

CONCLUSION

The δ -correction approach has great advantages: it takes the best from the numerical correction methods, and leaves behind most of their inconveniences; it is simple to apply and very accurate; it is particularly well suited to the analysis of industrial products where composition variations are usually not very large. The authors believe that the δ method will be in common use in the near future. A paper on the analysis of cements appears in this Journal (11); although that paper is not intended to be a typical example of application of the δ method, it nevertheless shows that the method offers definite advantages in relation with accuracy and simplicity.

LITERATURE CITED

- (1) G. R. Lachance and R. J. Traill, *Can. Spectrosc.*, **11**, 43 (1966).
- (2) S. D. Rasberry and K. F. J. Heinrich, *Anal. Chem.*, **46**, 81 (1974).
- (3) F. Claisse and M. Quintin, *Can. Spectrosc.*, **12**, 129 (1967).
- (4) J. W. Criss and L. S. Birks, *Anal. Chem.*, **40**, 1080 (1968).
- (5) R. Tertian, *X-Ray Spectrom.*, **2**, 95 (1973).

- (6) R. Tertian, *X-Ray Spectrom.*, **4**, 52 (1975).
- (7) W. K. Dejongh, *X-Ray Spectrom.*, **2**, 151 (1973).
- (8) G. R. Lachance, *Can. Spectrosc.*, **15**, 64 (1970).
- (9) R. Rousseau and F. Claisse, *X-Ray Spectrom.*, **3**, 31 (1974).
- (10) K. F. J. Heinrich and S. D. Rasberry, *Adv. X-Ray Anal.*, **17**, 309 (1974).
- (11) G. Fréchette, J. C. Hébert, T. P. Thinh, R. Rousseau, and F. Claisse, *Anal. Chem.*, **50**, following paper in this issue.
- (12) C. H. Anderson, J. E. Mander and J. W. Leitner, *Adv. X-Ray Anal.*, **17**, 217 (1974).
- (13) G. R. Lachance, Energy, Mines and Resources Canada, Ottawa, Canada, personal communication, 1978.
- (14) M. A. Amoury and K. S. Pryor, Denver X-Ray Conference, 1973.

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X-ray Fluorescence Analysis of Cements

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The combination of a borate fusion and "Delta-Coefficient" corrections for matrix effects is shown to yield a method for the analysis of cements in which high accuracy, rapidity, and simplicity are compatible. The features of the method are: (a) Counting statistics is nearly the only source of errors. (b) Weighing of flux and sample are nearly the only manipulations. (c) One standard only is required. (d) When cement composition is rather constant, the method described can be shortened significantly. The analysis of the six major elements in NBS-633-639 cements was performed with an average accuracy of 0.07%.

X-ray Fluorescence is currently used in the analysis of cements because of its rapidity and reproducibility. A complete analytical procedure incorporates the following steps: (a) sample preparation: grinding, pelletizing or fusion; (b) X-ray measurements; (c) determination of sample composition by comparison with other cements, by calibration lines, or by calculations with influence coefficients.

In addition, preparatory work must be done once only to work out the methods, for example, obtaining the required standards or determination of influence coefficients.

Accuracy and rapidity are both desirable but as they are usually incompatible one makes a compromise between the possible procedures. For example, pelletizing which is associated with some inaccuracies due to particle size effects is often adopted for sample preparation instead of the more accurate but sometimes slower fusion process. For similar

reasons, corrections for matrix effects are sometimes based on an empirical relation already in the computer instead of a more fundamental and more accurate relation.

The ideal situation is one where each step of the procedure is at the same time the simplest, the fastest, and the most accurate of all the available ways to make it; the purpose of this paper is to present a procedure which is close to this ideal situation.

That procedure is a combination of a borate fusion and corrections for matrix effects by the δ method described by Claisse and Thinh (1). It features rapid, simple, and reproducible sample preparation; complete freedom from particle size effects; simple and accurate corrections for matrix effects; calibration through one standard only; accuracy comparable to the better wet chemical methods.

First, a procedure is described with the objective of obtaining maximum accuracy. Second, it is shown how the procedure can be shortened considerably with nearly no loss in accuracy.

