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ABSTRACT

Quantitative X-ray powder diffraction analysis (QXRD) is being used within the cement industry for phase characterization of hydraulic cement. The current ASTM standard test method for powder diffraction analysis of cements provides guidance, but not an explicit method, for quantifying phase concentrations. The standard utilizes qualification criteria, where an analysis of a set of certified reference materials must fall within stated precision and bias limits. Validation of X-ray powder diffraction analyses by the Rietveld method is particularly important because the normalization inherent in the mass fraction calculations can obscure accuracy problems. Currently, the only certified reference materials for phase abundance are a set of NIST SRM clinkers, which lack the calcium sulfate and carbonate phases found in portland cements. A set of portland cements was distributed to 29 laboratories for analysis according to each lab's individual protocols. The objective was to provide each lab with quantitative feedback on its precision and accuracy performance. The results from all the labs are presented graphically with Youden plots that incorporate ranking to illustrate relative lab precision and accuracy based upon a consensus mean for each phase and ASTM C1365 performance qualification criteria. Labs that fall outside of the compliance limits are provided with information via the Youden plots to assess their systematic and random error. Proficiency testing of this sort provides

participating laboratories with a quantitative assessment of their performance relative to peers using a wider range of materials encompassing the broad spectrum of modern hydraulic cement production. These newer materials may include, for example, the calcium sulfate phases and the limestone additions that have become commonplace in today's cements. Such a quantitative assessment could be used to qualify laboratories and may be stipulated in a specification.

Introduction

Standard test method validation is generally accomplished through interlaboratory testing and development of a precision statement. If certified reference materials are available, a statement on bias may be possible. ASTM C1365 [1], standard test method for X-ray powder diffraction analysis of clinker and cement, provides guidance and performance criteria for X-ray powder diffraction analysis of cements. Rather than provide a specific set of steps to follow in the analysis of cement, C1365 provides performance criteria that labs and analysts must meet in order to claim compliance with the test requirements, a process called qualification. Qualification involves documented analyses of certified reference materials, such as NIST SRM 2686, 2687, and 2688 for cement clinkers, with precision and bias performance criteria previously established from an inter-laboratory study [2].

Being performance-based, ASTM C1365 provides flexibility in the selection of a protocol. If, however, a laboratory lacks an explicit procedural format, it may result in higher levels of random (precision) and systematic (bias) error, or uncertainty. Cement and clinker phases pose challenges in phase identification as most, if not all, of the intense diffraction peaks are subject to partial or complete overlap, and diffraction peaks from major phases can obscure low-concentration phase diffraction peaks. With few resolvable peaks for identification, an alternate approach is necessary for phase identification based upon key resolvable diffraction peaks. These key peaks are not typically the most intense peaks for a phase, but those that are less likely to have an overlap with other phases in the cement. ASTM C1365 does provide a list of important diagnostic peaks to facilitate phase identification.

The normalization of the mass fraction calculations in the Rietveld calculations and the lack of a representative range of certified cement reference materials make identification of bias difficult. Given that individual lab bias generally dominates method-specific biases, a statement on method bias becomes difficult to formulate, making comprehensive calibration essentially impossible [2,3].

In developing an individual lab protocol, identification and resolution of measurement issues typically involve the use of synthesized phases, in-house compounded samples, clinkers that have been subjected to a light microscope point count, or certified reference materials [4–7]. An alternative approach to developing and validating a lab protocol is to incorporate proficiency testing. This approach was developed by Youden [8], applied to cement testing [9], and used by the Cement and Concrete Reference Laboratory (CCRL) for a wide variety of chemical and physical cement analyses to assess laboratory precision and to rate laboratory performance based upon consensus means.

Adopting anonymous proficiency testing for X-ray powder diffraction analysis of hydraulic cements provides a number of advantages: (1) enabling a regular supply of new materials from actual industrial cements, which include calcium sulfate and carbonate phases lacking in the clinkers, (2) testing a laboratory protocol against consensus values from a large group of laboratories, (3) developing insight into individual lab precision and accuracy, (4) ranking performance by phase against precision and accuracy qualification criteria required by ASTM C1365 [1], (5) anonymously contributing and then comparing one's performance against the collective results of peers, and (6) identifying precision and accuracy problems in the test method.

A trial proficiency test program was initiated for quantitative X-ray powder diffraction of hydraulic cements by distributing two industrial cements to each of the participating laboratories. Participants were instructed to use their own laboratory preparation, data collection, and data reduction protocols, and to provide as much detail to the organizers as possible. The test program specified replicate analyses that are not generally used in routine proficiency testing, but which will be used in a subsequent report on refining precision and accuracy estimates for ASTM C1365 [1].

The Proficiency Test Program

CCRL provided a pair of cements for each lab (25 g samples sealed in glass vials) that were chosen from among those used in the chemical proficiency test program cements 177 (A) and 178 (B) (**Table 1**) [10]. These cements were taken from commercial production and were homogenized in a V-blender prior to packaging. Each lab participating in the trial test program was instructed to perform a quantitative

TABLE 1

CCRL oxide results and ASTM C150 phase estimates from chemical analyses for cements A and B. The manufacturers each reported a mass fraction of 3.7 % limestone.

	A	B
SiO_2	20.72	19.53
Al_2O_3	4.46	4.44
Fe_2O_3	2.87	3.09
CaO	63.58	63.68
MgO	2.26	2.50
SO_3	2.70	3.38
Na_2O	0.175	0.120
K_2O	0.559	0.496
Alite	53.2	61.5
Belite	19.0	9.4
Aluminate	7.0	6.5
Ferrite	8.7	9.4

analysis by XRD in triplicate. Each lab was assigned an identification number allowing it to identify its results while maintaining anonymity. Details on each lab's analytical procedures were requested in order to enable investigation of procedure-induced bias from factors like the use of specimen grinding, hydraulic press mounting, and preferred orientation corrections. Data were returned on pre-formatted spreadsheets to facilitate processing and analysis. Samples were sent to 36 participating laboratories, and 29 of these laboratories returned data.

This proficiency test program differs from that described in ASTM E2489 [11] in that the precision criteria for ranking are not being derived from the data, but from the qualification limits from ASTM C1365 [1]. The qualification criteria include repeatability (within-lab) and reproducibility (between-lab) standard deviations and accuracy limits against a known value using the mean of 2, 3, or 4 replicate determinations. The ranking system of proficiency testing [9] was adopted to expand the information from reproducibility results by assigning a rank based upon each lab's performance, rather than pass/fail criteria. The ASTM C1365 reproducibility criteria (d2s) would be approximately 2.5 standard deviations, or a ranking of 1.

