MISCELLANEOUS PAPER C-68-2

X-RAY EMISSION ANALYSIS OF PORTLAND CEMENT

Report 1

VARIANCES IN ANALYSIS

by

L. Pepper

July 1968

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Office, Chief of Engineers
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Foreword

The investigation reported herein is the second phase of the work covered by a project plan entitled "Investigation of X-ray Emission Analysis of Portland Cement." The project plan was approved by a first indorsement dated 23 September 1966 from the Office, Chief of Engineers (ENGCW-EC), to a U. S. Army Engineer Waterways Experiment Station (WES) letter dated 9 September 1966, subject, "Technical Surveillance of Cement and Pozzolan Testing Program."

The investigation is being conducted at the Concrete Division, WES, under the direction of Mr. Bryant Mather and Mr. R. V. Tye. The principal investigator is Mr. Leonard Pepper, author of this report.

COL John R. Oswalt, Jr., CE, was Director of WES during the investigation and the preparation of this report. Mr. J. B. Tiffany was Technical Director.

Contents

Summary

A balanced statistical experiment was conducted to evaluate the effect of four factors on the X-ray emission analysis for calcium (Ca), silicon (Si), iron (Fe), aluminum (Al), magnesium (Mg), and sulfur (S) in portland cement. The factors evaluated were: instrument conditions (optimized versus predetermined goniometer and counter-tube voltage settings); rounds; binders used to aid in grinding and pelletizing the cement (boric acid, sodium lauryl sulfate, Boraxo, and a Boraxo-cellulose mixture); and the sample pellet-making procedure.

The experimental results indicate that pellets have a direct effect on the analysis of portland cement. Binders were found to have a direct effect on the elemental analyses, and the effect was determined to be due to sodium lauryl sulfate. However, the effect is negated by the use of a ratio method of analysis. Instrument conditions and rounds were both found to have an effect on the analytical results either as direct factors or in the form of interactions, particularly the interaction of pellets and rounds. The precision of the X-ray analysis is apparently increased when optimized instrument settings are used.

Either sodium lauryl sulfate or Boraxo may be used as a binder for X-ray emission analysis. Only one pellet need be made with each sample. A replicate analysis will confound the pellet-round interaction with round variances, and the pellet effect will be confounded between samples. The decision as to whether the spectrometer is to be tuned prior to every analysis is deferred until the spectrometer calibration results are evaluated.

X-RAY EMISSION ANALYSIS OF PORTLAND CEMENT

VARIANCES IN ANALYSIS

Introduction

1. Specifications for portland cements require the cements to comply with a number of physical and chemical limits. The tests to determine compliance with the chemical limits are based on conventional gravimetric and titrimetric procedures. These conventional "wet" chemical procedures require highly trained personnel and also a long time to complete. New techniques and instrumentation, such as ultraviolet and visual spectroscopy, flame and X-ray emission spectroscopy, and absorption flame spectroscopy, are now available for determining elemental composition. Procedures involving such instrumentation are purported to be more economical than the conventional wet chemical procedures. The development of rapid methods of analysis has been a function of the National Bureau of Standards (NBS) in conjunction with their work of acceptance testing of cement for Federal agencies.

2. Acceptance testing of cement for Federal agencies was transferred to the Department of the Army, Corps of Engineers, on 1 January 1966. At the same time the responsibility for the development of rapid methods of analysis of cement was transferred to the U. S. Army Engineer Waterways Experiment Station (WES). As a result of this transfer of function, the work on X-ray emission analysis of cement that had been in progress at NBS under the direction of Mr. Leonard Bean was terminated.

3. NBS had begun the investigation of X-ray methods of analysis of portland cement in 1958 using an Applied Research Laboratories (ARL) emission spectrometer (Model PXQ). In 1963 the original instrument was converted to a vacuum emission spectrometer (Model VXQ). The modified instrument, spare parts, associated hardware, reference samples, pertinent data, correspondence, and record books maintained by Mr. Bean were all transferred to WES in January 1966. Mr. Bean's work indicated that satisfactory results could be obtained only by direct comparison of the test sample with a reference sample of the same type and produced by the same mill.

4. A General Electric XRD-6 vacuum emission spectrometer was purchased by WES in July 1965 to be used as a research instrument and to serve as a backup instrument to the ARL Model VXQ. The XRD-6 and VXQ spectrometers were both installed at WES in March 1966. However, little work could be done with the ARL equipment because of persistent component breakdown. During the latter part of July 1966, all work with the ARL equipment was halted. Investigations of methods for X-ray emission analysis are to be conducted solely with the XRD-6 spectrometer. After methods of analysis have been developed, the use of the VXQ spectrometer will be considered.

5. The results of a literature search, the work performed by Bean, and studies by the Subcommittee on Chemical Analysis of ASTM Committee C-1 indicate that cement samples need not necessarily be fused for X-ray emission analysis. In addition, it was noted that a simple calibration with known cement standards would not be satisfactory, but instead, that some ratio technique would be needed for analysis of portland cements. The ratio method of analysis is required for a number of reasons, one of which is instrument changes with time. To determine the effects of the instrument changes and other procedural variances and to gain experience in the use of the XRD-6 spectrometer, a balanced statistical experiment was designed. This report gives the results of the statistical study.

Experimental Design

6. The statistical design chosen for evaluation originally contemplated using both spectrometers. Termination of the use of the VXQ spectrometer did not alter the basic experimental design. The following four factors were selected for evaluation:

a. Instrument conditions (C) (i.e. predetermined and optimized instrument settings).

b. Rounds (R).

c. Binders (B).

d. Pellet and pellet preparation (P).

7. The first and second factors enumerated above are components of

the instrument fluctuations. The first factor, designated as test conditions, measures the effect of fluctuation in the settings of the goniometer and the counter-tube voltage of the pulse height selector. The second factor, rounds, measures the effect of all other instrument changes that may take place in two to three days.

8. A number of different binders have been used by different laboratories to assist in grinding and pelletizing cement samples. The binders used can be summarized as belonging in one of the following three groups: sodium lauryl sulfate, boric acid, and Boraxo (a mixture of sodium lauryl sulfate and boric acid). Sodium lauryl sulfate is the binder used by most of the laboratories involved in X-ray emission analysis of portland cement. A local laboratory was using a mixture of Boraxo and cellulose (2:1 by weight) as a binder and claiming many advantages for this mixture. The effects of these four binders on X-ray emission analysis of cement were determined.

