

# X-ray fluorescence analysis of Portland cement and clinker for major and trace elements: accuracy and precision

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**Abstract** Accurate, rapid methods for controlling and determining composition are necessary to aid in classification of cements and for correlation of performance characteristics with composition. X-ray fluorescence (XRF) is used to adjust the raw material proportions and to control the process conditions. The aim of the present study was to establish a reliable analytical program by X-ray fluorescence spectrometry, based on the choice of a well-defined range of standards, which are used to control the quality of the clinker. The results showed a second order polynomial regression model that could properly interpret the experimental data with an  $R^2$  value  $>0.97$  even after correction for some elements. The results obtained indicate the reliability, reproducibility, and the ease of use of the established program.

**Keywords** Clinker · X-ray fluorescence · Analytical program · Choice · Range of standards

Throughout this paper, the following notation for the cement was used: ( $C = \text{CaO}$ ;  $S = \text{SiO}_2$ ;  $A = \text{Al}_2\text{O}_3$ ;  $F = \text{Fe}_2\text{O}_3$ ;  $N = \text{Na}_2\text{O}$ ;  $K = \text{K}_2\text{O}$ ;  $S = \text{SO}_3$ ).

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## Introduction

Cement is the essential constituent of concrete, which is one of the most used materials in the world and according to some estimates. The second most consumed on the planet after water product. The production of cement occurred in three steps: the preparation of a raw meal which is a mixture of clay and limestone, the production of clinker by burning the raw meal [1], and finally, the making of cement by milling the clinker with about 5% of calcium sulfate [2]. Indeed, this raw meal would be burned in a rotary kiln tube. The cement powder would be gradually heated by shifting down towards the flame on the other side of the oven. Then, three parameters of the burning process affect the clinker quality: the heating rate, the maximum temperature, and the burning time. All raw meals were heated up to 1450 °C. After burning, the clinkers were immediately air-cooled by removal from the furnace [1]. This process results in a multi-phase solid consisting of round micron-sized calcium silicate particles of two different chemical compositions ( $(\text{CaO})_3(\text{SiO}_2)$  noted  $\text{C}_3\text{S}$  and  $(\text{CaO})_2(\text{SiO}_2)$  noted  $\text{C}_2\text{S}$ ), immersed in an interstitial matrix of aluminate and ferrite ( $(\text{CaO})_3(\text{Al}_2\text{O}_3):\text{C}_3\text{A}$  and  $(\text{CaO})_4(\text{Al}_2\text{O}_3)(\text{Fe}_2\text{O}_3):\text{C}_4\text{AF}$ ). These four components represent the main cement phases [3].

Therefore, the chemical composition of Portland clinker consists for about two thirds of calcium oxide ( $\text{CaO}$ ; 62–68%), another major oxide in a raw meal is silicon oxide ( $\text{SiO}_2$ ; 19–25%) which is found in sand and fly ash. The other components, aluminum oxide ( $\text{Al}_2\text{O}_3$ ; 2–9%) and iron oxide ( $\text{Fe}_2\text{O}_3$ ; 1–5%) are often present in the materials providing  $\text{CaO}$  and  $\text{SiO}_2$  [1].

The evaluation of the potential mineralogical composition of Portland clinker is so important and required. So, this task

**Table 1** The confidence interval for each compound

Oxides	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Cl <sup>-</sup>
Confidence interval	62–68	19–22	4–7	2–4	1–3	0.5–4	0.1–0.3	0.4–1.5	0–0.2

was found by using the formulas of Bogue on the chemical composition of a cement raw meal [4]:

$$C_3S = 4.07 C - 7.60 S - 6.72 A - 1.43 F.$$

$$C_2S = 2.87 S - 0.75 C_3S.$$

$$C_3A = 2.65 A - 1.69 F.$$

$$C_4AF = 3.04 F.$$

with  $C_3S$  (m%),  $C_2S$  (m%),  $C_3A$  (m%), and  $C_4AF$  (m%), the potential mass percentages of alite, belite, aluminate, and ferrite in the clinker, respectively; as by optimizing different parameters that determine the quality of a cement raw meal. A first set of parameters regards the lime saturation factor (LSF), the silica modulus (SM), and the alumina modulus (AM) [5]. Clinker that is the main component of Portland cement [3] requires a continuous and strict quality control to ensure compliance with the requirements of the standard. So, in this paper, we have to suggest a technical solution which aims to establish an analytical program by X-ray fluorescence (XRF) spectrometry used to control the quality of the clinker. Furthermore, the development of X-ray fluorescence has led to much more rapid analyses, and as many cement works use the method as part of their control processes, it is of some interest to examine the precision of the method [2]. Indeed, the purpose of this paper is to present a method in which those problems are overcome. So, the design of analytical program is divided into three steps: the choice of a well-defined range of standards, the determination of the chemical composition of standards solution, and the plotting of the calibration curve.