Accuracy is the "closeness of agreement between a test result and an accepted reference value" and contains random uncertainty compared to bias [12]. Uncertainty introduced by individual lab protocol appears to dominate that of method bias, particularly when the method does not explicitly specify the process. Use of a certified reference material is less helpful in these cases, as the computed bias will not represent most individual lab's performance [2] and, additionally, certified reference materials may not be available. An alternative may be found in using cements, for which certified reference materials are not available for phase abundance, and comparing each lab's performance against the consensus value of the participants. The consensus value is used because the individual lab uncertainties tend to cancel out, providing an improved estimate of the true value. Since there is a lab effect (outliers), the consensus value for each analyte is established using a trimmed mean of means. This is a modification of a mean of means model used in early SRM work using the 3-point mean from each lab and an 80 % trimmed mean across all laboratories. The 3-point mean reduces within–lab random uncertainty while the trimmed mean of means reduces the influences of outliers by the mean of the data excluding 10 % from the top and bottom of ranked mean determinations [13].

The ASTM C1365 [1] accuracy criteria are based upon a prediction interval developed from the composite results of an inter-laboratory study [2]. ASTM C1365 95 % prediction intervals should contain the measurement estimate for a single future observation and are based upon three-point means for this program. Falling within this interval indicates a lab's accuracy is similar to that of the collective results of the inter-lab study participants.

RECALCULATION OF CALCITE QUALIFICATION CRITERIA

New calcite ($CaCO_3$) qualification values were derived from these data, as an unusual number of labs failed the original ASTM C1365 [1] limits for calcite. The overly restrictive accuracy limit may be a result of the calcite qualification criteria in ASTM C1365 being based upon a single cement for and an unusual occurrence of

TABLE 2

Calcite repeatability (sr) and reproducibility (sR) values expressed as a single standard deviation and 95 % limits for repeatability (r) and reproducibility (R) where n = 24.

Material	Mean	s_r	s_R	r	R
A	2.58	0.1936	0.9498	0.54	2.66
B	2.51	0.2176	1.0517	0.61	2.94
pooled		0.2059	1.0020	0.57	2.78

the between-lab standard deviation being smaller than the within-lab standard deviation [2]. Following ASTM E691 [14], calcite precision was re-estimated (**Table 2**) based upon two cements and three replicates, each from 29 laboratories, and the qualification criteria were re-calculated. These values will be used for the qualification criterion in place of those given for calcite in ASTM C1365. A future report will evaluate all phases for consideration by ASTM in future revisions of the ASTM C1365 test method.

ASTM C1365 STANDARD TEST METHOD

ASTM C1365 [1] was first adopted in 1998 for quantitative X-ray powder diffraction analysis of portland cement and portland cement clinker. A novel feature of this standard test method is a requirement for demonstrating the ability to perform an analysis comparable to the consensus performance of a set of competent labs from an inter-laboratory study. This qualification process uses a set of three SRM clinkers available from NIST for the determination of proportions of alite, belite, aluminate, ferrite, and periclase, which are all the phases discussed in the ASTM C150 [15] cement specification. The ASTM C1365 qualification criteria consist of repeatability and reproducibility standard deviations (**Table 3**), and accuracy (**Table 4**) relative to the certified SRM values [1,2].

TABLE 3

Repeatability and reproducibility expressed as 1−σ and 95 % limit where the results of two tests by should not vary more than the 95 % limit (ASTM C1365).

	Repeatability Within-Lab	95 % Limit (r)	Reproducibility Between-Lab	95 % Limit (R)
alite	0.74	2.04	2.27	6.30
belite	0.64	1.77	1.40	3.87
aluminate	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[a]	0.21	0.58	1.00	2.78

[a]Revised values based upon current proficiency data.

TABLE 4

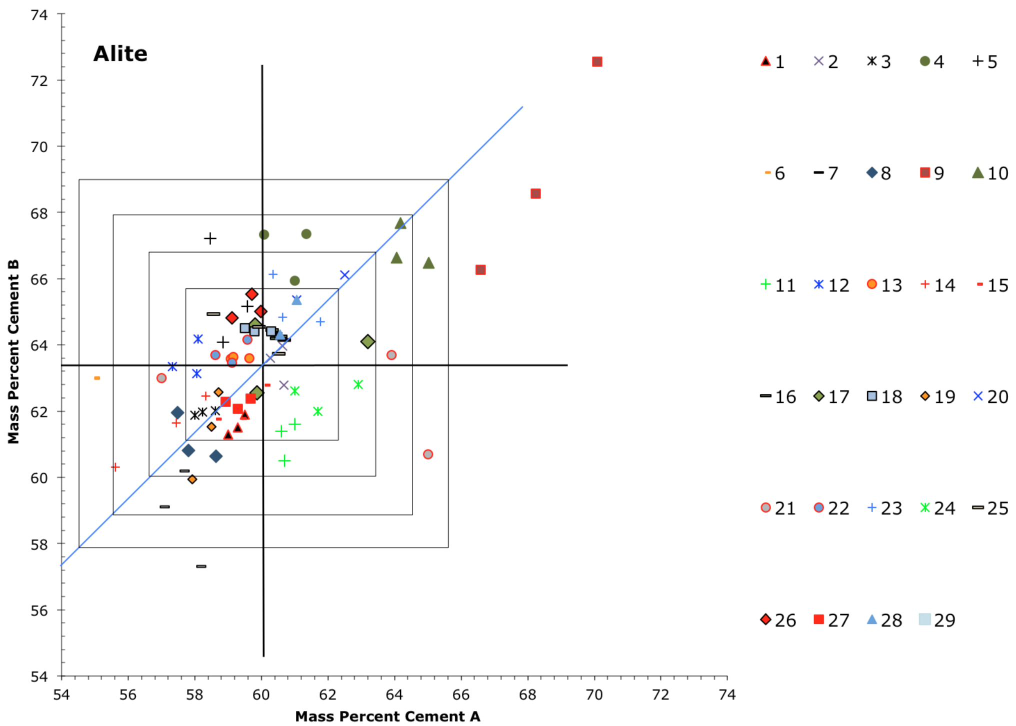
Prediction intervals for n = 2, 3, 4 replicate measurements, corrected from ASTM C1365.

	2	3	4
alite	3.38	2.80	2.45
belite	2.08	1.72	1.51
ferrite	1.32	1.10	0.96
aluminate	1.17	0.97	0.85
periclase	0.74	0.62	0.54
gypsum	0.88	0.73	0.64
bassanite	0.86	0.71	0.63
anhydrite	0.95	0.79	0.69
arcanite	0.51	0.42	0.37
calcite[a]	1.53	1.27	1.12

[a]Revised values based upon current proficiency data.