9. Sample preparation appears to be simple and straightforward. There did not appear to be any reason to separate the procedures into component parts. Each pellet in this experiment, therefore, represents the entire preparation procedure.

Test Procedure

10. Only one cement (type II, low-alkali, moderate heat of hydration) was used in this investigation. As mentioned earlier, four grinding aids were used: boric acid, sodium lauryl sulfate, Boraxo, and a Boraxo-cellulose mixture (2:1). Grinding aid was added to the cement in an amount equal to 5% by weight of the cement; the mixture was thoroughly mixed, and then ground in a Blueler mill for 6 min. Four grinds were made with each grinding aid, and one pellet was pressed from each grind at a pressure of 40,000 psi (2812.28 kg/sq cm). All pellets were made with a Boraxo backing. The 16 pellets were made in a random order on the same day.

11. Three rounds were run on the 16 pellets for each of six elements: calcium (Ca), silicon (Si), aluminum (Al), iron (Fe), magnesium (Mg), and

sulfur (S). For all elements except Ca, the first-order Kα line was used for analysis. The second-order Kα line was used for Ca. A Cr target tube was used as well as a 0.005 Soller slit and pulse height selection for all elements. Operating parameters are shown in table 1.

12. The procedure for each element in each round involved:

   a. Four consecutive readings of each pellet using predetermined instrument settings for the element.

   b. Tuning for optimum goniometer (2θ) and counter-tube voltage settings for the element using the appropriate standard for the element.

   c. Four consecutive readings of each pellet at the optimum settings. The pellet order was randomized for each set of settings, each element, and each round. A round consisted of all the above readings for all six elements. Each round had to be completed before the next could be started, and the interval between rounds was at least two days.

13. The following general linear model is applicable to the results obtained in the investigation:

$$x_{ijk\ell m} = \mu + C_i + B_j + CB_{ij} + P_{k(j)} + CP_{ik(j)} + R_\ell + CR_{i\ell} + BR_{j\ell}$$

$$+ CBR_{ij\ell} + PR_{k\ell(j)} + CPR_{ik\ell(j)} + e_{m(ijk\ell)} \qquad \text{(Model 1)}$$

where

μ = the average value

C_i = the test condition and i = 1 is the optimum setting and i = 2 is the predetermined setting

B_j = the binder factor and j = 1 is boric acid, j = 2 is sodium lauryl sulfate, j = 3 is Boraxo, and j = 4 is Boraxo plus cellulose (2:1)

P_k = the pellet factor where k = 1...4

R_ℓ = the round factor where ℓ = 1...3

$e_{m(ijk\ell)}$ = the residual error where m = 1...4

and all other symbols are interactions of the above factors. The general linear model to examine the data when only one binder is used is:

$$x_{ijk\ell} = \mu + C_i + P_j + CP_{ij} + R_k + CR_{ik} + PR_{jk} + CPR_{ijk} + e_{\ell(ijk)} \quad \text{(Model 2)}$$

where the symbols have the same meaning and levels noted on the preceding page. Finally, the general linear model for the work as it would normally be conducted, i.e. omitting both binder and test condition factors, is:

$$x_{ijk} = \mu + P_i + R_j + PR_{ij} + e_{k(ij)} \quad \text{(Model 3)}$$

where again the symbols have the same meaning and levels noted on the preceding page. The expected mean squares and the calculation formulas for each of the three models are given in Appendix A.

Analysis of Test Results

14. Using the data in terms of counts per second (intensity), the analyses of variance indicate that the following factors and interactions have a significant* effect on analytical results:

All six elements: CPR, PR, CR, R

Ca, Si, Fe, and S: B

Fe: C

Note: These factors and interactions were found to be significant at the 1% level, except the factor C in the analysis for Fe, the factor R in the analysis for Mg, and the interaction CR in the analysis for S which are significant only at the 5% level. Any factor or interaction found to be significant at the 1% level is also, necessarily, significant at the 5% level.

15. It is important to note that pellets can be disregarded as a source of variance as long as the sample and pellet preparation procedure is not changed. The significance of the R factor was expected, since its significance has been well documented in the literature. The PR interaction is the pellet face effect; that is, a different pellet face was presented for analysis for each round. The experimental design allowed for separation of

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* An effect is referred to as "significant" if it was found to be so at either the 5% or 1% level.

the pellet and pellet face effects. Although the C factor was significant only for Fe, and at the 5% level, interactions involving test conditions (CR and CPR) were found significant at the 1% level for all six elements. Test conditions, therefore, have a significant effect on X-ray analysis of portland cement.

16. Additional information concerning the effects of binders can be obtained by examination of the results using Duncan's method for separation of means.* The results obtained for the four elements for which B had a significant effect are shown in table 2. The results obtained with binder 2, sodium lauryl sulfate, are significantly different from those obtained with the other three binders, being lower for Ca, Si, and Fe, and higher for S. The results obtained with the other binders are statistically the same for Ca, Si, and Fe, but statistically different from each other for S. Sodium lauryl sulfate is excellent as a grinding aid and binder. However, the significant reduction in intensity in the analysis for Ca, Si, and Fe tends to make it undesirable for use for these elements. With the exception of the analysis of S, no difference in intensity measurements may be expected through the use of either boric acid, Boraxo, or the Boraxo-cellulose mixture. Boric acid is a poor grinding aid compared with the other two materials. The Boraxo-cellulose mixture requires extra weighings. Therefore, of the four materials evaluated, Boraxo appears to be the more desirable material for use as a grinding aid and binder.

17. The data were also analyzed by taking the ratio of the average counts obtained for pellet 1 of binder 3 for each test condition, round, and element to all the other values obtained for that round, test condition, and element. The following factors and interactions were found to have a significant effect:

All six elements: CPR, PR	Al, Fe, S: CR
Si, Al, Fe, Mg, S: R	Ca, Si: C
Ca, Si, Fe, S: B	

Note: These factors and interactions were found to be significant at the 1% level, except the factor C in the analysis for Si and the interaction CR in the analysis for S which are significant only at the 5% level.

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* D. B. Duncan, "Multiple Range and Multiple F Tests," Biometrics, Vol 11, No. 1, Mar 1955.

The significance of B, PR, and CPR is expected considering the results previously obtained. However, the significance of R for five elements and the interaction CR for three elements is unexpected, since the process of ratioing the counts is supposed to remove the effect of rounds. Test conditions are not significant for Fe, as found previously, but are significant for Ca and Si.