EXPERIMENTAL

Sample Preparation. The fusion method (2) was adopted using mixtures of 40% calcined cement and 60% pure lithium tetraborate as flux (2.8 and 4.2 g, respectively); the reasons for this choice are:

- (1) Complete elimination of particle size effects.
- (2) High ratio of sample to flux results in strong X-ray lines with easier detection of light elements in low concentrations such as Mg, and lower statistical errors on counting.
- (3) Absence of a heavy absorber or other additives in the flux also results in stronger X-ray lines and minimizes the number

Table I. Experimental Conditions^a

| X-ray line | analyzing crystal | line | counting time, s | | typical intensities, counts/s | |
|---------------|-------------------|----------------|------------------|---------------|-------------------------------|----------------------|
| | | | background | | background | net line/ % oxide |
| | | | low angle | high angle | | |
| Mg K α | ADP | 3 \times 100 | 100 | 100 | 13 | 5 |
| Al K α | EDDT | 3 \times 100 | 100 | | 9 | 18 |
| Si K α | EDDT | 3 \times 100 | 100 | 100 | 6 | 10 |
| S K α | EDDT | 3 \times 100 | 2 \times 20 | 2 \times 20 | 9 | 50 |
| K K α | EDDT | 3 \times 100 | 20 | 20 | 30 | 1700 |
| Ca K α | LiF | 3 \times 100 | 20 | | 18 | 190 |
| Fe K α | LiF | 3 \times 40 | 20 | 20 | 28 | 300 |

^a Philips Spectrograph PW 1540, chromium tube, 44 kV, 20 mA.Table II. δ Coefficients for Use with Philips Spectrograph PW 1540, Chromium Tube, 44 kV and with Calcined NBS-634 as Reference Standard^a

| analyzed oxide | interfering oxide | | | | | | |
|--------------------------------|-------------------|--------------------------------|------------------|-----------------|------------------|---------|--------------------------------|
| | MgO | Al ₂ O ₃ | SiO ₂ | SO ₃ | K ₂ O | CaO | Fe ₂ O ₃ |
| MgO | | -0.1041 | -0.1316 | 0.1165 | -0.0235 | -0.0152 | 0.4932 |
| Al ₂ O ₃ | 0.8325 | | -0.0144 | 0.0491 | -0.0512 | -0.0089 | 0.7774 |
| SiO ₂ | 0.5837 | 0.8381 | | 0.0041 | -0.0645 | 0.0638 | 0.6030 |
| SO ₃ | 0.4970 | 0.5914 | 0.6801 | | -0.0448 | -0.1015 | 0.4751 |
| K ₂ O | 0.0481 | 0.1305 | 0.2066 | 0.4028 | | -0.3374 | 0.0514 |
| CaO | -0.0684 | -0.0006 | 0.0615 | 0.2233 | 1.7411 | | -0.0605 |
| Fe ₂ O ₃ | -0.2629 | -0.2301 | -0.2055 | -0.1174 | 0.6269 | 0.5339 | |

^a Samples fused with 1.5 times their weight of lithium tetraborate.

of weighings to only two, the sample and the flux.

(4) Rapidity, simplicity, and reproducibility of sample preparation could be obtained by using a Claisse Fluxer (3) to produce six Claisse (glass) disks simultaneously and automatically in about 10 min including cooling. Fusion and homogenization time was set at 6 min although 4 min is usually sufficient for cements. One drop of a solution containing 20 mg NaBr was put into the mixture before fusion to prevent the glass from sticking to the Pt-5% Au crucibles and molds, minimizing the need of cleaning. It was not found necessary to use better nonwetting agents such as KI or LiI. The Claisse disks, 30 mm in diameter, were used in the spectrometer as they came out of the Fluxer without any further preparation. This sample preparation is faster than grinding and pelletizing, and faster than most other fusion techniques, even when the samples are processed one by one instead of six at a time. The Claisse disks were made from samples calcined at 1000 °C but it is also possible to work with raw cements (4). In this paper, the reported concentrations always refer to the raw cements; "loss on ignition" values reported on the certificates of analysis were used to make the appropriate corrections.