Most of the participants in this study indicated that they were not currently qualified, so this was not made a prerequisite for participation. The qualification limits from ASTM C1365 and the recalculated calcite criteria were applied to results of their analyses of the two cements, with the trimmed mean of means value representing the consensus estimate of phase abundance for each analyte as described previously.

FIG. 1 Alite Youden plot delineated by 1, 1.5, 2, and 2.5 standard deviations from the means.



Graphical Illustration Using the Youden Plot

The Youden plot is a scatter plot used to compare within- and between-laboratory variability and to identify labs with repeatability (within-lab) and reproducibility (between-lab) problems. Measurements on a specific phase, from the two cements, constitute the *x*- and *y*-coordinates to form a point on the plot. Given that three replicate determinations are made, each lab will have three points per plot, the clustering providing a visual indication on their repeatability. Two perpendicular lines bisect the overall cloud of points, marking the trimmed mean of means for each across-lab sample, dividing the plot into four quadrants. A third line runs diagonally from the lower left to upper right quadrant, passing through the trimmed mean of means coordinates as a 1:1 line. The scatter of the points and their position along the diagonal illustrates the random and systematic error components in the overall uncertainties of the individual lab's measurements.

Youden observed that the systematic error of each lab, rather than random error tends to dominate the results. If random error predominates, any point would have an equal chance of falling either above or below the mean, generating a roughly equal number of points in each quadrant and appearing in a roughly circular pattern. Generally, however, the cloud of points appears elongated along the diagonal line, reflecting the dominance of the systematic error. Points far along the diagonal represent a positive (upper-right) or negative (lower-left) systematic error, reflecting the fact that a lab that gets a high result on one material

FIG. 2 Belite Youden plot delineated by 1, 1.5, 2, and 2.5 standard deviations from the means.

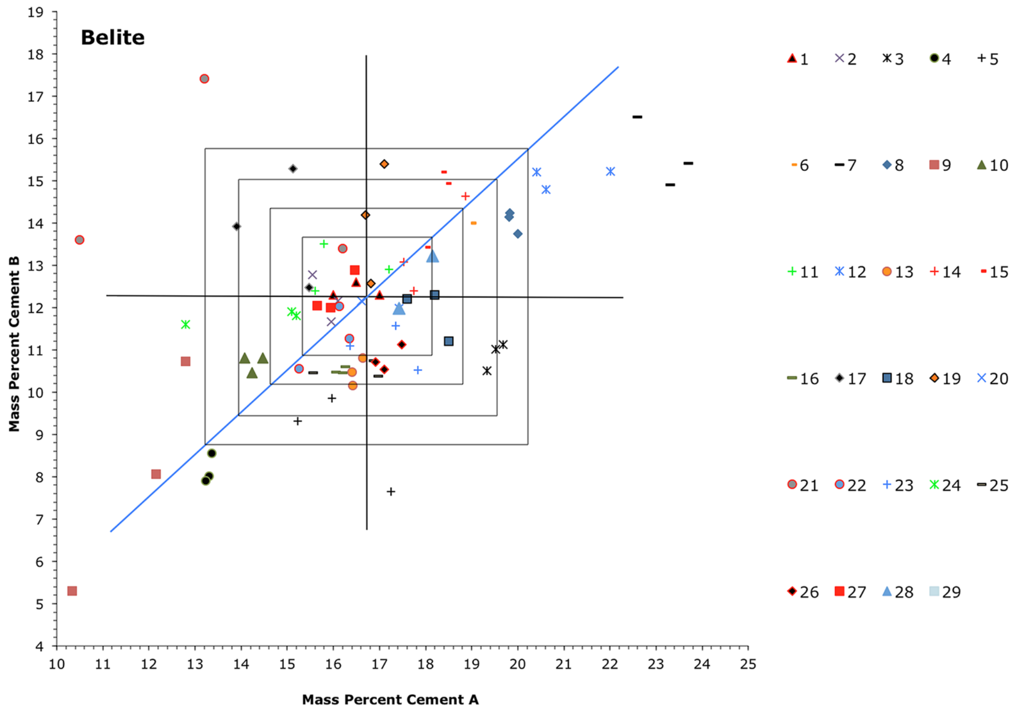
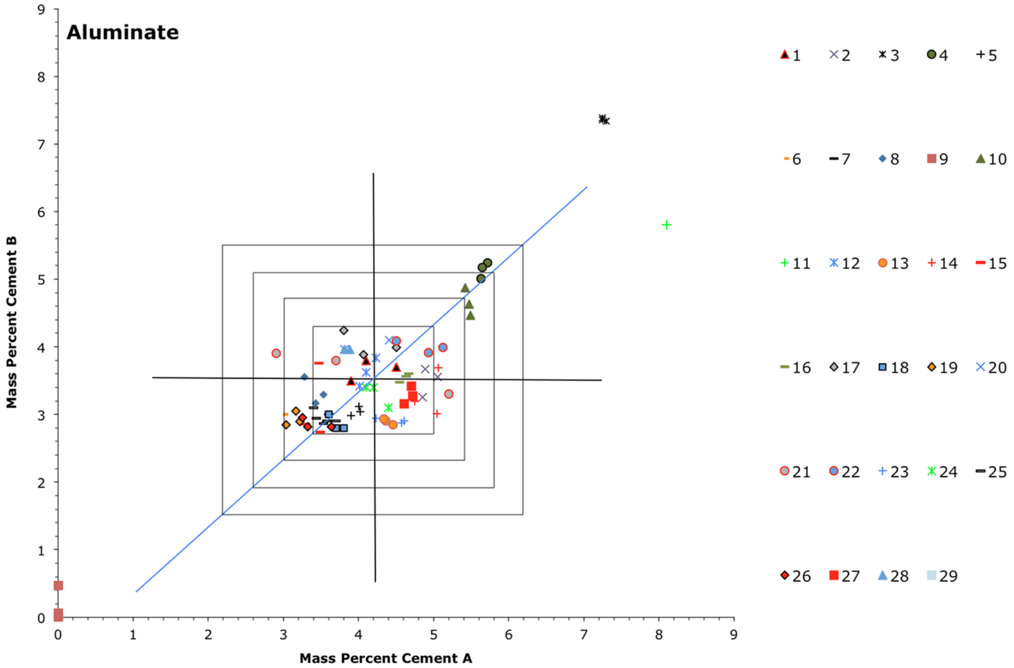


FIG. 3 Aluminate Youden plot delineated by 1, 1.5, 2, and 2.5 standard deviations from the means.