18. The unexpected significant variances of R and CR require additional data analyses using linear models 2 and 3. The significant R and CR variances may be due to the test conditions and perhaps to the data obtained with the different binders. The analyses conducted in accordance with models 2 and 3 were based on the data obtained with binders 2 and 3. Analyses with model 3 were made separately for each test condition, i.e. pretuned and optimum. All analyses were made using both the intensity data and ratios obtained as described previously as applicable for each model. The results of the calculations are shown in tables 3-8. The values shown are the calculated variances that were found to be significant. In all six tables the first column of variances was obtained using Model 1, the second and third columns were obtained using Model 2, and the last four columns were obtained using Model 3.

Ca results

19. The significant variances in the determination of Ca are shown in table 3. Comparison of the variances obtained using Model 1 with those obtained using Model 2 indicates that:

a. For both intensity data and ratio data, the binder 2 and binder 3 error variances are statistically the same and significantly less than the Model 1 error variance.

b. For both intensity data and ratio data, the binder 2 PR and CPR variances are significantly less than the respective binder 3 and Model 1 variances. The binder 3 CPR variance is statistically the same as the Model 1 CPR variance; however, the binder 3 PR variance is significantly higher than the Model 1 PR variance.

c. For both intensity data and ratio data, binder 2 P variance was found to be significant whereas the P variance for binder 3 and also Model 1 was not found to be significant. The significance of binder 2 P variance accounts for the significantly lower CPR and PR variances found for binder 2.

d. The three CR variances and also the three R variances are

statistically the same when the intensity data are used. The CR and R variances are not significant when the ratio data are used. Finally the C variance was significant only for Model 1 ratio data.

20. Comparison of the significant variances obtained for optimum test conditions and those obtained for pretuned test conditions, all calculated in accordance with Model 3, in the determination of Ca indicates that:

a. For both intensity data and ratio data, the binder 2 and binder 3 error variances are statistically the same for optimum test conditions. The binder 2 and binder 3 error variances are also the same for pretuned test conditions. However, the error variances obtained for pretuned test conditions are significantly lower than those obtained for optimum test conditions.

b. For both intensity data and ratio data, the binder 2 and binder 3 PR variances are statistically the same for optimum test conditions. For pretuned test conditions, binder 2 PR variance is significant only at the 5% level and is significantly less than the binder 3 PR variance and the two PR variances obtained for optimum test conditions. The binder 3 PR variance for pretuned test conditions is significantly higher than the two PR variances obtained for optimum test conditions and accounts for the high PR variance obtained for binder 3 calculated in accordance with Model 2.

c. For intensity data, pretuned test conditions, binder 2 and binder 3 R variances are statistically the same. For intensity data, optimum test conditions, only binder 2 R variance is significant, at the 5% level, and it is significantly lower than the two R variances obtained for pretuned test conditions. The R variances were not significant for the ratio data.

d. The P variances were not significant for either binder, condition, or type of data (i.e. intensity data or ratio data). These results appear anomalous since, as noted above, binder 2 P variance was found to be significant when calculated in accordance with Model 2 using either intensity or ratio data. Examination of the results of the analysis of variance calculated in accordance with Model 3, for both test conditions and types of data, indicated that the binder 2 P F ratio is greater than the binder 3 P F ratio, but the binder 2 P variance is just below the level of significance. Additional tests, which would increase the degrees of freedom for pellets, may indicate that the binder 2 P variance is significantly greater than random error.

Si results

21. The significant variances in the determination of Si are shown in table 4. Comparison of the variances obtained with Model 1 with those obtained with Model 2 indicates that:

a. For both intensity data and ratio data, the three error variances are statistically the same. The three CPR variances are also statistically the same.

b. For both intensity data and ratio data, the binder 2 PR variance was not significant and the PR variance for binder 3 and that calculated for Model 1 are statistically the same.

c. The CR variance was significant only when Model 1 intensity data were used. The P variance was not significant in the determination of Si.

d. When the intensity data were used, the three R variances were found to be statistically the same. When the ratio data were used, binder 3 R variance was not significant, and the remaining two R variances are statistically the same.

e. The C variance was not significant when calculated in accordance with Model 1 using intensity data, and significant only at the 5% level using ratio data. Binder 2 and binder 3 C variances were significant and statistically the same when the intensity data were used, and not significant when the ratio data were used.

f. Binder 2 significant variances tend to appear for direct factors (R and C), whereas binder 3 significant variances tend to appear for interactions (CPR and PR).

22. In the determination of Si, comparison of the significant variances obtained for optimum test conditions and those obtained for pretuned test conditions, all calculated in accordance with Model 3, indicates that:

a. For both intensity data and ratio data, the binder 2 and binder 3 error variances are statistically the same for optimum test conditions and also for pretuned test conditions, and finally, comparison of the two test conditions indicates that the error variances are statistically the same.

b. For both intensity data and ratio data, binder 2 PR variance for optimum test conditions was not significant and the remaining three PR variances are significant and statistically the same.

c. Binder 3 R variance was not significant for optimum test conditions when intensity data were used, nor were any of the R variances significant when ratio data were used. The three R variances calculated using intensity data (binder 2 optimum, binder 2 pretuned, and binder 3 pretuned) are all statistically the same.

Fe results

23. The significant variances in the determination of Fe are shown in table 5. Comparison of the variances obtained using Model 1 with those obtained using Model 2 indicates that:

a. For both intensity data and ratio data, the Model 1, binder 2, and binder 3 error variances are statistically the same. Also, the Model 1, binder 2, and binder 3 CPR variances are statistically the same.

b. For both intensity data and ratio data, the binder 2 PR variance was not significant. Model 1 and binder 3 PR variances are significant and statistically the same.

c. The three CR variances obtained using the intensity data are all statistically the same. When the ratio data were used, only the Model 1 CR variance was found to be significant.

d. For the intensity data, the three R variances are significant and statistically the same. Binder 3 R variance calculated using the ratio data was not significant; however, Model 1 and binder 2 R variances for the ratio data are significant and statistically the same.

e. For both intensity data and ratio data, the P variance was found to be significant only for binder 2.

f. The C variances were significant only for Model 1 and binder 2 (intensity data). The tendency noted in paragraph 21 f for binder 2 significant variances to appear for direct factors (R, P, and C) and for binder 3 variances to appear for interactions (CPR, PR, and CR) is also noted in the determination of Fe.