## Materials and methods

### Materials

Calibration standards were prepared in the laboratory from analytical grade pure reagents. They were formulated to provide a series of calibration standards covering the range of maximum and minimum values for each element to be analyzed, and they were distributed between those limits. The variation in concentration of the elements is independent of each other. There is a minimum of seven calibration standards in a series. First, samples of clinker were obtained from 13 different works and collected by work staff. They were taken from ends of a grinding mill; the clinker samples being labeled CK1 to CK13. Second, materials were crushed twice to reduce particle size. Finally, bottles containing samples were labeled and conserved for analyzing. Table 1 shows the confidence interval for each component.

### Chemical analysis

For all clinkers sample, chemical analysis was performed. In accordance with European standard EN 196-2 and chemical analysis instruction in Bizerte Cement CB (North of Tunisia), the amounts of CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and MgO were determined by complexometric titration, the sulfate content was determined by nephelometric turbidity, and chloride content was quantified by back titration. The silica content was determined by gravimetric method, and finally, Na and K ions were determined by flame spectrophotometry.

### Decomposition of samples

Mineralization of sample was conducted by HCl and NH<sub>4</sub>Cl: the beaker, which contains the sample was placed on a hot plate and boiled for 20 min. After that, the contents of the beaker were diluted and filtered through a filter paper. The precipitate and the filter were used to determine the mass percentage of silicon oxide by the gravimetric method, and the obtained solution was conserved to the chemical analysis.

### Complexometric titration

The determination of single metals was carried out at similar pH values to those for EDTA titration. In many cases, two or even three methods of determination are chosen to ascertain the eventual influence on the formation of bimetallic complexes [6]. The titration process is summarized in Table 2.

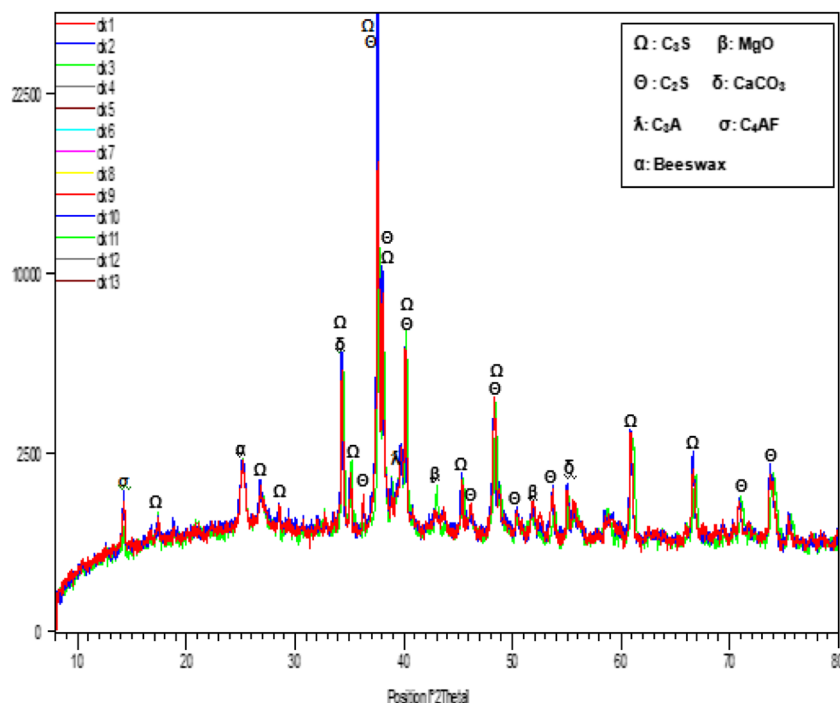
### Determination of silicon oxide

The filter paper and its contents as obtained above have been transferred into a platinum crucible and ignited in an electric

**Table 2** Titration of various metals with EDTA

Metal	pH of the solution	Indicator	Buffer solution
Ca	11–13	Calcéine	Triethanolamine/hydroxylammonium chloride
Mg	10–12	Blue methylthymol	ammonia/ammonium chloride
Al	2.6–4.8	PAN: 2'-pyridyl-1-azo-2-naphthol	—
Fe(III)	1.4–2.8	Salicylic acid	Glycocoll

**Fig. 1** XRD pattern of clinker samples (\*) *beeswax* was mixed with the sample as a binder



furnace at  $(1000 \pm 25)^{\circ}\text{C}$  for 60 min. The mass percentage of silicon oxide was obtained by the difference between weights before and after ignition.