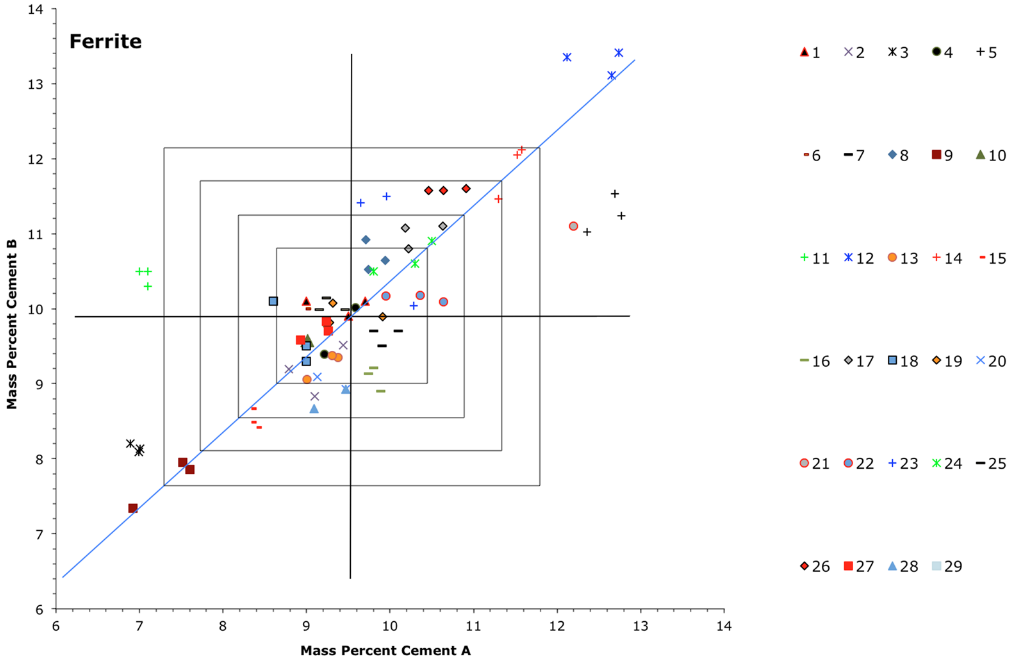
will likely have a high result on the other. Points that fall away from the diagonal indicate some inconsistency for that lab; for example, poor within-lab precision or a problem with one specimen. In general, the width of the data projected onto a perpendicular to the diagonal is proportional to the test random error, while the width of the data projected onto the diagonal itself is proportional to the systematic error [11].

The modified Youden plots presented here (**Figs. 1–6**) have been augmented with boxes representing 1, 1.5, 2, and 2.5 standard deviations from the mean, based upon the ASTM C1365 [1] 1σ reproducibility precision. These bounds define rankings from 4 to 0, respectively, with higher numerical ranking representing better laboratory performance. Each lab is anonymously identified by a color and shape-coded symbol. The rankings can also be presented in tabular form. Graphical representation of single-phase data in the form of a strip plot (**Figs. 7–10**) is similar to a histogram with lab results coded by lab number, organized horizontally according to value.

OBSERVATIONS ON TEST RESULTS

The dispersion of the data within the Youden plots for alite, belite, and aluminate appear generally circular with some elongation along the 45° line. Plots for ferrite, periclase, and calcite show a more pronounced elongation. In the case of calcite and possibly ferrite, the propensity for preferred orientation due to calcite's rhombic and ferrite's tabular crystal habits may result in a greater incidence of systematic error if an orientation correction is not made, or made in a way where the bias increases.

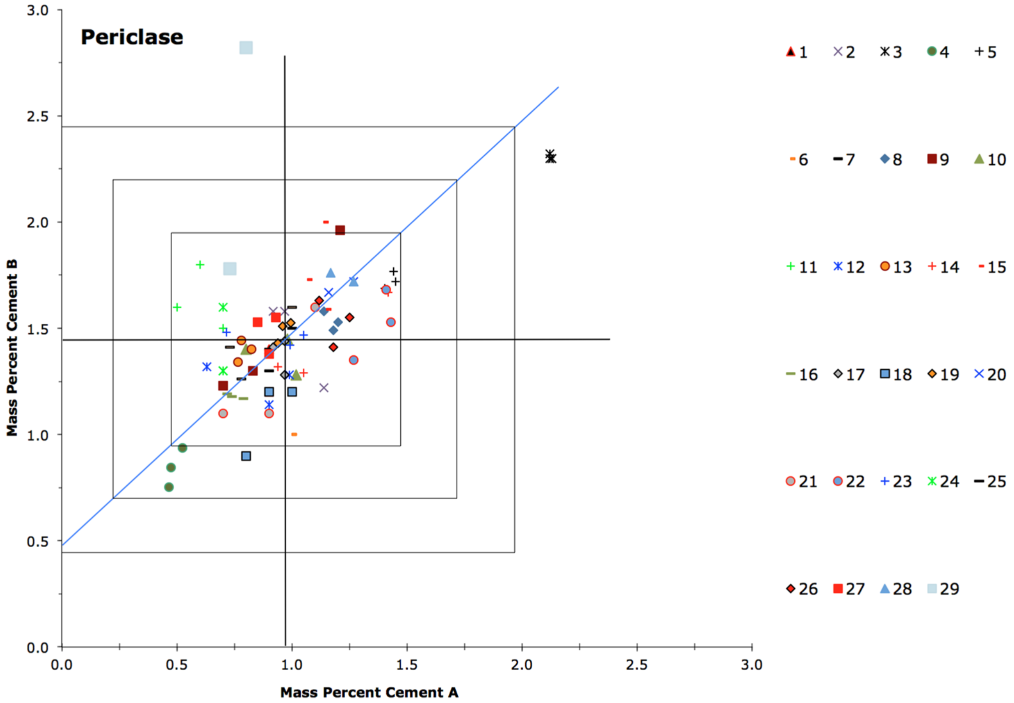
FIG. 4 Ferrite Youden plot delineated by 1, 1.5, 2, and 2.5 standard deviations from the means.



An example of a lab that scores well for all analytes is lab 27, where the all the reported values lie close to the 45° lines and to the intersection of the mean lines. This lab's results fell inside the smallest box ($\pm 1\sigma$) for all phases but bassanite (as seen in tabulation), where they fell inside the 1.5 σ box. In **Fig. 1** of the alite Youden plot, Lab 21 exhibits a large random error (relatively wide point clustering), and greater difficulty with cement A, suggesting that Lab 21 should consider improving its sample preparation and measurement processes to achieve more consistent results. Averaging test results can reduce lab bias due to imprecision. While the individual determinations for Lab 21 exhibit relatively poor repeatability, a test result being an average of multiple determinations would reduce bias in their case, as seen later in the prediction interval plot that utilizes the mean of three replicates.