24. In the determination of Fe, comparison of the significant variances obtained for optimum test conditions and those obtained for pretuned test conditions, all calculated in accordance with Model 3, indicates that:

a. For both intensity data and ratio data, the binder 2 and binder 3 error variances are statistically the same for optimum test conditions and also for pretuned test conditions, and finally, comparison of the two test conditions

indicates that the error variances are statistically the same.

b. For intensity data and optimum test conditions, the binder 2 PR variance was not significant. Using the intensity data, the binder 3 PR variance for optimum test conditions is of the same magnitude as the binder 2 PR variance for pretuned test conditions, and both of these variances are significantly lower than the binder 3 PR variance for pretuned test conditions. Using the ratio data, the binder 2 and binder 3 PR variances for optimum test conditions and also the binder 2 PR variance for pretuned test conditions are all of the same magnitude. In addition, these three variances are significantly lower than the binder 3 PR variance for pretuned test conditions.

c. R variances were significant only for intensity data. Binder 2 and binder 3 R variances are statistically the same for optimum test conditions, and also for pretuned test conditions. Although the magnitudes of the R variance for optimum and pretuned test conditions are different, the variances are statistically the same.

d. The P variance was significant only for binder 2, optimum test conditions, intensity data. As noted for Ca, these results appear to be anomalous since binder 2 P variance was found to be significant when calculated in accordance with Model 2 using either intensity or ratio data. Examination of the results of the analysis of variance, calculated in accordance with Model 3, for both test conditions and both intensity and ratio data, indicated that the binder 2 P F ratio is greater that the binder 3 P F ratio, but that the binder 2 P variance is just below the level of significance.

Al results

25. The significant variances in the determination of Al are shown in table 6. Comparison of the variances obtained using Model 1 with those obtained using Model 2 indicates that:

a. For both intensity data and ratio data, the binder 2, binder 3, and Model 1 error variances are statistically the same, the binder 2, binder 3, and Model 1 CPR variances are statistically the same, and finally, binder 2, binder 3, and Model 1 PR variances are statistically the same.

b. Using the intensity data, binder 2 CR variance is statistically the same as the Model 1 and binder 3 CR variances. Using the ratio data, the CR variance was found to be significant only for Model 1.

c. For the intensity data, the three R variances are statistically the same. For the ratio data, the R variance was found to be significant only for Model 1.

26. Comparison of the significant variances obtained for optimum test conditions and those obtained for pretuned test conditions, all calculated in accordance with Model 3, in the determination of Al indicates that:

a. For both intensity data and ratio data, the binder 2 and binder 3 error variances are statistically the same for optimum test conditions and also for pretuned test conditions, and finally, comparison of the two test conditions indicates that the error variances are statistically the same.

b. For both intensity data and ratio data, the binder 2 and binder 3 PR variances for optimum test conditions are statistically the same. Binder 2 and binder 3 PR variances for pretuned test conditions are also statistically the same; however, the PR variances for pretuned test conditions are significantly higher than the PR variances for the optimum test conditions.

c. Using ratio data, the R variances were not found to be significant. Binder 3 R variance for optimum test conditions, intensity data, was not significant. Binder 2 and binder 3 R variances for pretuned test conditions, intensity data, are statistically the same and significantly higher than the binder 2 R variance for optimum test condition.

Mg results

27. The significant variances in the determination of Mg are shown in table 7. Comparison of the variances obtained using Model 1 with those obtained using Model 2 indicates that:

a. For both intensity data and ratio data, Model 1, binder 2, and binder 3 error variances are all statistically the same.

b. For both intensity data and ratio data, binder 3 CPR variance is significantly less than the CPR variance determined for Model 1. Binder 2 CPR variance is statistically the same as Model 1 CPR variance.

c. For both intensity data and ratio data, Model 1, binder 2, and binder 3 PR variances are statistically the same.

d. The CR variances are significant for intensity data only,

and all three are statistically the same. The R variance is significant only for Model 1, for both intensity data and ratio data. However, the R variance is significant only at the 5% level for the intensity data.

28. Comparison of the significant variances obtained for optimum test conditions and those obtained for pretuned test conditions, all calculated in accordance with Model 3, in the determination of Mg indicates that:

a. For both intensity data and ratio data, the binder 2 and binder 3 error variances are statistically the same for optimum test conditions and also for pretuned test conditions, and finally, comparison of the two test conditions indicates that the error variances are statistically the same.

b. The observations made above with regard to the error variances are also true for the PR variances for both intensity and ratio data. Finally, the same observations are true for the R variances for the intensity data. The R variances were not significant for the ratio data.

S results

29. The significant variances in the determination of S are shown in table 8. The effects of the binders are most evident in the determination of S. Variances that were found to be significant with one binder were generally not significant with the other. Specific comparisons of the variances obtained using Model 2 and Model 1 are:

a. For both intensity data and ratio data, binder 2, binder 3, and Model 1 error variances are statistically the same.

b. Using the intensity data, the variances found to be significant for binder 2 are: CR, R, CP, and P; the CP variance is significant only at the 5% level, whereas CPR, PR, and C variances were not significant. The variances found to be significant for binder 3 using the intensity data are: PR and C, the latter only at the 5% level, whereas the CPR, CR, R, CP, and P variances were not significant. The variances found to be significant for Model 1 using the intensity data are: CPR, PR, CR, R, and B, with the CR variance significant only at the 5% level, whereas the CP, P, and C variances were not significant.

c. Using the ratio data, the variances found to be significant for binder 2 are CP (only at the 5% level) and P, whereas CPR, PR, CR, and R variances were not significant. The variances found to be significant for binder 3 using the ratio data are PR, CR, R, and P, the latter two only at the 5% level, whereas

only CPR and CP were not significant. The variances found to be significant for Model 1 using the ratio data are CPR, PR, CR (only at the 5% level), R, and B.

30. The effects of binders are also evident in the variances that are found to be significant when the results obtained in the S determination are analyzed in accordance with Model 3. Specific comparisons of the variances obtained using Model 3 are as follows:

a. For both intensity data and ratio data, the binder 2 and binder 3 error variances are statistically the same for optimum test conditions and for pretuned test conditions, and finally, comparison of the two test conditions indicates that the error variances are statistically the same.

b. Using intensity data, the variances found to be significant for binder 2 for both optimum and pretuned test conditions are R and P, with the P variance for optimum test condition being significant only at the 5% level. In contrast, for binder 3, the PR variance was found to be significant for optimum test conditions, whereas the P variance was found to be significant for pretuned test conditions.

c. Using ratio data, only the P variance was found to be significant for binder 2 for optimum test conditions (only at the 5% level) and pretuned test conditions. In contrast, for binder 3, both PR and R are significant, the latter only at the 5% level, for optimum test conditions, whereas for the pretuned test conditions only the P variance was significant.

