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APPLICATION NOTES

The analysis of tile glaze

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Introduction

Tile glaze is a complex mixture of refractory oxides. Its composition must be carefully monitored since its properties can vary considerably with changes in composition. The range of concentration of the major constituents is shown in Table 1.

Compound	Concentration
SiO ₂	30 – 50%
Al ₂ O ₃	5 – 15%
Na ₂ O	10 – 20%
K ₂ O	0.5 – 5%
B ₂ O ₃	15 – 30%
CaO	5 – 15%

Table 1: Composition of glaze

This sample requires careful sample preparation to ensure complete dissolution and careful analysis to avoid interferences. The sample was obtained in powder form and two sample preparation methods were used – an acid digestion and a sodium hydroxide fusion. The method of standard additions was used for calibration in order to avoid interferences.

Experimental

Sample preparation

Method 1: Acid digestion

A 0.5 g sample was weighed into a 50 mL screw-top, wide-mouth plastic bottle. 20 mL of concentrated HCl was added and the sample allowed to stand for 35 minutes (with occasional shaking). 4 mL of 40% HF was added and the solution maintained at 50 – 60°C for 30 minutes. 0.5 g of boric acid was added and the solution was allowed to cool. It was then transferred to a 100 mL volumetric flask and made up to volume.

Because of the addition of boric acid, this sample could not be used for boron determination. If boric acid had not been added, the method could have been used for all elements. However, it was preferable to passivate the hydrofluoric acid to minimize the needed to handle highly corrosive solutions and to allow standard glassware to be used for preparation of the standard additions.

Method 2: Sodium hydroxide fusion

A 0.5 g sample was fused with 2 g NaOH in a platinum crucible. This was cooled and dissolved in 100 mL of warm water, then acidified by slow addition of 15 mL concentrated HCl. 5 mL of 10 vol H₂O₂ was added and the solution warmed to 60°C and diluted to 250 mL. This solution was used for the boron determination. It could have been used for all but the sodium determination. It could not be used for sodium because of the NaOH used in the fusion.

Table 2 shows the expected concentration range of the elements in the prepare solutions. These correspond to the oxide concentrations in Table 1.

Element	Concentration in Solid	Volume of Solution (mL)	Concentration in Solution (mg/L)
Si	14 – 24%	100	700 – 1200
Al	2.7 – 7.9%	100	130 – 400
Na	7.5 – 15%	100	370 – 740
K	0.4 – 4%	100	21 – 210
B	4.7 – 9.3%	250	90 – 180
Ca	3.6 – 11%	100	180 – 540

Table 2: Composition of prepared solutions (0.5 g of glaze powder was used)

Due to the complex nature of the sample, it was necessary to use the method of standard additions for calibration with all elements. Since this method is only appropriate for the linear part of the calibration curve, dilution factors were chosen to put the sample concentration near the bottom of the normal working range. Table 3 shows the optimum working range for the wavelength used with each element, as listed in in the GBC Flame Methods Manual, and the selection dilution factor.

Element	Wavelength (nm)	Optimum Working Range (mg/L)	Dilution Factor
Si	251.6	68 – 275	20
Al	309.2	25 – 135	10
Na	330.2	100 – 380	10
K	766.5	0.4 – 1.5	100
B	249.8	340 – 1400	1
Ca	422.7	1 – 4	100

Table 2: Dilution factors

A range of addition standards was prepared for each element as shown in Table 4.

Element	Addition 1	Addition 2	Addition 3
Si	50	100	150
Al	20	40	60
Na	50	100	150
K	3	6	9
B	100		
Ca	3	6	9

Table 4: Concentrations of added standard (mg/L)

An ionization suppressant comprising 0.1% caesium was added to samples and additions for calcium and potassium.

Instrumentation

A GBC atomic absorption spectrophotometer was used for all measurements. This instrument allows direct calibration in the standard additions mode using a least squares regression, and it provides a printout of the standard additions calibration plots. It also prints the largest deviation from the fitted line to alert the analyst to calibration curvature or faulty standard preparation.

The wavelengths used were as listed in Table 3 and the other conditions as in Table 5. A nitrous oxide-acetylene burner was used for all measurements, including those with the air-acetylene flame.

Element	Bandwidth (nm)	Lamp Current (mA)	Background Corrector	Flame
Si	0.2	15	On	N ₂ O-acet
Al	0.5	7	On	N ₂ O-acet
Na	0.5	5	Off	air-acet
K	1.0	5	Off	air-acet
B	0.2	18	On	N ₂ O-acet
Ca	0.5	5	Off	N ₂ O-acet

Table 5: Operating conditions

Results

The prepared samples and series of additions were aspirated in turn and a standard additions graph obtained for each element. The graph for calcium is shown in Figure 1 and similar graphs were obtained for the other elements. As usual with the standard additions method, it was important to check the linearity of these calibrations.

Table 6 shows the concentrations in the prepared samples as determined from the standard additions calibration, the concentrations of the elements in the solid sample and the computed concentrations of the oxides in the solid sample.

Element	Measured Conc. (mg/L)	Conc. of Element in Solid	Conc. of Oxide in Solid
Si	52	20.7%	44.2%
Al	19.2	3.8%	7.2%
Na	52	10.1%	13.6%
K	0.6	1.2%	1.4%
B	159	9.06%	29.2%
Ca	2.76	5.5%	7.7%

Table 6: Analytical results

The oxide concentrations in Table 6 add up to slightly over 100% but the accuracy is considered acceptable for this analysis, considering the relatively complex sample preparation and the fact that all the major components were determined by standard additions. Possible sources of error could include incomplete compensation for chemical interferences or slight curvature of the calibration graphs.

Conclusion

A method for analysing the complex mixture of refractory oxides comprising a glaze sample has been developed. The method requires two separate sample preparation procedures, but this is unavoidable if both sodium and boron are to be determined and hydrofluoric acid is to be passivated. A potassium hydroxide fusion could be used as an alternative to the sodium hydroxide fusion but then potassium could not be determined, and two procedures would still be necessary.

The method outlined in this report can be used for samples other than glaze. The most common use for this type of method is in the analysis of rocks and ores.

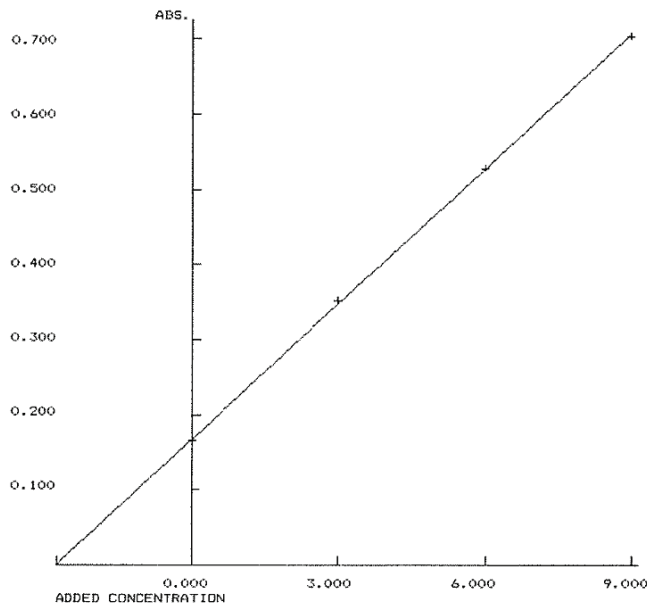


Figure 1: Standard additions graph for calcium