Measurements. Measurements were made on seven NBS standards of cements (NBS-633-639) under the conditions specified in Table I. One Claisse disk only was prepared for each cement. Background intensities at line peaks were obtained by linear interpolation of background readings on both sides of the lines when possible (Table I). An additional correction was necessary for the Mg K α line because that line is close to a strong Ca line which produces a curved background (Figure 1). That correction was obtained by measuring the background at three points on sample NBS-634 and fitting a quadratic curve of the type $y = a + bx + cx^2$; the calculated background under the Mg line was found to be 0.5 count/s. lower than that obtained by linear interpolation. Since all the samples had similar backgrounds, this correction was applied to all the Mg K α measurements.

As counting statistics is the major source of errors in the proposed procedure, experimental conditions were chosen (Table I) so as to accumulate large numbers of counts to reach the maximum accuracy. In routine work, it is obvious that shorter measurements can be made, specially background measurements. Corrections for dead time were made.

CALCULATION AND SAMPLE COMPOSITION

The Delta-Coefficient method of correction for matrix effects discussed by Claisse and Thinh (1) was chosen for its high accuracy and simplicity. Concentrations are obtained

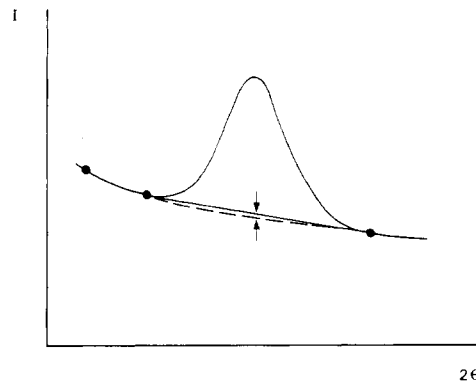


Figure 1. Determination of background correction due to curvature (see text)

by comparing the X-ray intensities of the unknown with those of a reference cement (standard) and applying the following equations to each element in an iterative manner:

$$C_A = C_A^{\text{app}} (1 + \delta_B \Delta C_B + \delta_C \Delta C_C + \dots) \quad (1)$$

with

$$C_A^{\text{app}} = C_A^* \frac{I_A}{I_A^*} \quad (2)$$

$$\Delta C_B = C_B - C_B^* \quad (3)$$

where C is the weight fraction in the original sample, A is the element analyzed, δ are influence coefficients, and $*$ refers to the reference cement.

A typical set of δ coefficients that were used is given in Table II.

An example of calculation, considering three elements only, is given in Table III. Lines 1, 2, and 3 contain the required information, namely the X-ray fluorescence intensities of the two cements and the composition of the standard. From these figures, the apparent composition of the unknown (line 4) is calculated by means of Equation 2. Using this approximate composition, Equations 3 and 1 are applied to yield ap-

Table III. Example of Calculation of a Sample Composition

| line no | units | SiO ₂ | CaO | Fe ₂ O ₃ |
|------------------------------------|----------|------------------|-------|--------------------------------|
| 1 <i>I</i> * (standard) | counts/s | 235 | 11734 | 470 |
| 2 <i>I</i> (sample) | counts/s | 213 | 11468 | 1053 |
| 3 <i>C</i> * (standard) | % | 23.49 | 64.29 | 1.63 |
| 4 <i>C</i> ^{app} (sample) | % | 21.29 | 62.83 | 3.65 |
| 5 ΔC | % | -2.20 | -1.46 | 2.02 |
| 6 <i>C</i> (1st iteration) | % | 21.54 | 62.67 | 3.64 |
| 7 ΔC | % | -1.95 | -1.62 | 2.01 |
| 8 <i>C</i> (2nd iteration) | % | 21.53 | 62.68 | 3.64 |

proximate ΔC 's (line 5) and an approximate but better composition (line 6). The latter calculations are repeated (lines 7 and 8) to obtain a still more accurate composition. Usually, the first iteration is nearly sufficient but two iterations give a more reliable composition.

PREPARATORY WORK

Some preparation is always necessary in working out a method. As one standard only is required in the application of the δ method, no problem exists in finding a reliable cement standard.

The δ coefficients are calculated once only from α coefficients by means of simple equations (*I*); we used the equation based on the Claisse-Quintin relation:

$$\delta_B = \frac{\alpha_B + 2\alpha_{BB}C_B^*}{1 + \alpha_B C_B^* + \alpha_C C_C^* + \dots + \alpha_{BB} C_B^{*2} + \alpha_{CC} C_C^{*2} + \dots}$$

where * refers to the composition of the standard.