Discussion and Conclusions

31. As a result of the analysis of all the data in accordance with Model 1, it was concluded that pellets can be disregarded as a source of variance as long as the sample and pellet preparation procedure is not changed. It was also concluded that of the four materials evaluated Boraxo is the more desirable material for use as a grinding aid and binder. However, detailed analysis of portions of the data, in accordance with Models 2 and 3, tends to refute these two conclusions. Separate statistical analyses of the sodium lauryl sulfate and Boraxo data indicate that the significant variances found for sodium lauryl sulfate tend to appear for the direct factors (R, C, and P), particularly in the determination of Ca, Si, Fe, and S, whereas the significant variances found for Boraxo tend

to appear for interactions (CPR, PR, and CR). Significant interaction variances may mask the significance of the direct factors, particularly when the degrees of freedom associated with the interaction are low as they are in the Model 3 analysis. Pellets cannot therefore be disregarded as a source of variance in the X-ray emission analysis of portland cement.

32. Boraxo was previously considered as a more desirable grinding aid and binder, principally because of the lower intensities obtained with the use of sodium lauryl sulfate in the determination of Ca, Si, and Fe. However, the lower intensities have little meaning since the analysis will be based on a calibration which involves a standard prepared with the same grinding aid and will have even less meaning if a ratio method of analysis is used. The statistical analysis has indicated that both sodium lauryl sulfate and Boraxo have errors of equal magnitude associated with their use. The statistical information developed in this investigation indicates that either material can be advantageously used for X-ray emission analysis.

33. Instrument variations have an influence on the results, either as a direct factor (test conditions and rounds) or in the form of interactions (CPR, PR, and CR). Using optimum test conditions, the face effect (PR) variance is less than or equal to the variance obtained using pretuned test conditions for five of the six elements. The face effect variance is higher for optimum test conditions than for pretuned test conditions in the determination of S when Boraxo is used or in the determination of Ca when sodium lauryl sulfate is used. Using optimum test conditions, the round variance is less than or equal to the variance obtained using pretuned test conditions for all six elements. There appears to be an apparent increase in precision when optimum test conditions are used. However, it is questionable whether the increased precision warrants the increased work of tuning the spectrometer prior to each analysis. The decision as to whether optimum test conditions should be used will be made after the results obtained by calibration are evaluated.

34. Instrument variances must be considered in any calibration procedure. Since the round variance has been found to be significant under certain conditions, several rounds should be run. Replicating pellets in the calibration would confound the face and pellet effects

within a round. It would be less costly to confound the face effect with rounds by using only one pellet per standard and confound the pellet effect between standards. The calibration procedure to be used in this laboratory is as follows:

a. Make one pellet with each standard.

b. Randomize the pellets, and determine the radiation intensity of each pellet using pretuned instrument settings for the element being calibrated.

c. Tune the spectrometer for optimum instrument setting for the element.

d. Rerandomize the pellets, and determine the radiation intensity of each pellet.

e. Using steps a. to d., determine the radiation intensity of the six elements for each of the pellets.

f. Replicate the procedure a. to e. three times.

Table 1

Operating Parameters

Element	Analyzing Crystal	KVP	ma	Count Duration, sec	2θ, deg	Counter-Tube Potentiometer Setting
Ca	PET	40	25	10	100.16	8.80
Si	PET	75	25	20	108.80	8.92
Fe	PET	75	25	20	25.48	8.66
Al	PET	75	25	40	144.26	9.00
Mg	ADP	75	25	200	136.48	9.02
S	PET	75	25	40	75.58	8.88

Table 2

Separation of Binder Means

A. Calcium — Standard error = 15.567 counts/sec

	2 Means	3 Means	4 Means
Least significant (1%) range	61.6	64.4	66.0

	Binder 2	Binder 3	Binder 1	Binder 4
Average counts/sec	9505.6	9586.8	9606.6	9638.3

B. Silicon — Standard error = 2.814 counts/sec

	2 Means	3 Means	4 Means
Least significant (1%) range	11.2	11.6	12.0

	Binder 2	Binder 3	Binder 1	Binder 4
Average counts/sec	3237.9	3277.4	3279.4	3285.2

C. Iron — Standard error = 3.122 counts/sec

	2 Means	3 Means	4 Means
Least significant (1%) range	12.4	12.9	13.2

	Binder 2	Binder 3	Binder 1	Binder 4
Average counts/sec	2913.9	2926.8	2930.5	2932.9

D. Sulfur — Standard error = 1.438 counts/sec

	2 Means	3 Means	4 Means
Least significant (1%) range	5.7	5.9	6.1

	Binder 1	Binder 3	Binder 4	Binder 2
Average counts/sec	641.2	704.9	714.8	1128.3

Note: The lines under the average counts/sec indicate those means that are statistically the same.

Table 3

Error Variances and Variances Found to be Significant in the Determination of Ca*

	Both Test Conditions			Optimum Test Condition		Pretuned Test Condition	
	All Binders	Binder 2	Binder 3	Binder 2	Binder 3	Binder 2	Binder 3
Intensity Data							
Code, counts/sec	-8,900	-8,900	-9,000	-8900	-9000	-8,900	-9,000
Variances, $(counts/sec)^2$							
Error	1,113.56	780.94	773.71	1046.06	1059.44	515.86	488.00
CPR	3,405.20	413.56	3,353.99	NA	NA	NA	NA
PR	2,768.90	347.92	7,571.62	853.61	3283.89	255.74*	15,213.29
CR	62,293.69	59,906.52	65,487.83	NA	NA	NA	NA
R	34,640.76	40,817.30	23,402.71	2665.22*	--	138,875.92	111,974.68
P	--	633.90*	--	--	--	--	--
B	2,868.67	NA	NA	NA	NA	NA	NA
Ratio Data							
Variances, $\times 10^{-6}$							
Error	11.9	8.7	8.3	11.4	11.3	6.0	5.4
CPR	35.4	4.6	34.4	NA	NA	NA	NA
PR	28.8	3.8	78.8	9.5	34.7	2.7*	157.3
P	--	7.0*	--	--	--	--	--
B	31.2	NA	NA	NA	NA	NA	NA
C	5.6	--	--	NA	NA	NA	NA

Note: NA = not applicable; factor or interaction does not appear in model.