#### Determination of sulfate

Sulfate ions produced by the decomposition of clinker with hydrochloric acid are precipitated by a solution of barium chloride and transferred in the turbidimeter to measure the turbidity. The mass percentage of sulfate in clinker sample can only determine by plotting a calibration curve for the turbidimeter.

#### Determination of chloride

Clinker was treated with boiling dilute nitric acid to decompose it and to remove sulfides. The dissolved chloride was precipitated using a known volume of a standard silver nitrate solution. Chloride content was determined by back titration.

#### Determination of alkali

Flame spectrophotometry relies upon the fact that the compounds of the alkali can be thermally dissociated in a flame

**Table 3** Chemical analysis for standard solution

Echantillon	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Cl <sup>-</sup>
CK1	65.57	21.80	5.93	3.45	1.25	1.55	0.22	0.58	0.15
CK2	65.42	21.85	5.36	3.65	2.22	1.93	0.22	0.56	0.05
CK3	67.88	20.46	5.48	3.04	2.28	2.58	0.26	0.65	0.10
CK4	65.11	20.10	5.85	2.95	2.37	1.83	0.25	0.69	0.16
CK5	64.45	20.39	5.29	3.52	2.00	1.37	0.24	1.07	0.14
CK6	64.32	21.61	5.70	3.44	2.18	1.10	0.18	0.47	0.07
CK7	62.63	21.93	6.23	3.48	2.20	1.85	0.17	0.48	0.02
CK8	64.50	20.15	5.32	3.33	2.16	3.54	0.18	0.57	0.06
CK9	64.39	21.57	5.67	3.70	1.90	1.40	0.19	0.55	0.12
CK10	65.24	20.18	5.87	3.24	1.93	1.51	0.15	0.49	0.04
CK11	64.52	20.47	4.94	3.51	2.56	1.58	0.15	0.51	0.03
CK12	64.89	20.12	5.58	3.47	1.56	0.97	0.13	0.46	0.02
CK13	66.21	19.51	5.30	3.28	1.45	2.04	0.14	1.08	0.01
Maximum	67.88	21.93	6.23	3.70	2.56	3.54	0.26	1.08	0.16
Minimum	62.53	19.51	4.94	2.95	1.25	0.97	0.13	0.46	0.01

**Table 4** Analysis results of sample CK6

Elements	Number of experience					Average	Standard deviation
	1	2	3	4	5		
CaO	64.31	64.43	64.21	64.46	64.18	64.32	0.13
SiO <sub>2</sub>	21.57	21.64	21.7	21.53	21.6	21.61	0.07
Al <sub>2</sub> O <sub>3</sub>	5.73	5.72	5.72	5.69	5.63	5.72	0.12
Fe <sub>2</sub> O <sub>3</sub>	3.48	3.53	3.36	3.37	3.44	3.44	0.07
MgO	2.18	2.17	2.17	2.18	2.18	2.18	0.01
SO <sub>3</sub>	1.2	1.08	1.15	1.04	1.03	1.1	0.07
Na <sub>2</sub> O	0.25	0.14	0.14	0.18	0.17	0.18	0.05
K <sub>2</sub> O	1.05	1.06	1.1	1.09	1.04	1.07	0.03
Cl	—	—	—	—	—	0.07	—

and that some of the atoms produced will be further excited to a higher energy level. When these atoms return to the ground state, they emit radiation which lies mainly in the visible region of the spectrum. Each element will emit a radiation, characterized by a specific wavelength.

In this work, the determination of Na and K was performed with a commercial instrument JENWAY PFP7; a calibration of this instrument is required. So, Na and K levels in clinker sample can only be determined by plotting a calibration graph.

### X-ray fluorescence spectrometry

X-ray fluorescence was applied to quantify the elemental composition of the clinker [7]. The XRF system consists of an X-ray tube which is produced the primary beam (production system) with a principals collimators, Crystals, secondary collimators and detectors. X-rays produced excite the sample atoms; consequently, they emit radiation when they are returning to the ground state. Thus, an XRD system analyzes this emitted radiation.

