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XRF THIN FILM COPPER DISC EVAPORATION TEST FOR THE ELEMENTAL ANALYSIS OF CONCRETE TEST SOLUTIONS

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ABSTRACT

A modified XRF thin film analytical approach to the analysis of solution extracts from concretes has been developed and tested. Small volumes of solutions (1ml) are evaporated on suitably machined copper discs. The thin film of evaporated salts produced is virtually free of absorption effects and provides a reproducible linear relationship between instrumental response and element concentration. this copper disc evaporation test (CDET) is currently applied for analysis of Sulphate and chloride ions in solution.

Introduction

In the development of new research projects within the Concrete Technology Unit, University of Dundee, a need arose for an analytical programme to allow the rapid determination of a range of element concentrations in solutions. In particular, there was a requirement for a method of time-sequential analysis of the effluent solutions from a newly developed confined cell leaching test, designed for an accelerated evaluation of the behaviour of cementitious materials when used in the long term containment of hazardous wastes. Standard analytical techniques were found inadequate for multi-element analysis of the small volume solution samples produced from the leaching test. Other applications envisaged were the analysis of expressed concrete pore solutions and the determination of soluble chlorides. It was decided to approach the problem through development of a procedure of thin-film X-ray Fluorescence Spectrometry on salts precipitated by evaporation from the solutions.

Thin film techniques allow the analysis of milligram samples. The procedure has a high sensitivity and, within limits, is free from absorption effects (1,2,3). The method has been successfully applied to the analysis of microgram samples of suspended mineral sediment from fluvial and marine water samples (4,5). Emission and absorption of thin deposits of selected elements, produced by evaporation from solution, give a linear relation between instrumental response and element concentration, even at moderately high levels (2).

Sample Preparation

Copper discs with a machined recess of 1 mm depth and 50 mm diameter were initially selected as the evaporation substrate. Three ml of solution were transferred by burette into the disc recess and the solution evaporated to dryness on a hot plate at 60^{o}C. With this regime, the instrumental response was found to be non-linear, indicating that the thin film criterion had not been achieved i.e. an even distribution of the evaporated salts, with a sample thickness allowing elimination of absorbence of the X-rays.

The substrate copper disc format was redesigned to give a recess depth of 0.2 mm and a diameter of 30 mm (allowing 98.6% surface coverage by the incident X-rays). These discs were loaded with 1 ml of solution using a Transferpette 1 ml pipettor. This design proved successful both in terms of fluorescent response and signal linearity when tested with a variety of solutions, and was adopted for calibrations and subsequent analyses.

Analytical Machine Conditions

All analyses were carried out using a Philips PW1410 Sequential X-ray Fluorescence Spectrometer employing wave length dispersion (WD) and pulse height analysis (PHA) with a sinθ potentiometer attached. The machine conditions adopted after experimentation are as shown in Table 1. Voltage and current settings were adjusted to ensure that all elements analysed using the same wavelength dispersing crystal would use the same setting, allowing automation within the constraints of the available equipment.

TABLE 1
Machine Conditions

Crystal	Power Settings	Element	Angle (°2θ)
Pe *	30mA 40KV	Potassium	50.67
		Chlorine	65.32
		Sulphur	75.79
		Silicon	108.86
		Aluminium	145.07
TlAP	40mA 40KV	Magnesium	45.14
		Sodium	55.10
LiF 200	10mA 20KV	Iron	57.62
		Manganese	62.99
		Calcium	113.15
LiF 220	40mA 40KV	Zinc	60.70

* Approximate Angles

X-ray fluorescence intensity is strongly controlled by atomic number (Z), with the weakest intensities produced by low Z elements. The sensitivity of the technique was tested using solutions of Na and Mg, the lowest Z elements under consideration, using the TlAP diffraction crystal. The initial high power levels adopted (60mA, 40KV), to accommodate the low response of these elements, was found to lead to element volatilisation, as shown by decreasing response on repeated analysis of the same preparation. This conforms with the findings of McGill and Hubbard (4). A reduction of the current input to 30 mA was required to combat this effect. As a consequence, however, the lowest level of detection (LLD) was limited to 6 ppm for Na and 3 ppm for Mg.