Labs showing an alite inaccuracy tend to have an opposing anti-correlated estimate for belite. For example, Lab 9 shows a positive alite estimate, having its values fall outside the upper-right quadrant, resulting in a ranking of 0 for all the replicates. Lab 9 exhibits a similar inaccuracy in the opposite direction for belite, ferrite and aluminate. Given the far right quadrant point placement and distance from the 45° line for alite, Lab 9 exhibits both systematic and random error. Lab 9 used unground samples, top loading using a high-pressure mounting press, and a preferred orientation correction, which while not explicitly so noted, was presumably for alite. In contrast, Lab 7 shows a negative inaccuracy for alite and a positive inaccuracy for belite. Lab 21 shows poor repeatability, and a positive alite inaccuracy with corresponding low belite estimates in two of its three replicates, particularly for cement A. This anti-correlation may be the result of the

FIG. 5 Periclase Youden plot delineated by 1, 1.5, 2, and 2.5 standard deviations from the means.



substantial peak overlap and the correlation between their scale (intensity) variables or it could be the result of the normalization in calculation of mass fractions. Attempts to correlate processing and analysis procedures with accuracy problems were not successful as most summary reports provided few details on the use of preferred orientation correction.

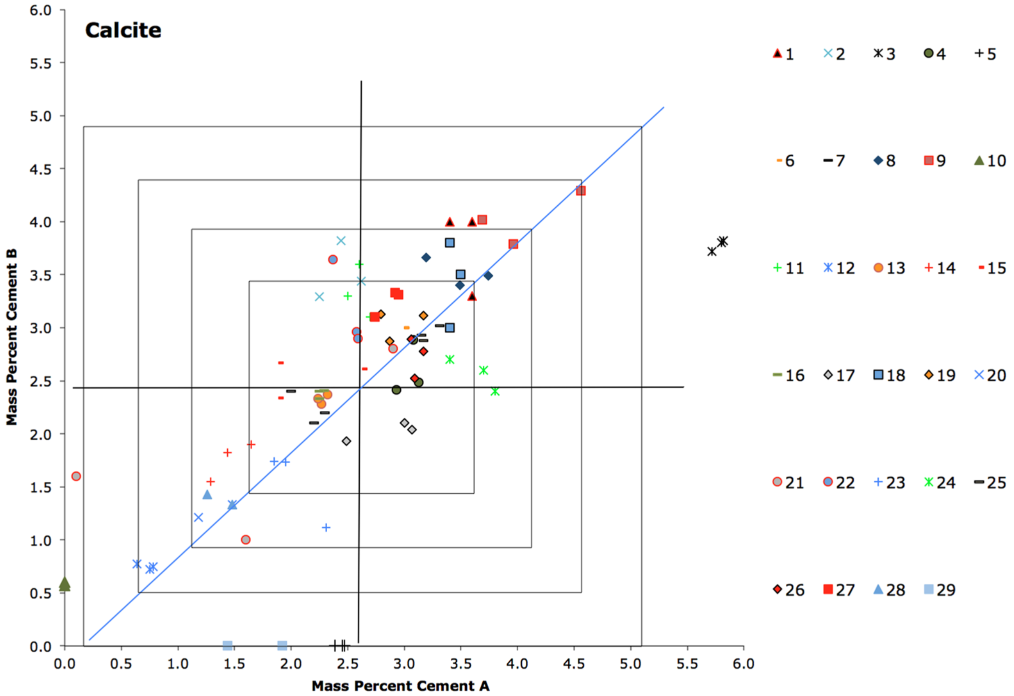
PLOTS FOR SINGLE-OCCURRENCE PHASES

In the cases where a phase is identified in only one of the two cements, a point plot is useful for visualizing the test results. Plots for gypsum, bassanite, anhydrite, and arcanite are presented in **Figs. 7–10**. The vertical axis represents the mass percentage of the phase with replicates for each lab stacked in columns along the *x*-axis. The consensus mean value is indicated with a horizontal solid line parallel to the *x*-axis and the performance interval bounds noted by numerical values on the dashed lines. This presentation provides each lab with a sense of its within-lab precision (repeatability) based upon their point clustering and accuracy relative to the consensus mean.

PRECISION

Table 5 shows how individual labs compared to the ASTM C1365 [1] repeatability criteria, broken out by phase and designated by P/F for pass or fail. Currently within C1365, the pass/fail criteria apply to individual phases. Therefore, a fail on a single phase will not invalidate the entire analysis, but it does indicate that the analyst should review the lab's analysis protocol.

FIG. 6 Calcite Youden plot delineated by 1, 1.5, 2, and 2.5 standard deviations from the means.



New calcite precision criteria were established using these data, so that few labs would fail for this phase. Labs 28 and 29 exhibited some difficulty in meeting the within-laboratory precision criteria for many of the phases for both cements, while labs 5, 9, and 21 had difficulties with one of the two cements. Labs 11 and 17 missed the limits for tricalcium aluminate and belite, respectively, for a single cement. No single cement appears to have exclusively presented precision problems, indicating that for these analyses the samples were probably relatively homogeneous.

Proficiency scores are presented in **Table 6** based upon the ASTM C1365 95 % limits, r and R, (**Table 2**) [1]. In this example, the difference between the first two replicates and the consensus mean were evaluated based upon the maximum allowed for qualification. Proficiency scores are presented for the first replicate by cement (A, B) and phase for each participant where 4, 3, 2, 1, and 0 represent $\leq$1, 1.5, 2, 2.5, and $\geq$2.5 standard deviations, respectively, from the mean, with the sign indicating the direction of inaccuracy. A score of 1 is approximately the same as the 95 % limits from ASTM C1365, as reported in **Table 1** of ASTM C1365. If proficiency testing becomes part of a qualification scheme for ASTM C1365, the Subcommittee will need to specify what constitutes a reasonable performance limit before requiring a re-evaluation of the laboratory procedures and re-certification using the SRM clinkers.

BIAS QUALIFICATION USING PREDICTION INTERVALS

For each lab, the mean of the three replicates was calculated and compared to the limits in **Table 4** for the appropriate number of replicates to check conformance to

FIG. 7 Gypsum plot by lab for cement B, with a solid consensus mean arrow and dashed lines bounding performance levels.