* All factor and interaction variances are significant at the 1% level, except those marked with an asterisk which are significant only at the 5% level.

Table 4

Error Variances and Variances Found to be Significant in the Determination of Si*

	Both Test Conditions			Optimum Test Condition		Pretuned Test Condition	
	All Binders	Binder 2	Binder 3	Binder 2	Binder 3	Binder 2	Binder 3
Intensity Data							
Code, counts/sec	-3150	-3150	-3200	-3150	-3200	-3150	-3200
Variances, $(counts/sec)^2$							
Error	168.05	215.76	157.14	213.45	178.86	218.08	135.44
CPR	155.75	85.73*	146.51	NA	NA	NA	NA
PR	73.97	--	183.75	--	195.85	154.30	318.17
CR	137.91	--	--	NA	NA	NA	NA
R	288.55	484.06	321.68*	308.69	--	739.71	609.43*
B	459.38	NA	NA	NA	NA	NA	NA
C	--	274.62	253.36	NA	NA	NA	NA
Ratio Data							
Variances, $\times 10^{-6}$							
Error	15.7	20.5	14.7	20.3	16.6	20.7	12.8
CPR	14.6	8.2*	13.8	NA	NA	NA	NA
PR	6.9	--	17.2	--	18.2	15.1	30.0
R	14.9	4.8	--	--	--	--	--
B	43.0	NA	NA	NA	NA	NA	NA
C	1.7*	--	--	NA	NA	NA	NA

Note: NA = not applicable; factor or interaction does not appear in model.

* All factor and interaction variances are significant at the 1% level, except those marked with an asterisk which are significant only at the 5% level.

Table 5

Error Variances and Variances Found to be Significant in the Determination of Fe*

	Both Test Conditions			Optimum Test Condition		Pretuned Test Condition	
	All Binders	Binder 2	Binder 3	Binder 2	Binder 3	Binder 2	Binder 3
			Intensity Data				
Code, counts/sec	-2800	-2800	-2800	-2800	-2800	-2800	-2800
Variances, $(counts/sec)^2$							
Error	131.79	135.54	127.33	151.47	135.45	119.61	119.22
CPR	153.77	88.34	152.23	NA	NA	NA	NA
PR	100.50	--	126.75	--	67.60*	73.38	338.14
CR	448.87	223.38*	607.78	NA	NA	NA	NA
R	674.22	528.34	735.54	180.80	296.78	1099.26	1782.09
P	--	9.86	--	89.64	--	--	--
B	56.23	NA	NA	NA	NA	NA	NA
C	2870.73*	3313.33*	--	NA	NA	NA	NA
			Ratio Data				
Variances, $\times 10^{-6}$							
Error	15.5	16.0	15.0	17.4	15.5	14.6	14.4
CPR	18.5	10.4	18.5	NA	NA	NA	NA
PR	12.0	--	15.1	6.3*	7.9*	8.9*	40.8
CR	26.6	--	--	NA	NA	NA	NA
R	11.9	1.7	--	--	--	--	--
P	--	15.1	--	--	--	--	--
B	6.6	NA	NA	NA	NA	NA	NA

Note: NA = not applicable; factor or interaction does not appear in model.

* All factor and interaction variances are significant at the 1% level, except those marked with an asterisk which are significant only at the 5% level.

Table 6

Error Variances and Variances Found to be Significant in the Determination of Al*

	Both Test Conditions			Optimum Test Condition		Pretuned Test Condition	
	All Binders	Binder 2	Binder 3	Binder 2	Binder 3	Binder 2	Binder 3
			Intensity Data				
Code, counts/sec	-450	-475	-450	-475	-450	-475	-450
Variances, $(counts/sec)^2$							
Error	15.22	16.78	14.45	15.70	10.22	17.86	18.68
CPR	147.41	189.58	142.66	NA	NA	NA	NA
PR	59.44	76.20	72.52	26.32	49.50	315.67	238.22
CR	618.07	467.98*	769.36	NA	NA	NA	NA
R	470.93	616.11	408.19	78.69	--	1621.51	1571.10
			Ratio Data				
Variances, $\times 10^{-6}$							
Error	53.9	55.8	53.4	48.0	31.8	63.7	74.9
CPR	570.6	621.7	615.2	NA	NA	NA	NA
PR	234.2	245.1	301.7	81.5	152.1	1030.4	1066.4
CR	837.8	--	--	NA	NA	NA	NA
R	282.6	--	--	--	--	--	--

Note: NA = not applicable; factor or interaction does not appear in model.

* All factor and interaction variances are significant at the 1% level, except those marked with an asterisk which are significant only at the 5% level.

Table 7

Error Variances and Variances Found to be Significant in the Determination of Mg*

	Both Test Conditions			Optimum Test Condition		Pretuned Test Condition	
	All Binders	Binder 2	Binder 3	Binder 2	Binder 3	Binder 2	Binder 3
Intensity Data							
Code, counts/sec	-65	-65	-65	-65	-65	-65	-65
Variances, $(counts/sec)^2$							
Error	0.78	0.85	0.61	0.83	0.68	0.88	0.55
CPR	17.71	9.31	3.74	NA	NA	NA	NA
PR	11.31	5.20	11.18	5.67	11.87	14.03	14.23
CR	129.01	80.73	124.10	NA	NA	NA	NA
R	2.55*	--	--	31.45	38.37	49.56	90.34
Ratio Data							
Variances, $\times 10^{-6}$							
Error	96.8	121.5	73.8	100.7	81.0	142.4	66.7
CPR	2077.5	1362.4	466.3	NA	NA	NA	NA
PR	1264.4	745.2	1156.3	718.1	1356.6	2134.8	1422.3
R	1153.7	--	--	--	--	--	--

Note: NA = not applicable; factor or interaction does not appear in model.

* All factor and interaction variances are significant at the 1% level, except those marked with an asterisk which are significant only at the 5% level.