Obtaining the required α coefficients for use in Equation 4 may represent a considerable amount of work when it is done the way we did (high accuracy was the objective), but our work does not have to be repeated by those who can apply our coefficients, and there are also easier ways to obtain these coefficients (*I*). To determine our α coefficients, binary mixtures of MgO, Al₂O₃, SiO₂, CaO, and Fe₂O₃ were prepared as glass disks as described above and the α values were obtained as described in reference 1. When the glass disks produced at the nominal sample/flux ratio of 2/3 were not of acceptable quality, the α coefficients were obtained by extrapolation from α values found at lower sample/flux ratios. The other α coefficients were calculated from fundamental parameters (5).

RESULTS

In a first round of analyses, sample NBS-634 was used as the reference cement because its composition is close to the average composition of the other NBS cements. The δ -coefficients which apply when the sample is used as a reference are listed in Table II. The six other samples were considered as unknowns and were compared to that standard; their calculated compositions are reported in Table IV. The largest absolute error is 0.18% (CaO at the 60% level) and the average error is 0.06%. Considering the fact that the composition of the reference standard is known to about $\pm 0.04\%$, we must recognize that the other causes of errors, namely weighing, counting, and residual matrix effects are extremely small.

A graphical illustration of the high accuracy obtained in the analysis of SiO₂ and CaO is given in Figures 2 and 3. The dark points represent the results when it is assumed that the concentrations are directly proportional to the X-ray intensities (Equation 2); the white points are obtained when corrections for matrix effects are made (Equation 1).

The analysis of SO₃ in sample NBS-635 is remarkable. This represents a more than threefold extrapolation from the

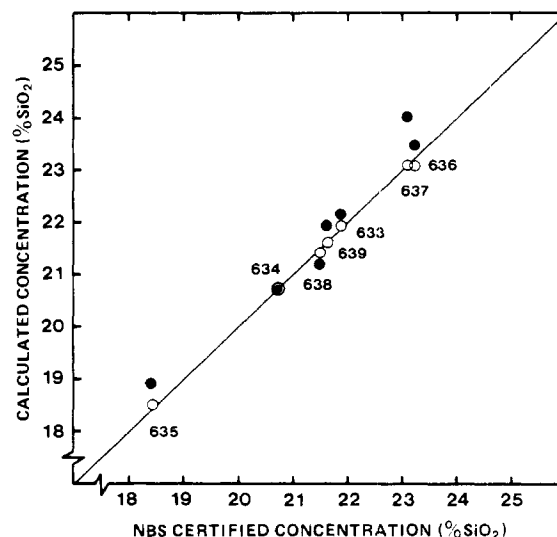


Figure 2. Analysis of SiO₂ in NBS 633-639 cements (NBS-634 as reference standard). (●) Apparent concentrations (Equation 2). (○) Corrected concentrations (Equation 1)

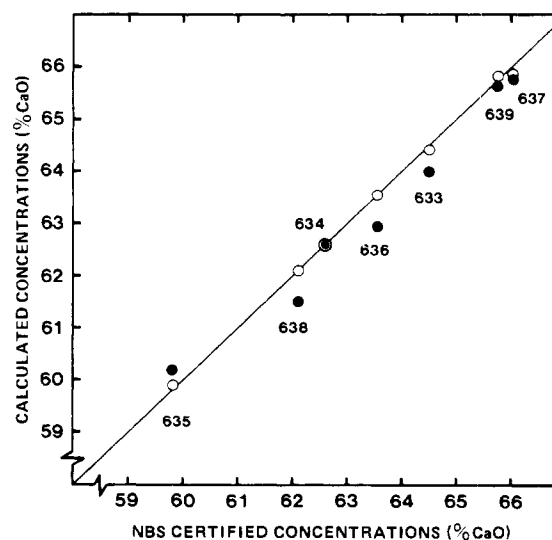


Figure 3. Analysis of CaO in NBS 633-639 cements (NBS-634 as reference standard). (●) Apparent concentrations (Equation 2). (○) Corrected concentrations (Equation 1)

reference composition. Also the analysis of Fe₂O₃ in sample NBS-633 represents about 50% extrapolation.