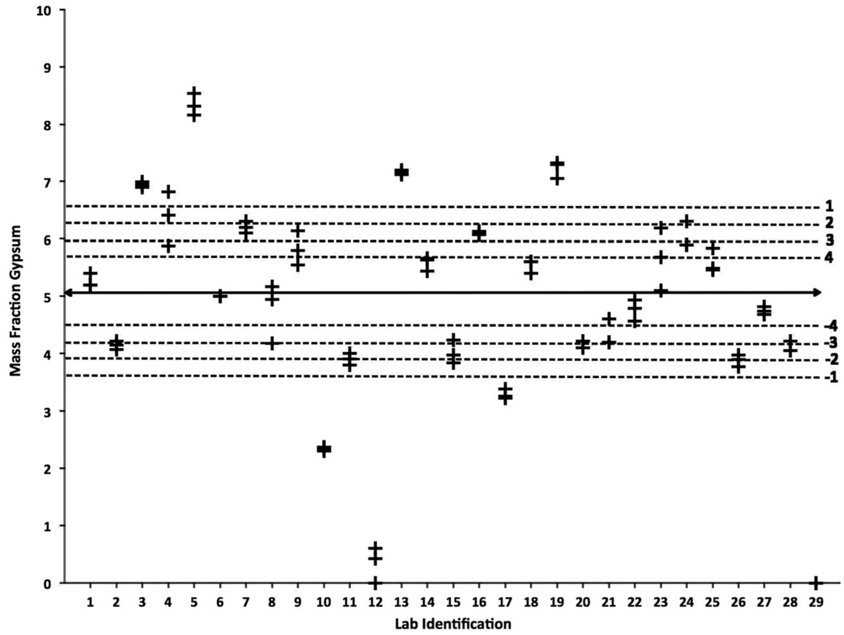


FIG. 8 Bassanite plot by lab for cement A, with solid consensus mean arrow and dashed lines bounding performance levels.

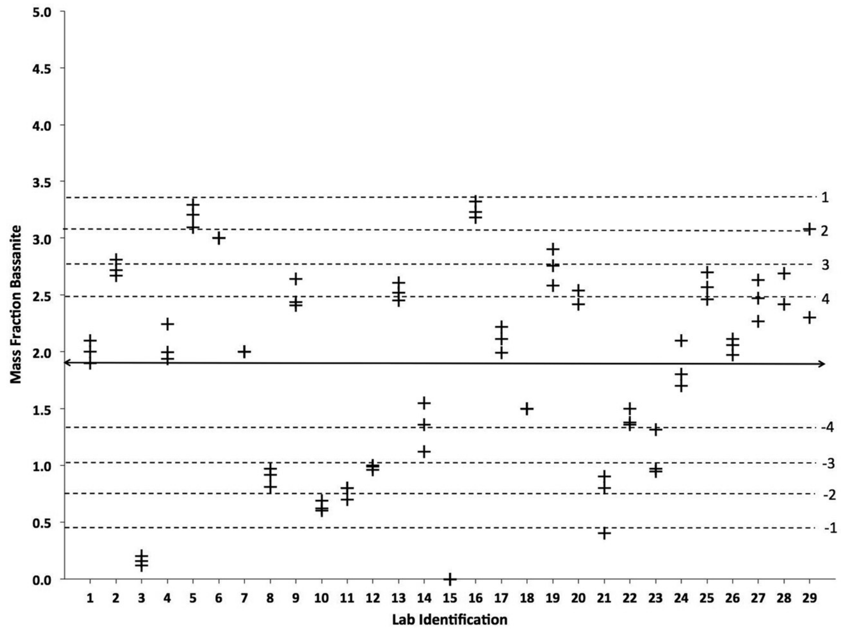


FIG. 9 Anhydrite plot by lab for cement A, with solid arrow consensus mean marker and dashed lines bounding performance levels.

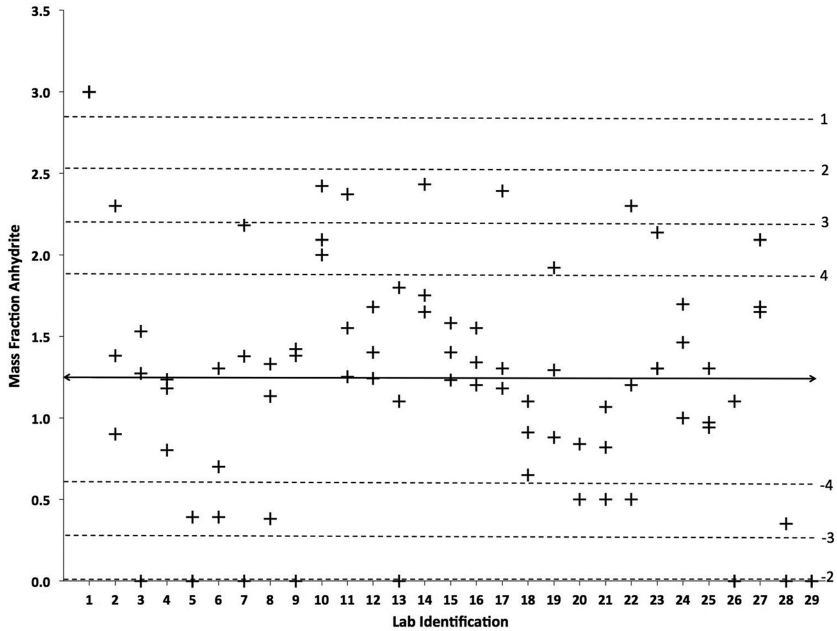


FIG. 10 Arcanite plot by lab for cement A, with solid arrow consensus mean marker and dashed lines bounding performance levels.

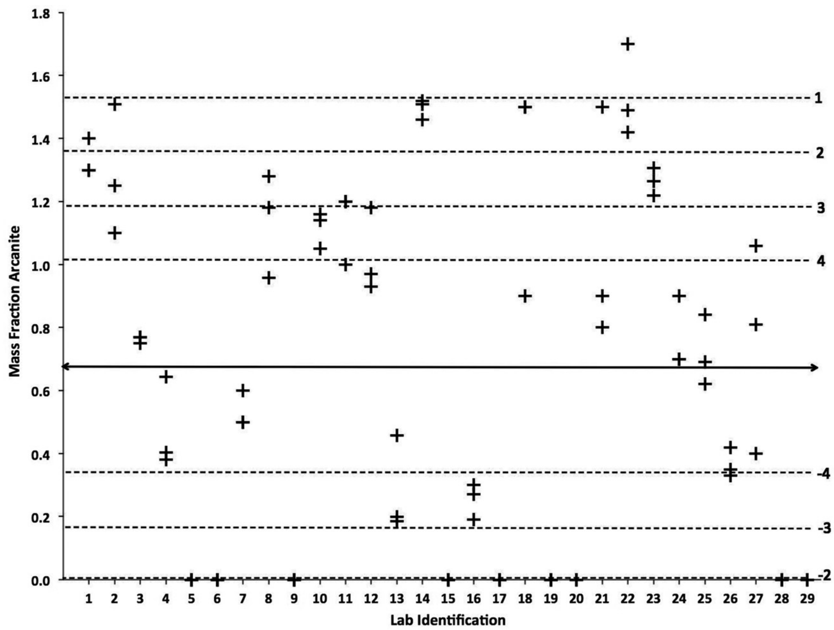


TABLE 5

Pass (P)–Fail (F) precision qualification by phase based upon the C1365 repeatability (within-lab) 95 % limits on maximum difference between duplicates from the first two replicates.