All XRF measurements were performed with a commercial instrument (ARL 9900 of THERMOFISHER), using monochromatic radiation  $K_{\alpha 1}$  of cobalt ( $\lambda = 1.788996\text{\AA}$ ). The key to their

versatility is the patented technology which allows two X-ray techniques: X-ray fluorescence and X-ray diffraction (XRD) combined in one instrument.

In this work, using the XRF technique is based upon fused bead. Preparing this bead was released through an automatic fusion apparatus “PERL’X3” to improve the homogeneity of the phase distribution and the quality of the top surface of the powder packing.

### X-ray diffraction spectrometry

X-ray diffraction was applied to identify and measure the mass fractions of various crystalline phases in Portland clinker and cement [7, 8]. The sample was a compressed disc of finely ground material: pressed pellet.

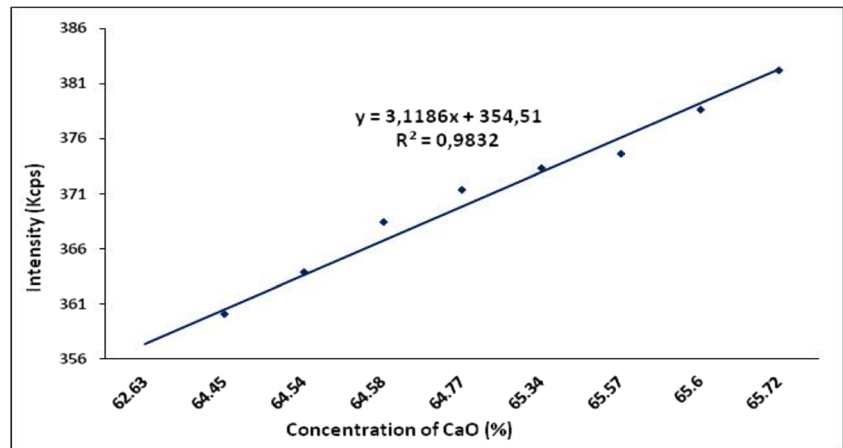
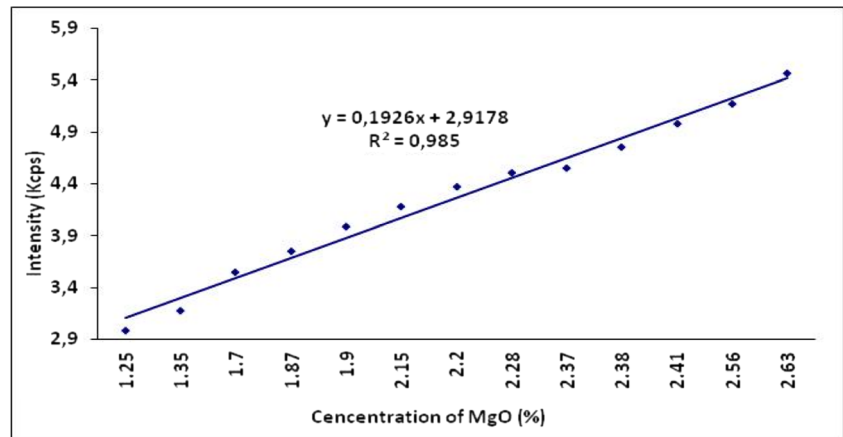
## Results and discussion

### X-ray diffraction

Crystalline components may be identified using the traditional approach of measuring location and relative intensities of the

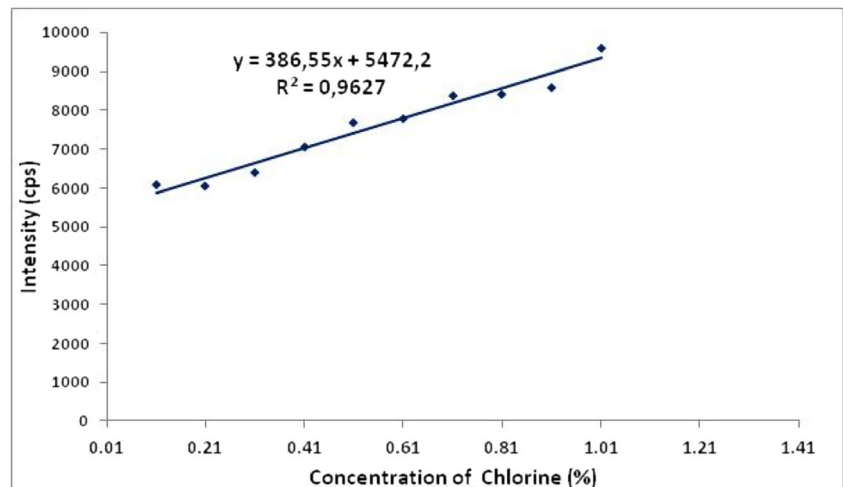
**Table 5** Relative intensities of X-ray for all components