Results similar to those in Table IV were obtained when any of the six other standards was used as a reference; in each case a new table of δ coefficients was calculated although this was not really necessary because the differences with the values in Table II are very small. Only three unacceptable errors of 0.30, 0.42, and 0.46% (absolute) were observed out of a total of 294 results (7 cement standards; each standard was used in turn as a reference to analyse the 6 other cements for 7 elements), but these three errors occurred in conditions of severe extrapolation. Needless to say, in any circumstance, results obtained by severe extrapolation should never be considered as reliable.

One case where exceptionally large extrapolations have been made without significant errors is that of K₂O which ranges in concentrations from 0.06% to 0.59%. Since the line intensities are relatively high compared to the background, they are accurate even at the 0.06% level, so that the cement containing 0.59% K₂O could be analyzed by comparing it to the cement with 0.06% K₂O (NBS-639 taken as the reference standard); this represents a tenfold extrapolation. When the

Table IV. Comparison between Certified and Calculated Concentrations of NBS 633-639 Cements^a

| | MgO | | | Al ₂ O ₃ | | | SiO ₂ | | | SO ₃ | | | K ₂ O | | | CaO | | | Fe ₂ O ₃ | | |
|---------|------------------|------------------|-------|--------------------------------|--------|-------|-------------------|--------|-------|------------------|--------|-------|------------------|--------|-------|-------------------|--------|-------|--------------------------------|--------|-------|
| | cert. | calcd. | diff. | cert. | calcd. | diff. | cert. | calcd. | diff. | cert. | calcd. | diff. | cert. | calcd. | diff. | cert. | calcd. | diff. | cert. | calcd. | diff. |
| NBS-633 | 1.0 ₄ | 0.98 | -0.06 | 3.7 ₈ | 3.90 | 0.12 | 21.8 ₈ | 21.95 | 0.07 | 2.2 ₀ | 2.21 | 0.01 | 0.17 | 0.17 | 0.00 | 64.5 ₀ | 64.37 | -0.13 | 4.20 | 4.18 | -0.02 |
| NBS-634 | 3.3 ₀ | 5.2 ₁ | 1.91 | 18.4 ₁ | 18.52 | 0.11 | 20.7 ₃ | 20.73 | 0.00 | 7.0 ₇ | 6.95 | -0.12 | 0.42 | 0.46 | 0.04 | 62.5 ₈ | 59.91 | -2.67 | 2.84 | 2.64 | -0.20 |
| NBS-635 | 1.2 ₃ | 1.18 | -0.05 | 6.2 ₉ | 6.29 | 0.00 | 18.4 ₁ | 18.52 | 0.11 | 7.0 ₇ | 6.95 | -0.12 | 0.42 | 0.46 | 0.04 | 59.8 ₃ | 59.91 | 0.08 | 2.61 | 2.64 | 0.03 |
| NBS-636 | 3.9 ₅ | 3.83 | -0.12 | 3.0 ₂ | 3.17 | 0.15 | 23.2 ₂ | 23.05 | -0.17 | 2.3 ₁ | 2.41 | 0.10 | 0.59 | 0.56 | -0.03 | 63.5 ₄ | 63.54 | 0.00 | 1.61 | 1.59 | -0.02 |
| NBS-637 | 0.6 ₇ | 0.65 | -0.02 | 3.2 ₈ | 3.32 | 0.04 | 23.0 ₇ | 23.12 | 0.05 | 2.3 ₈ | 2.41 | 0.03 | 0.25 | 0.25 | 0.00 | 66.0 ₄ | 65.86 | -0.18 | 1.80 | 1.75 | -0.05 |
| NBS-638 | 3.8 ₁ | 3.74 | -0.09 | 4.4 ₅ | 4.58 | 0.13 | 21.4 ₈ | 21.37 | -0.11 | 2.3 ₁ | 2.46 | 0.15 | 0.59 | 0.59 | 0.00 | 62.0 ₀ | 62.10 | 0.10 | 3.55 | 3.56 | 0.01 |
| NBS-639 | 1.2 ₆ | 1.18 | -0.08 | 4.2 ₈ | 4.35 | 0.07 | 21.6 ₁ | 21.61 | 0.00 | 2.4 ₈ | 2.45 | -0.03 | 0.06 | 0.06 | 0.00 | 65.7 ₆ | 65.83 | 0.07 | 2.40 | 2.36 | -0.04 |