	Alite		Belite		Ferrite		Aluminate		Periclase		Arcanite	Anhydrite	Bassanite	Gypsum	Calcite	
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**A**	**A**	**B**	**A**	**B**
1	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
2	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
3	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
4	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
5	P	**F**	P	**F**	P	P	P	P	P	P	P	P	P	P	P	P
6	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
7	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
8	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
9	P	**F**	P	**F**	P	P	P	P	P	P	P	P	P	P	P	P
10	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
11	P	P	P	P	P	P	**F**	P	P	P	P	P	P	P	P	P
12	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
13	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
14	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
15	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
16	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
17	P	P	P	**F**	P	P	P	P	P	P	P	P	P	P	P	P
18	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
19	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
20	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
21	**F**	P	**F**	P	**F**	P	P	P	P	P	P	P	P	P	P	P
22	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
23	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
24	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
25	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
26	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
27	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
28	P	**F**	**F**	**F**	P	P	P	P	P	P	P	P	P	P	**F**	P
29	**F**	**F**	**F**	P	P	**F**	P	P	P	P	P	P	P	P	P	P

the accuracy qualification criteria, using mean values as the consensus. This table is a modification of that in ASTM C1365 [1] to correct an error in the original calculation of the intervals. **Tables 7** and **8** show results of the prediction interval qualification, with the mean values on the bottom row and boldface for values exceeding the prediction interval bounds. In some cases, no value was reported and the slot is left empty. In others, a value of zero was reported as such. Averaging the replicate determinations improved the apparent quality of the results from some participants because the averaging can offset a relatively high random error; for example, with alite in cement A for lab 21. In other instances with high systematic error (e.g., Labs 9 and 10), averaging did not help a lab to meet the prediction interval qualification criteria. Proficiency test reporting criteria making explicit the distinction between

TABLE 6

Proficiency scores for the first replicate by cement (A, B) and phase for each participant where 4,3, 2, 1, and 0 represent ≤ 1, 1.5, 2, 2.5, and ≥ 2.5 standard deviations from the median, with the sign indicating the direction of bias.

	Alite		Belite		Ferrite		Aluminate		Periclase		Arcanite	Anhydrite	Bassanite	Gypsum	Calcite	
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**A**	**A**	**B**	**A**	**B**
1	−4	−4	4	4	−4	4	−4	−4	−4	−4	2	1	4	4	3	2
2	4	4	−4	4	−4	−4	4	4	−4	−4	2	1	3	4	4	2
3	−4	−4	−4	4	4	4	−4	4	−4	−4	2	1	−1	−4	3	4
4	4	2	−4	−4	−4	−3	4	4	−4	4	3	4	−4	3	4	4
5	−4	2	−4	−4	−4	−4	3	−4	4	4	1	2	2	3	−4	4
6	−2	−4	−4	−4	−4	−4	4	−4	4	−4	2	−4	2	3	−4	3
7	−3	−4	2	−4	−1	−2	0	0	1	2	4	−2	0	−1	0	3
8	−3	−4	2	−4	−1	−2	0	0	1	2	4	4	−2	−1	0	3
9	1	3	2	−3	−1	−2	0	0	1	2	4	4	3	−1	0	3
10	2	3	−1	−1	−4	−4	0	2	−4	−3	−4	−4	−1	−4	4	4
11	4	−4	−1	−1	−4	−4	0	2	−4	−3	−4	−4	−2	−4	4	4
12	−3	−4	−1	−1	4	4	0	2	−3	−3	−4	4	−2	4	4	−4
13	−4	4	4	−1	1	3	−4	−4	4	4	0	−3	3	2	−4	0
14	−2	−3	−4	−2	0	2	−4	−4	4	4	0	−2	−4	2	−4	0
15	−4	−4	−3	−2	0	3	−4	−4	4	4	0	−2	0	2	−4	0
16	4	4	2	3	−4	4	0	−4	4	−4	0	−4	−3	2	4	4
17	−4	4	2	3	−4	4	0	−4	4	−4	0	−3	−4	2	4	4
18	−4	4	2	3	−4	4	0	−4	4	−4	0	4	−4	2	4	4
19	−4	−2	0	2	4	−4	−3	−4	−4	−4	−4	−2	4	0	−4	−4
20	4	4	0	2	4	−4	−4	−4	4	4	−4	4	4	0	−4	−4
21	−3	−4	0	1	4	−4	−4	−4	−4	−4	−4	3	−2	0	−4	−4
22	−4	4	1	3	4	4	−4	−4	4	4	3	−3	−4	−2	4	4
23	4	3	2	3	4	3	−4	−4	4	4	4	4	−3	−2	3	3
24	4	−4	2	3	4	4	−3	−4	4	4	2	−4	−4	−2	4	3
25	−4	4	−1	−3	−1	−2	0	0	4	3	0	4	3	3	3	3
26	−4	4	−1	−1	−2	−1	0	0	−4	−4	0	4	4	4	3	2
27	−4	−4	0	0	−1	−1	0	0	−4	−4	0	−2	3	4	1	2
28	4	4	−2	−3	−4	−4	0	3	4	−4	3	3	3	−1	0	−2
29	3	0	−2	−3	−4	−4	0	3	4	−4	3	3	2	−1	0	−2

phases determined to be absent in the pattern compared to those not identified would improve data reporting and subsequent analysis. This is most evident with the low concentration phases where the occurrence of multiple zeros can skew the consensus mean value if that phase was not actually evaluated but simply reported to be zero.

Conclusions

A proficiency test program involving X-ray powder diffraction analysis of two portland cements was initiated to evaluate laboratory performance in phase abundance

TABLE 7

Prediction Interval qualification for alite, belite, aluminate and ferrite where boldface indicates a k = 3 mean exceeding the 95 % confidence bounds. Un-reported values are blank.