Table 8

Error Variances and Variances Found to be Significant in the Determination of S*

	Both Test Conditions			Optimum Test Condition		Pretuned Test Condition	
	All Binders	Binder 2	Binder 3	Binder 2	Binder 3	Binder 2	Binder 3
			Intensity Data				
Code, counts/sec	-650	-1100	-675	-1100	-675	-1100	-675
Variances, $(\text{counts/sec})^2$							
Error	22.59	28.53	24.91	34.27	16.06	22.78	33.76
CPR	46.74	--	--	NA	NA	NA	NA
PR	22.00	--	6.34	--	13.02	--	--
CR	8.65*	11.18	--	NA	NA	NA	NA
R	10.20	42.68	--	32.36	--	64.18	--
CP	--	5.06*	--	NA	NA	NA	NA
P	--	17.52	--	7.53*	--	32.56	12.66
B	45,187.19	NA	NA	NA	NA	NA	NA
C	--	--	1.17*	NA	NA	NA	NA
			Ratio Data				
Variances, $\times 10^{-6}$							
Error	45.6	22.4	50.2	27.0	32.5	17.8	67.9
CPR	94.6	--	--	NA	NA	NA	NA
PR	44.5	--	12.9	--	26.2	--	--
CR	19.8*	--	11.4	NA	NA	NA	NA
R	54.8	--	16.0*	--	43.8*	--	--
CP	--	3.9*	--	NA	NA	NA	NA
P	--	13.8	20.5*	5.9*	--	25.5	25.6
B	91,252.6	NA	NA	NA	NA	NA	NA

Note: NA = not applicable; factor or interaction does not appear in model.

* All factor and interaction variances are significant at the 1% level, except those marked with an asterisk which are significant only at the 5% level.

Appendix A: Estimator and Calculation Formulas for Three Models Used in This Study

1. All the values shown in this report were obtained from the results of an analysis of variance (ANOVA). The procedures involved in ANOVA are well known and explained in many texts on statistical analysis. The ANOVA formulas for Model 1 of this study are, however, rather complex. It is, therefore, desirable to list the formulas for future reference, and for completeness the formulas for all three models used in this study are given. Fundamental to the ANOVA is the determination of the estimated mean square (E(MS)). Rules for this determination and derivation of the calculation formulas can be found in Bennett and Franklin.*

2. Model 1 is a mixed design with four main factors tested at levels shown in the main text of this report. Test condition (C) and binder (B) are fixed factors, whereas pellets (P) and rounds (R) are random factors. The following degrees of freedom (ν) and E(MS) were determined for the factors and interactions of this model.

Parameter	ν	E(MS)
C_i	1	$\sigma^2 + 4\sigma^2_{CPR} + 64\sigma^2_{CR} + 12\sigma^2_{CP} + 192\sigma^2_{C}$
B_j	3	$\sigma^2 + 8\sigma^2_{PR} + 32\sigma^2_{BR} + 24\sigma^2_{P} + 96\sigma^2_{B}$
CB_{ij}	3	$\sigma^2 + 4\sigma^2_{CPR} + 16\sigma^2_{CBR} + 12\sigma^2_{CP} + 48\sigma^2_{CB}$
$P_{k(j)}$	12	$\sigma^2 + 8\sigma^2_{PR} + 24\sigma^2_{P}$
$CP_{ik(j)}$	12	$\sigma^2 + 4\sigma^2_{CPR} + 12\sigma^2_{CP}$
R_{ℓ}	2	$\sigma^2 + 8\sigma^2_{PR} + 128\sigma^2_{R}$
$CR_{i\ell}$	2	$\sigma^2 + 4\sigma^2_{CPR} + 64\sigma^2_{CR}$

(Continued)

* Bennett, C. A. and Franklin, N. L., Statistical Analysis in Chemistry and the Chemical Industry, Wiley, New York, 1954.

Parameter	ν	E(MS)
$BR_{j\ell}$	6	$\sigma^2 + 8\sigma^2_{CPR} + 32\sigma^2_{BR}$
$CBR_{ij\ell}$	6	$\sigma^2 + 4\sigma^2_{CPR} + 16\sigma^2_{CBR}$
$PR_{k\ell(j)}$	24	$\sigma^2 + 8\sigma^2_{PR}$
$CPR_{ik\ell(j)}$	24	$\sigma^2 + 4\sigma^2_{CPR}$
$e_{m(ijk\ell)}$	288	σ^2

The estimator and calculation formulas for Model 1 are as follows:

Parameter	Estimator	Calculation Formula
μ	$(x_{ijk\ell m} - \bar{x}_{.....})$	$(\Sigma_{ijk\ell m} x^2_{ijk\ell m}) - (T^2_{...../384}) = (1) - (2)$
C_i	$(\bar{x}_{i....} - \bar{x}_{.....}) = I$	$(\Sigma_i T^2_{i..../192}) - (2) = (3) - (2) = I$
B_j	$(\bar{x}_{.j...} - \bar{x}_{.....}) = II$	$(\Sigma_j T^2_{.j.../96}) - (2) = (4) - (2) = II$
CB_{ij}	$(\bar{x}_{ij...} - I - II - \bar{x}_{.....}) = III$	$(\Sigma_{ij} T^2_{ij.../48}) - I - II - (2) = (5) - I - II - (2) = III$
$P_{k(j)}$	$(\bar{x}_{.jk..} - x_{.j...}) = IV$	$(\Sigma_{jk} T^2_{.jk../24}) - (4) = (6) - (4) = IV$
$CP_{ik(j)}$	$(\bar{x}_{ijk..} - IV - \bar{x}_{ij...}) = V$	$(\Sigma_{ijk} T^2_{ijk../12}) - IV - (5) = (7) - IV - (5) = V$
R_ℓ	$(\bar{x}_{...\ell.} - \bar{x}_{.....}) = VI$	$(\Sigma_\ell T^2_{...\ell./128}) - (2) = (8) - (2) = VI$
$CR_{i\ell}$	$(\bar{x}_{i..\ell.} - I - VI - \bar{x}_{.....}) = VII$	$(\Sigma_{i\ell} T^2_{i..\ell./64}) - I - VI - (2) = (9) - I - VI - (2) = VII$
$BR_{j\ell}$	$(\bar{x}_{.j.\ell.} - II - VI - \bar{x}_{.....}) = VIII$	$(\Sigma_{j\ell} T^2_{.j.\ell./32}) - II - VI - (2) = (10) - II - VI - (2) = VIII$
$CBR_{ij\ell}$	$(\bar{x}_{ij.\ell.} - I - II - III - VI - VII - VIII - \bar{x}_{.....})$	$(\Sigma_{ij\ell} T^2_{ij.\ell./16}) - I - II - III - VI - VII - VIII - (2) = (11) - I - II - III - VI - VII - VIII - (2)$
$PR_{k\ell(j)}$	$(\bar{x}_{.jk\ell.} - IV - \bar{x}_{.j.\ell.}) = IX$	$(\Sigma_{jk\ell} T^2_{.jk\ell./8}) - IV - (10) = (12) - IV - (10) = IX$
$CPR_{ik\ell(j)}$	$(\bar{x}_{ijk\ell.} - IV - V - IX - \bar{x}_{ij.\ell.})$	$(\Sigma_{ijk\ell} T^2_{ijk\ell./4}) - IV - V - IX - (11) = (13) - IV - V - IX - (11)$
$e_{m(ijk\ell)}$	$(x_{ijk\ell m} - \bar{x}_{ijk\ell.})$	$(1) - (13)$

