorption effects are reduced by borate fusion because the sample is diluted. However, the dilution must be low to retain sufficient sensitivity for trace analysis. That is one reason for the quantities of cement and flux given in the Sample preparation section.

A specimen is infinitely thick if it transmits less than 1% of the X-rays that strike its surface. Borate beads 3 mm thick (7.5 g, 30 mm diameter) are not infinitely thick when the X-ray energy exceeds 9300 eV. Thus, it is a problem because the count rate of Sr $K-L_{2,3}$ X-rays depends on both the thickness of the bead and the mass fraction of Sr. To correct the problem, the count rate of the Rh $K-L_{2,3}$ Compton scatter peak from the X-ray tube, which depends in part on the thickness of the sample, was used as an internal reference.

Line overlaps were corrected by measuring another X-ray line from the interfering element and using the XRF software to subtract the interference. The software calculates an estimate of the interference or overlap as part of the calibration regression for the analyte element, in this case, either Ti or Mn.

5.2. Calibration

XRF calibration can be accomplished in several ways. For portland cement, CTL prepared calibration curves using SRMs from the 633 and 1880 series. NIST created synthetic standards that bracket the unknowns. Both approaches have the potential to be equally accurate. However, the NIST approach is characterized by lower uncertainty because it eliminates the need for matrix absorption corrections and it relates the calibration to ultra-high purity compounds, which have significantly lower uncertainties in their assigned mass fraction values than certified reference materials [6]. Fig. 2 is a calibration curve created using existing cement SRMs of the original 1880 series and is similar to the CTL approach. Fig. 3 is an NIST calibration curve created using four synthetic standards that bracket the compositions of fused samples of SRM 1880a. The bracketing standards were prepared to the mass fractions in Table 4 using high-purity compounds, typically 99.99% purity or better. Some components were weighed as the oxide and some were first diluted by borate fusion to keep all weights above 0.04 g, which minimizes the uncertainty due to the analytical balance.

Figs. 2 and 3 display Working-Hotelling-Scheffé (WHS) confidence bands [7,8] (dashed curves) to illustrate the magnitude of the uncertainty associated with a value obtained from each calibration curve for a hypothetical unknown specimen containing 1.00% by mass Fe_2O_3. Vertical arrows mark the upper and lower limits of the 95% confidence interval as estimated by the WHS method. In Fig. 2, the confidence interval is from 0.066% mass above to 0.063% mass below the found value. In Fig. 3, the

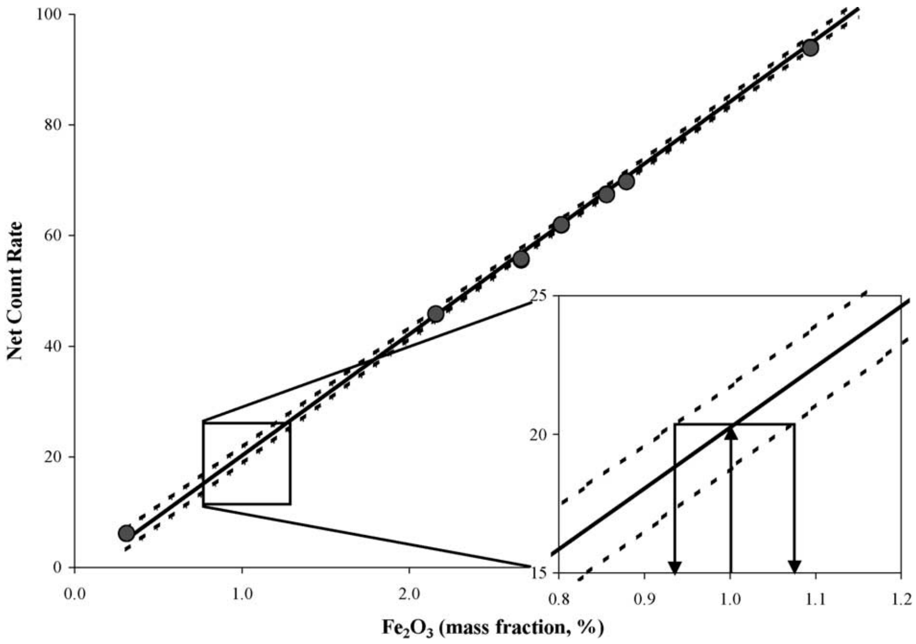

Fig. 2. Calibration by SRM 1880 series, Fe_2O_3 in Portland cement.