	Alite		Belite		Aluminate		Ferrite	
	A	B	A	B	A	B	A	B
1	59.27	61.57	16.50	12.40	4.17	3.67	9.40	10.03
2	60.52	63.45	15.86	12.20	4.93	3.49	9.11	9.18
3	58.28	61.95	**19.51**	10.88	**7.27**	**7.36**	**6.96**	**8.14**
4	60.82	**66.87**	**13.30**	**8.15**	**5.67**	**5.14**	9.35	9.73
5	58.96	65.49	16.15	**8.94**	3.98	3.05	**12.61**	**11.26**
6	**55.00**	63.00	**19.00**	14.00	**3.00**	3.00	9.00	10.00
7	57.67	**58.87**	**23.20**	**15.60**	3.57	3.00	9.93	9.63
8	57.98	61.13	**19.88**	**14.04**	3.41	3.34	9.80	10.69
9	**68.30**	**69.13**	**11.76**	**8.03**	**0.00**	**0.18**	**7.35**	**7.72**
10	**64.43**	**66.93**	**14.26**	10.68	**5.46**	**4.66**	9.01	9.57
11	60.77	61.17	16.20	12.93	**9.37**	**5.50**	**7.07**	10.43
12	57.83	63.55	**21.01**	**15.07**	4.11	3.63	**12.50**	**13.29**
13	59.29	63.60	16.49	**10.48**	4.39	2.89	9.23	9.26
14	**57.13**	61.47	18.04	13.37	4.95	3.30	**11.47**	**11.88**
15	59.39	62.11	18.27	**14.52**	3.42	3.12	**8.37**	**8.53**
16	60.45	64.30	16.17	**10.51**	4.62	3.55	9.81	9.08
17	60.95	63.75	**14.83**	13.89	4.12	4.04	10.34	10.99
18	59.87	64.43	18.10	11.90	3.70	2.87	8.87	9.63
19	58.38	61.35	16.87	**14.05**	**3.14**	2.93	9.50	9.93
20	61.79	65.73	17.02	12.07	4.11	4.03	9.30	9.01
21	61.97	62.47	**13.30**	**14.80**	3.93	3.67	**14.53**	10.90
22	59.10	63.78	15.91	11.28	4.85	4.00	10.32	10.15
23	60.92	65.22	17.18	11.06	4.47	2.91	9.96	10.98
24	61.87	62.47	**14.37**	11.77	4.23	3.30	10.20	10.67
25	59.67	64.41	16.47	**10.52**	3.52	2.90	9.28	10.04
26	59.60	65.12	17.17	10.79	3.40	2.86	**10.67**	**11.58**
27	59.30	62.24	16.02	12.31	4.68	3.28	9.14	9.70
28[a]	59.75	63.30	17.05	12.60	3.85	3.96	9.28	8.80
29[a]	**65.76**	**26.23**	17.11	**43.97**	4.53	**21.37**	**5.65**	**2.31**
Mean	60.0	63.42	16.74	12.28	4.21	3.57	9.53	9.92

[a]Qualification based on k = 2 as only two replicate values provided.

analysis of cements. By contrast to reference clinkers, cement samples contain additional calcium sulfate and calcium carbonate phases, and a "blind" test that requires a qualitative analysis followed by a quantitative analysis. Objective quality measures of a laboratory's measurement process can be obtained by comparing individual results against the consensus values using the ASTM C1365 [1] qualification criteria via graphical and numerical ranking of lab performance through Youden plots and strip plots. Comparing an individual lab's results to the collective consensus provides each lab with an opportunity to identify and resolve precision and bias problems in their analyses.

TABLE 8

Prediction interval qualification for periclase, calcite, arcanite, gypsum, bassanite, and anhydrite where boldface indicates a k = 3 mean exceeds the 95 % confidence bounds. Unreported values are blank.

	Periclase		Calcite		Arcanite	Gypsum	Bassanite	Anhydrite
	A	B	A	B	A	B	A	A
1	0.90	1.33	3.53	**3.77**	**1.3**	5.27	2.00	**3.00**
2	1.01	1.46	2.44	3.52	**1.3**	**4.14**	**2.73**	1.53
3	**2.12**	**2.31**	**5.78**	**3.78**	0.8	**6.95**	**0.16**	0.93
4	0.49	**0.84**	3.05	2.59	0.5	**6.37**	2.06	1.07
5	1.43	1.72	2.44	–	–	**8.34**	**3.20**	**0.13**
6	1.00	1.00	3.00	3.00	–	5.00	**3.00**	0.80
7	0.93	1.40	2.17	2.23	0.5	**6.20**	2.00	1.19
8	1.17	1.53	3.47	3.52	**1.1**	4.76	**0.90**	0.95
9	0.91	1.50	**4.07**	**4.03**	–	**5.83**	2.50	0.93
10	0.93	1.38	–	**0.59**	**1.1**	**2.34**	**0.64**	**2.17**
11	0.60	1.63	2.60	3.33	**1.1**	**3.90**	**0.77**	1.72
12	0.84	1.25	**0.72**	**0.75**	1.0	**0.34**	**0.98**	1.44
13	0.79	1.40	2.28	2.33	0.3	**7.16**	2.53	0.97
14	1.14	1.43	1.46	1.76	**1.5**	5.58	1.34	1.94
15	1.12	1.77	2.14	2.54	–	**4.01**	**0.00**	1.40
16	0.75	1.18	2.26	2.38	**0.3**	**6.10**	**3.24**	1.36
17	0.95	1.38	2.85	2.02	–	**3.28**	2.11	1.62
18	0.90	1.10	3.43	3.43	**1.3**	5.53	1.50	0.89
19	0.96	1.49	2.95	3.04	–	**7.22**	**2.75**	1.36
20	1.22	1.70	1.33	1.27	–	**4.16**	2.48	0.67
21	0.90	1.27	1.53	1.80	1.1	4.33	**0.70**	0.80
22	1.37	1.52	2.51	3.17	**1.5**	4.76	1.41	1.33
23	0.92	1.46	2.04	1.53	**1.3**	5.66	**1.08**	1.58
24	0.70	1.40	3.63	2.57	0.8	**6.03**	1.87	1.39
25	0.84	1.42	3.21	2.94	0.7	5.60	2.58	1.07
26	1.18	1.53	3.11	2.73	0.4	**3.88**	2.05	**0.37**
27	0.89	1.49	2.87	3.25	0.8	4.75	2.46	1.81
28[a]	1.22	1.74	1.37	1.38	–	**4.13**	2.56	**0.18**
29[a]	0.77	**2.30**	1.68	-	-	–	2.69	
mean	0.97	1.46	2.53	**2.46**	0.68	5.03	1.91	1.25

[a]Qualification based on k = 2 as only two replicate values provided.

In future proficiency testing, a requirement is necessary for distinguishing phases identified as not present compared to those not included in the analyses. In addition, ASTM C1365 should provide a list of required phases, optional phases, and a required phase identification protocol. Providing an option to use means of multiple test results in C1365 (though it is not precluded) would improve measurement precision.

One goal of this study was to identify potential problem areas in the analyses. However, identifying correlations between sample preparation, orientation corrections and mass fraction accuracy was inconclusive, in part due to lack of complete data describing the exact procedures employed by each lab. Evaluation of the impact of sample preparation and data analysis factors are probably best studied with a single laboratory using a ruggedness test. XRD proficiency testing may ultimately be included in the CCRL proficiency test program as part of the test regime, and may be considered as an addition to the existing ASTM C1365 qualification criteria as part of a routine testing program.

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