3. Model 2 is a crossed design with three main factors. Levels and definitions are as described previously. The following degrees of freedom (ν) and E(MS) were determined:

Parameter	ν	E(MS)
C_i	1	$\sigma^2 + 4\sigma^2_{CPR} + 16\sigma^2_{CR} + 12\sigma^2_{CP} + 48\sigma^2_{C}$
P_j	3	$\sigma^2 + 8\sigma^2_{PR} + 24\sigma^2_{P}$
CP_{ij}	3	$\sigma^2 + 4\sigma^2_{CPR} + 12\sigma^2_{CP}$
R_k	2	$\sigma^2 + 8\sigma^2_{PR} + 32\sigma^2_{R}$
CR_{ik}	2	$\sigma^2 + 4\sigma^2_{CPR} + 16\sigma^2_{CR}$
PR_{jk}	6	$\sigma^2 + 8\sigma^2_{PR}$
CPR_{ijk}	6	$\sigma^2 + 4\sigma^2_{CPR}$
$e_{\ell(ikj)}$	72	σ^2

The estimators and calculation formulas for Model 2 are as follows:

Parameter	Estimator	Calculation Formula
μ	$(x_{ijk\ell} - \bar{x}_{....})$	$(\Sigma_{ijk\ell}x^2_{ijk\ell}) - (T^2_{..../96}) = (1) - (2)$
C_i	$(\bar{x}_{i...} - \bar{x}_{....}) = I$	$(\Sigma_i T^2_{i.../48}) - (2) = I$
P_j	$(\bar{x}_{.j..} - \bar{x}_{....}) = II$	$(\Sigma_j T^2_{.j../24}) - (2) = II$
CP_{ij}	$(\bar{x}_{ij..} - I - II - \bar{x}_{....}) = IV$	$(\Sigma_{ij} T^2_{ij../12}) - I - II - (2) = IV$
R_k	$(\bar{x}_{..k.} - \bar{x}_{....}) = III$	$(\Sigma_k T^2_{..k./32}) - (2) = III$
CR_{ik}	$(\bar{x}_{i.k.} - I - III - \bar{x}_{....}) = V$	$(\Sigma_{ik} T^2_{i.k./16}) - I - III - (2) = V$
PR_{jk}	$(\bar{x}_{.jk.} - II - III - \bar{x}_{....}) = VI$	$(\Sigma_{jk} T^2_{.jk./8}) - II - III - (2) = VI$
CPR_{ijk}	$(\bar{x}_{ijk.} - I - II - III - IV - V - VI - \bar{x}_{....})$	$(\Sigma_{ijk} T^2_{ijk./4}) - I - II - III - IV - V - VI - (2)$
$e_{\ell(ijk)}$	$(x_{ijk\ell} - \bar{x}_{ijk.})$	$(1) - (\Sigma_{ijk} T^2_{ijk./4})$

4. Model 3 is a two-factor crossed design. Levels and definitions are as defined previously. The following degrees of freedom (ν) and E(MS) were determined.

Parameter	ν	E(MS)
P_i	3	$\sigma^2 + 4\sigma^2_{PR} + 12\sigma^2_P$
R_j	2	$\sigma^2 + 4\sigma^2_{PR} + 16\sigma^2_R$
PR_{ij}	6	$\sigma^2 + 4\sigma^2_{PR}$
$e_{k(ij)}$	36	σ^2

The estimator and calculation formulas for Model 3 are as follows:

Parameter	Estimator	Calculation Formula
μ	$(x_{ijk} - \bar{x}_{...})$	$(\Sigma_{ijk}x^2_{ijk}) - (T^2_{...}/48) = (1) - (2)$
P_i	$(\bar{x}_{i..} - \bar{x}_{...}) = I$	$(\Sigma_i T^2_{...}/12) - (2) = I$
R_j	$(\bar{x}_{.j.} - \bar{x}_{...}) = II$	$(\Sigma_j T^2_{.j.}/16) - (2) = II$
PR_{ij}	$(\bar{x}_{ij.} - I - II - \bar{x}_{...})$	$(\Sigma_{ij} T^2_{ij.}/4) - I - II - (2) = (3)$ $- I - II - (2)$
$e_{k(ij)}$	$(x_{ijk} - \bar{x}_{ij.})$	$(1) - (3)$

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13. ABSTRACT

A balanced statistical experiment was conducted to evaluate the effect of four factors on the X-ray emission analysis for calcium (Ca), silicon (Si), iron (Fe), aluminum (Al), magnesium (Mg), and sulfur (S) in portland cement. The factors evaluated were: instrument conditions (optimized versus predetermined goniometer and counter-tube voltage settings); rounds; binders used to aid in grinding and pelletizing the cement (boric acid, sodium lauryl sulfate, Boraxo, and a Boraxo-cellulose mixture); and the sample pellet-making procedure. The experimental results indicate that pellets have a direct effect on the analysis of portland cement. Binders were found to have a direct effect on the elemental analyses, and the effect was determined to be due to sodium lauryl sulfate. However, the effect is negated by the use of a ratio method of analysis. Instrument conditions and rounds were both found to have an effect on the analytical results either as direct factors or in the form of interactions, particularly the interaction of pellets and rounds. The precision of the X-ray analysis is apparently increased when optimized instrument settings are used. Either sodium lauryl sulfate or Boraxo may be used as a binder for X-ray emission analysis. Only one pellet need be made with each sample. A replicate analysis will confound the pellet-round interaction with round variances, and the pellet effect will be confounded between samples. The decision as to whether the spectrometer is to be tuned prior to every analysis is deferred until the spectrometer calibration results are evaluated.

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