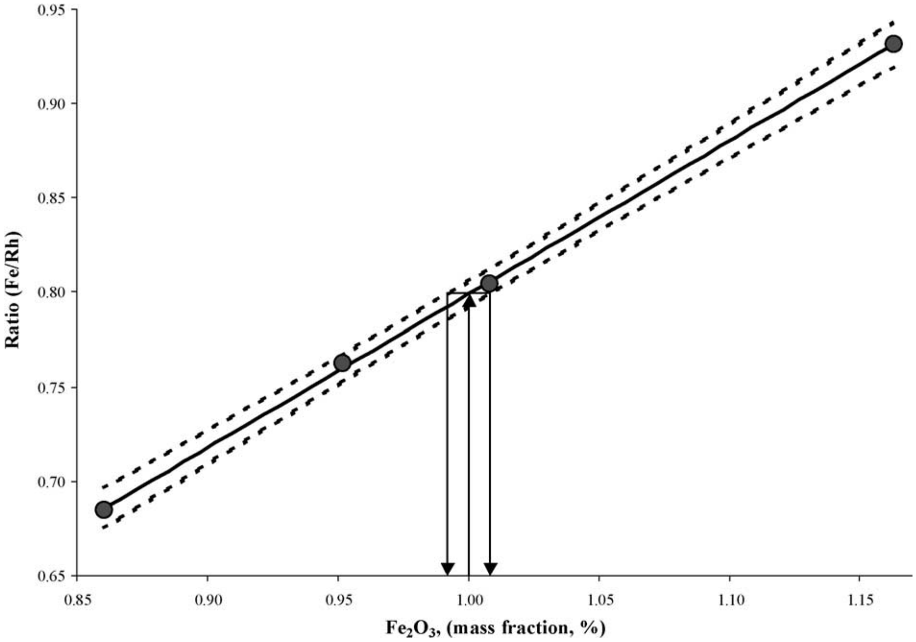

Fig. 3. Calibration by synthetic bracketing standards, Fe_2O_3 in Portland cement.

confidence interval is from 0.008% mass above to 0.008% mass below the found value of 1.00% mass Fe_2O_3. In this example, the estimated uncertainty using synthetic standards is smaller by a factor of eight than the estimated uncertainty using reference materials. The reader is cautioned that the WHS curves are just a means to estimate and illustrate the relative improvement in uncertainty possible with synthetic, bracket standards. A careful assessment of uncertainty is required with every analytical determination and the resulting estimates of uncertainty may be of different magnitudes than of those illustrated. However, the bracket standard approach will always be superior in terms of combined uncertainty.

The principal reason the bracketing approach to calibration works so well is that it simplifies the calibration model in XRF. The synthetic standards are designed to bracket the unknown so closely that a straight-line model is adequate for calibration. The compositions shown in Table 4 are designed to give a spread of $\leq \pm 3.5\%$ relative to the target composition for major components Ca and Si. For minor components Al, Fe, S and other elements, the bracket standards are $\leq \pm 15\%$ away from the target composition. For trace components, the bracket standards are designed to calibrate the linear response range of the matrix, usually from 0 to 0.02% by mass. Finally, the compositions are adjusted so that no single standard contains most of the high or low mass fractions for the elements to be calibrated so that the sample mass absorption coefficients of all standards are nearly equal. With this design, matrix effects are not eliminated, but they are tightly controlled. A comparison of the range of Fe_2O_3 mass fractions in Figs. 2 and 3 shows how much narrower the range is for the synthetic standards. In addition, the SRMs used in Fig. 2 do not provide a calibration point near to the target mass fraction of 1.00%, which causes the WHS bounds to diverge more rapidly.

There are additional advantages and some disadvantages to the bracket standard approach to calibration. The calibration is based on primary compounds, which allows the analyst to reserve SRMs for validation of the analytical results. It also reduces the uncertainty associated with the assigned value for the analyte in the new reference material. For high-purity compounds, the relative uncertainty in the assay is typically 0.1% or better versus the typical relative

Table 4
Compositions of synthetic calibration standards for analysis of portland cement SRM 1880a using XRF spectrometry