^a NBS-634 was taken as the reference standard. Concentrations in weight %.Table V. Analysis of NBS 633-639 Cements Using Accurate^a and Inaccurate^a α and δ Coefficients (NBS-634 as Reference)

| analysed oxide | average concn, % | average absolute errors, % | | | |
|--------------------------------|------------------|----------------------------|-------------------------|------------------------------|-------------------------|
| | | δ method | | α method ^b | |
| | | accurate ^a | inaccurate ^a | accurate ^a | inaccurate ^a |
| MgO | 2.2 | 0.07 | 0.07 | 0.07 | 0.10 |
| Al ₂ O ₃ | 4.3 | 0.08 | 0.08 | 0.08 | 0.17 |
| SiO ₂ | 21.5 | 0.08 | 0.17 | 0.08 | 0.96 |
| SO ₃ | 3.0 | 0.06 | 0.08 | 0.06 | 0.24 |
| K ₂ O | 0.4 | 0.005 | 0.007 | 0.005 | 0.013 |
| CaO | 63.5 | 0.09 | 0.17 | 0.09 | 0.63 |
| Fe ₂ O ₃ | 2.7 | 0.03 | 0.02 | 0.03 | 0.33 |

^a See text for definition of "accurate" and "inaccurate".^b Adjusted to give zero error on NBS-634.

cement NBS-639 was used in this way to analyze the six other samples for K₂O, the average error was 0.02%.

Our calculations indicate that the average error on the 294 calculated concentrations is 0.07%. This includes all the results, even those with the larger deviations which could be rejected on the ground that severe extrapolations are not acceptable.

The high accuracy observed is not unexpected. It has been shown in reference 1 that the δ method is accurate in principle, the main sources of errors being the reliability of the reference standard and the counting statistics.

In order to confirm that matrix effect corrections are a minor source of errors only, large experimental errors on δ coefficients were simulated by increasing arbitrarily each α value by 40%. This set of "inaccurate α " values led to a set of "inaccurate δ " values. A comparison between the average errors on concentrations when "accurate" and "inaccurate" δ coefficients are used, is given in Table V, columns 3 and 4; the differences are very small.

As a comparison, the concentrations were also calculated using the better known α method based on the Claisse-Quintin relation (6), with "accurate" and "inaccurate" α coefficients; the results are shown in Table V, columns 5 and 6. In this case, the deviations are very different.

It will be observed that the deviations in columns 3 and 5 are the same; this is due to the fact that the α method was applied in a rather unconventional manner. Since fluorescence intensities for the pure elements were not available, they were calculated from the composition and the intensities of the standard; this means that no error is observed when the composition of the standard is recalculated. If the intensities of the pure elements had been measured the errors listed in columns 5 (and 6 also) would be significantly larger.

An interesting consequence of the above observations is that the α coefficients do not need to be known with high accuracy; they can be obtained by interpolation (7), they can be taken from previous works in similar experimental conditions, and sometimes they can be reasonably estimated.

In routine analysis, the method described above can be shortened considerably with almost no sacrifice on accuracy because the variations in cement composition are usually small in any given cement factory.

(a) Background intensities are usually constant when the samples are fused and when the concentration of any element does not vary by more than 5 to 10% absolute; in such a case background measurements are omitted and a constant value is used in the calculations. When the line to background ratio is low, background measurements must be made however.

(b) If a sample of the currently produced cement is used as the reference standard, most of the corrections for matrix effects will be very small; we estimate that about half of the

42 δ coefficients of Table II can be ignored in most cases.

(c) Calcination of the cements prior to fusion is not necessary when the loss on ignition is already known. Corrections for loss on ignition is done in the same way as for matrix corrections for elements (4, 8), through a δ coefficient.

(d) Calcination of the cements prior to fusion is not necessary and prior determination of loss of ignition is not necessary either if a small sacrifice on accuracy is acceptable. The loss on ignition can be obtained indirectly from X-ray measurements (8) and corrections can be made as in (b).