Calibration

Calibration was carried out using the standard AAS solutions. These were selected as far as possible as simple salts with high elemental concentration and the lowest possible acidity (10,000 ppm in M nitric acid giving, on dilution, a maximum concentration of 0.02M HNO_3) Concentrated acid solutions were found to cause pitting, damaging the disc surface and leading to experimental error. The hydrophilic nature of calcium nitrate caused problems with evaporation and a neutral solution of calcium carbonate in sulphuric acid was substituted.

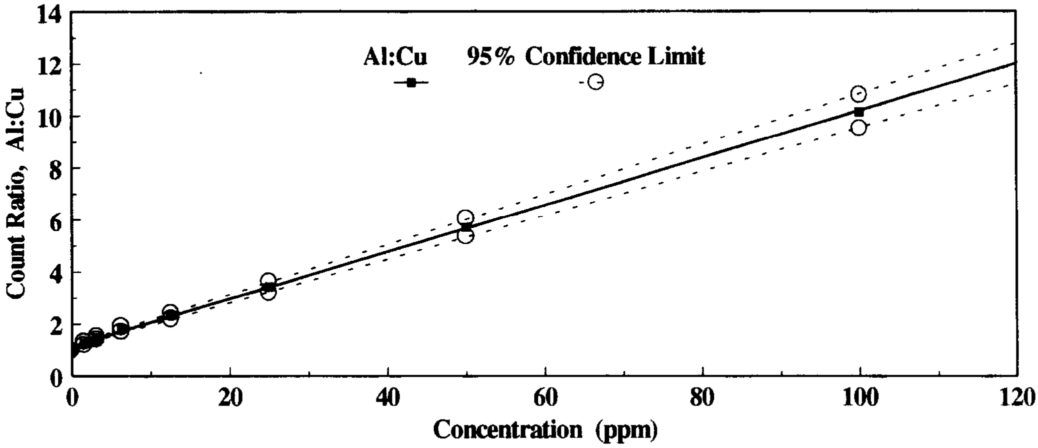

FIG. 1 Aluminium Calibration Graph

Solutions of varying concentration were prepared from these stock solutions, with elemental concentrations varying from 400 to 1.56 ppm. 10 copper discs were loaded for each solution, analysed and calibrations calculated for each element (Fig. 1 and Table 2). Calibration curves were constructed using the relationship:

$$\text{Concentration (ppm)} \propto \frac{\text{Element peak intensity } \lambda}{\text{Copper disc blank intensity } \lambda_1}$$

The copper disc blank intensity (λ_1) is that derived from a series of blank discs, determined under identical analytical conditions at the element 2θ positions. The calibrations achieved for the Pe crystal are indicated graphically in Fig. 2 and all calibration results are tabulated in Table 3. To test the possible influence of inter-element and matrix effects, three complex solutions were prepared containing Ca, K, Al and S, four elements that would be expected to be present in the pore solutions from cementitious materials. Results showed no deviation from the calibrations upto a total elemental concentration of 400 ppm, beyond which thin film analytical conditions were no longer present.

TABLE 2
Calibration Data for Sulphur

Conc. PPM	S:Cu Ratio	Std.Dev.	Error +/- PPM
100.0	47.52	1.79	6.9
50.0	24.80	0.84	3.5
25.0	13.14	0.43	1.8
12.5	7.25	0.23	0.9
6.3	4.15	0.15	0.5
3.1	2.30	0.07	0.3
1.6	1.79	0.07	0.2