Constituent	Standard 80a1	Standard 80a2	Standard 80a3	Standard 80a4
CaO	21.1968	22.2520	21.7037	20.6514
SiO_2	6.73398	6.91144	6.57541	7.06158
Al_2O_3	1.72998	1.65157	1.81281	1.90527
Fe_2O_3	1.00831	1.16303	0.95212	0.86077
SO_3	0.23839	1.02505	1.13406	0.29160
MgO	0.67686	0.63081	0.57722	0.51582
K_2O	0.28050	1.20610	1.33437	0.34310
TiO_2	0.09740	0.07064	0.07956	0.10606
Na_2O	0.04454	0.05950	0.02984	0.07165
SrO	0.01487	0.02241	0.03807	0.02995
P_2O_5	0.10201	0.13628	0.06834	0.16410
ZnO	0.00000	0.00118	0.00235	0.00356
Cr_2O_3	0.00292	0.00000	0.00147	0.00442

All values are mass fraction (%) in the borate bead.
Composition values are presented to the same number of digits as the mass values used in creating them or the nearest 0.1 mg/kg in order to preserve information. The number of significant digits in the final result of a determination is a function of the expanded uncertainty estimate.

Table 5
Results and value assignment for Fe_2O_3 in SRM 1880a

Replicate	NIST XRF	CTL XRF	CTL AAS
1	2.779	2.789	2.80
2	2.787	2.820	2.83
3	2.787	2.817	2.80
4	2.784	2.820	2.84
5	2.779	2.815	2.81
6	2.772	2.819	
7	2.781	2.814	
8	2.788	2.824	
9	2.794	2.786	
10	2.797	2.806	
11	2.780	2.812	
12	2.790	2.822	
13	2.774	2.903	
14	2.775	2.920	
15	2.787	2.807	
16	2.782	2.813	
Laboratory mean	2.783	2.824	2.816
s	0.022	0.113	0.018
n	16	16	5
Unweighted mean	2.808	Mean of three laboratory means	
Expanded uncertainty	0.025	$= 2s/\sqrt{3}$	
Weighted mean	2.806	Maximum likelihood estimate	
Expanded uncertainty	0.041	$= 2\sqrt{v_b + v_w}$	

All values in mass fraction, %.
v_b = variance among labs and v_w = pooled within lab variance.

uncertainty in a certified value for an SRM of 1% or higher. Nettles [9] used high-purity compounds to simulate the SRM 1880 series cements. Calibrations made using the simulated cements demonstrated improvements of the standard error of estimate when weighing errors were under control. One disadvantage of the bracket approach is the labor required to create synthetic standards including drying and heat-treating high-purity compounds [10,11], careful weighing of, in this case, 15 ingredients and careful design of the compositions using a spreadsheet. It is also necessary to establish reliable estimates of the unknown's composition to use when designing synthetic standards. A calibration made from a set of certified reference materials was used for this purpose.

6. Value assignment

Value assignment was done by combining results from two or more methods to create a certified value with an associated estimate of uncertainty. As stated above, certified values for cement SRMs were obtained using XRF results from NIST and CTL and classical determinations by CTL. Once again, iron can be used as an illustrative example of the value assignment process for all analytes. Table 5 contains the results of three different determinations of Fe in SRM 1880a, one done at NIST and two at CTL. These results were evaluated by the statisticians, who provided a consensus value and an estimate of expanded uncertainty at the 95% confidence level using different published meta-analysis methods [12,13]. The weighted mean and its associated expanded uncertainty were assigned as the certified values for Fe_2O_3 in SRM 1880a.

7. Conclusion

NIST is replacing the SRM 1880 series of portland cement and calcium aluminate cement certified reference materials. The new 1880a series includes ordinary portland cement, portland cement with slag and fly ash admixture, white cement and calcium aluminate cements (see http://srmcatalog.nist.gov/srmcatalog/tables/113-1.htm/ for a complete listing of these SRMs). XRF spectrometry was used to demonstrate that all materials are characterized by sufficiently low heterogeneity to be used for the purpose of qualification for ASTM C 114. Certified, reference and information values were assigned from determinations at NIST and CTL. NIST developed and applied a new matrix-independent borate fusion/bracket standard XRF method characterized by significantly lower levels of uncertainty than normal calibration approaches that use artifact standards (reference materials) as calibration standards.

Acknowledgements

The Cement and Concrete Reference Laboratories program donated materials for four of the cement SRMs. R. Haupt of the NIST Building and Fire Research Laboratory provided CCRL reports and consultation. D. Friend of the NIST Standard Reference Materials Program designed the vial loading chamber shown in Fig. 1. Certain commercial services, instruments and chemicals are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the services, equipment and chemicals are necessarily the best available for the purpose.

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