(e) Weighing of flux and sample can be omitted when all the elements of the sample are determined (9). In such a case, an approximate quantity of sample and an approximate quantity of flux are fused together, and the data are processed as when the loss on ignition is unknown as in (d). The result is the composition of the sample in the calcined state.

(f) Elements whose concentrations are already known do not need to be measured. Their known concentrations are used in Equation 1 for the calculation of the concentrations of the other elements. No relation is written for the calculation of the concentration of these known elements.

CONCLUSION

The combination of fusion with corrections by the δ method has been shown to be an accurate, rapid, and simple method of analysis, specially in routine work when the cement composition varies little.

It is accurate because: (a) modern X-ray spectrometers are capable of accurate measurements; (b) the delta approach is, in principle, the more accurate way to make correction for matrix effects.

It is rapid because: (a) an automatic machine is now available for the simultaneous preparation of six samples as homogeneous glass buttons; (b) measurements on one standard only are necessary; (c) the corrections for matrix effects are easy to make.

It is simple because: (a) the sample preparation requires two weighings only, the sample and the flux, the other operations being automatic; (b) the corrections for matrix effects are done by means of a very simple expression.

It has also been shown that the δ coefficients can be calculated from α coefficients that are not very accurate. As a result, the δ coefficients listed in Table II can be used directly when the experimental conditions are close to those specified in that Table. We estimate that the same coefficients apply rather well with nearly all makes of spectrographs because the α coefficients do not change significantly with the spectrometer geometry (10).

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LITERATURE CITED

- (1) F. Claisse and T. P. Thinh, *Anal. Chem.*, **51**, preceding paper in this issue.
- (2) F. Claisse, *Norelco Rep.*, III, (1), 3 (1957).
- (3) Claisse Scientific Corporation, 7-1301 Place de Mérici, Québec, P.Q., Canada, G1S 4N8.
- (4) In preparation.
- (5) R. Rousseau and F. Claisse, *X-ray Spectrom.*, **3**, 31, (1974).
- (6) F. Claisse and M. Quintin, *Can. Spectrosc.*, **12**, 129 (1967).
- (7) R. J. Traill and G. R. Lachance, *Can. Spectrosc.*, **11**, 63 (1966).
- (8) R. LeHouillier, S. Turmel, and F. Claisse, *Adv. X-Ray Anal.*, **20**, 459 (1977).
- (9) S. Turmel, R. LeHouillier, and F. Claisse, *Can. J. Spectrosc.*, **23**, 125 (1978).
- (10) G. R. Lachance, *Can. Spectrosc.*, **15**, 64 (1970).

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Effective Sample Weight from Scatter Peaks in Energy-Dispersive X-Ray Fluorescence

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A method is presented for the energy-dispersive X-ray fluorescence analysis of samples with irregular shape or heterogeneous thickness. Based on the intensity of the coherently and the incoherently scattered excitation radiation, the procedure permits the calculation of an "effective thickness" of samples with unknown composition. Within certain restrictions, the method avoids weighing of the sample and allows the analysis of thin non-uniform targets. These features have been checked by analyzing simulated highly heterogeneous samples and thin targets simply prepared by drying a slurry of standard reference material on a Mylar carrier.

The use of thin or intermediate thickness samples in X-ray fluorescence analysis presents several advantages over the more usual method involving infinitely thick targets. Indeed,

in the former case, the absorption and enhancement effects are small and can be corrected simply. Moreover, in tube excited energy-dispersive X-ray fluorescence, optimal detection limits are obtained (for the most commonly determined elements in usual matrices) for a sample thickness of a few mg cm⁻² only; above this level the increase of the background produced in the detector by incomplete charge collection of the exciting radiation dominates over the gain in characteristic line intensity resulting from the increase of sample thickness.

Since in energy-dispersive X-ray fluorescence setups, the excitation-detection efficiency varies strongly from point to point over the sample area (1), it is generally accepted that the sample to be analyzed should be present as a homogeneous and thin layer for accurate analyses. Preparation of such specimen presents important practical problems for, e.g., biological and geological samples.

The method, presented in this paper, allows the analysis of samples of heterogeneous thickness and irregular shape,