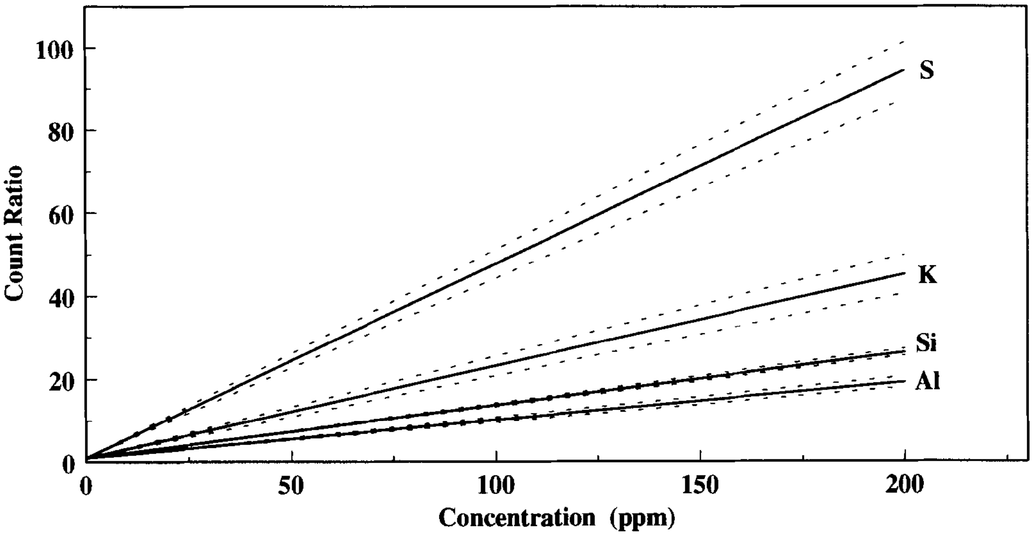

FIG. 2 Calibration Graph For Pe Crystal, showing 95% Confidence limits

Technique Verification

Since it is proposed to adopt this new CDET thin film XRF technique to predict the long term chemical behaviour of cementitious material used in containment of hazardous wastes, it was felt essential to obtain some control of the potential accuracy of the procedure by external "round robin" testing. To this end, effluent solution was collected over a long period from a Confined Cell Leach Test of an OPC concrete. The product was filtered through a 0.45 μm filter, to remove any dislodged solid matter, thoroughly mixed and then packaged in identical plastic bottles. The sealed bottles were despatched to five independent analytical facilities for analysis and comparison with the results obtained by CDET. The received data are given in Table 4, this provides confidence in substituting the CDET procedure as an alternative for AAS and ICP in our test program.

TABLE 3
Calibrations For All Analysed Elements

Crystal	Element	Calibration (x in ppm, y = count ratio)		Error @ 100ppm, ± % (95% Confidence Limit)
Pe	Potassium	$x = 4.555y - 5.634$,	$r^2 = 0.996$	10.0
	Chlorine	$x = 7.512y - 12.760$,	$r^2 = 0.997$	8.5
	Sulphur	$x = 2.146y - 2.544$,	$r^2 = 0.997$	6.9
	Silicon	$x = 7.973y - 9.352$,	$r^2 = 0.999$	4.8
	Aluminium	$x = 11.056y - 12.702$,	$r^2 = 0.995$	6.8
Tlap	Magnesium	$x = 81.326y - 82.827$,	$r^2 = 0.998$	8.1
	Sodium	$x = 101.031y - 103.523$,	$r^2 = 0.995$	18.7
LiF 200	Iron	$x = 40.722y - 41.654$,	$r^2 = 0.994$	6.5
	Manganese	$x = 16.577y - 17.045$,	$r^2 = 0.998$	5.3
	Calcium	$x = 4.053y - 4.893$,	$r^2 = 0.996$	8.2
LiF 220	Zinc	$x = 140.619y - 138.582$,	$r^2 = 0.991$	6.5

TABLE 4
Verification Results

Element/ (ppm)	Dundee (CDET)	Glasgow (AAS)	St Andrews (AAS)	Rugby Cement	Blue Circle Cement	TBV Stanger (ICP)	Mean*
Ca	266	268	248	276	292	281	273
K	28.6	29	24.6	30	29.1	27.1	28
Na	$<6^{+}$	7	3.7	4.3	5.2	4.6	5
SO_4	6.4	NT	NT	4^{**}	7.4^{**}	10^{**}	7.1
Mg	$<3^{+}$	$<1^{+}$	$<0.05^{+}$	1	0.66	NT	0.4
Si	$<0.5^{+}$	$<1^{+}$	$<2^{+}$	NT	0.35	0.37	0.36

Note: * Excluding CDET analysis ** Determined by Barium Chloride titration
NT Not Tested + Below the detection limit for that element

Conclusions

1. The CDET XRF procedure provides a means of quantitative analysis of a wide range of dissolved components, with good reproducibility where thin film conditions are maintained. With high total concentrations, dilutions may be required.

2. The small volume of solution required (3 ml allows analysis of three aliquots), makes the test suitable not only for use in leaching tests but also for expressed concrete pore solution analysis.

3. The method can be calibrated for both cations and anions.

4. Given the correct configuration of X-ray tube target metal, wavelength dispersion crystal and detector, a wide range of heavy metals can be quantitatively analysed.

5. In common with all XRF procedures, however, the method is less suitable for the analysis of elements of low atomic number at low concentrations.

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