Samples	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Cl <sup>-</sup>
CK1	375,193.03	43,806.87	9447.25	91,355.45	2528.64	7965.65	5956.01	722.89	8996.50
CK2	374,334.72	43,907.34	8498.93	94,798.20	4686.35	10,429.88	11,587.09	697.96	6679.15
CK3	388,410.90	41,279.12	8555.44	77,969.48	4731.96	14,612.01	15,063.22	810.13	7775.42
CK4	372,620.20	40,552.81	9066.28	75,661.18	4794.31	9045.61	14,265.29	859.99	9207.55
CK5	368,441.04	41,137.90	8278.66	93,413.70	4358.61	6877.13	12,166.45	1240.01	8405.95
CK6	368,040.50	43,599.31	9026.65	90,530.93	4607.10	5520.34	9849.03	585.79	7070.48
CK7	357,232.57	44,068.10	9925.19	92,424.05	4639.74	9751.77	9269.67	598.25	6218.21
CK8	368,784.36	40,653.68	8339.15	85,407.36	4401.55	16,835.20	10,428.38	710.43	7041.23
CK9	368,070.46	43,377.38	8826.93	95,797.07	3984.65	7741.54	11,007.74	685.50	8171.95
CK10	373,304.76	40,714.21	9351.66	84,495.33	4058.34	7796.24	7489.15	610.72	6393.70
CK11	371,302.10	41,299.30	7870.05	92,845.19	4921.97	8892.70	8699.19	635.64	6258.94
CK12	371,905.43	40,593.16	8747.00	91,741.41	3155.75	4613.04	7206.49	573.33	6220.06
CK13	377,652.38	39,362.45	8305.62	84,638.34	2933.23	10,979.99	7326.87	1346.07	6175.64

**Fig. 2** Calibration curve of CaO**Fig. 3** Calibration curve of MgO

most intense diffraction peaks. An alternative for the complicated cement diffraction patterns is to employ diagnostic characteristics of the composite diffraction pattern, which may be either a single key diffraction peak or groups of peaks that are typical for a specific mineral, with subsequent confirmation

using a powder diffraction pattern database. The obtained patterns were shown on Fig. 1. It can be explicitly considered that the same diffraction peaks have appeared in the XRD spectra of all samples. Some diffractions were related to the presence of  $C_3S$  (alite) (JCPDS numbers: 31–301/42–551),  $C_2S$  (belite)

**Fig. 4** Calibration curve of Chlorine

**Table 6** Calibration results for some elements

Elements	<i>A</i>	<i>F</i>	<i>S</i>	<i>N</i>	<i>K</i>	<i>s</i>
Correlation coefficient	0.9881	0.9865	0.9851	0.9828	0.9967	0.9995

(JCPDS numbers: 33–302), C<sub>3</sub>A (JCPDS numbers: 38–1429), and C<sub>4</sub>AF (JCPDS numbers: 30–226) clinker phases. On the other hand, typical peaks of periclase (MgO) (JCPDS numbers: 4–829) and calcite (CaCO<sub>3</sub>) phases were detected. X-ray diffraction analysis revealed the similarity of the mineralogical composition of studied samples.

### Chemical analysis

An overview of the chemical composition of the used standard solution is given in (Table 3). Extensive how it is expressed by the maximum and minimum shows that all of the components of the standard solution were included in the range game and covered widely clinker. Thus, each value is the average for five determinations to verify reproducibility and repeatability. We report in this investigation as an example that standard solution of CK6 sample (Table 4), in within, appears the average of five determinations of each element concentration, and the standard deviation for this analysis was calculated. This value is less than 0.5 how confirm the precision and fidelity of these results.

### X-ray fluorescence

The relative intensities for all components of the standard solution were measured by X-ray fluorescence (Table 5), and each value is the average for three determinations. It can be seen that the relative intensities increase with increasing concentration in each component. So, we concluded that these samples allow obtaining calibration curve.

### Calibration of X-ray spectrometer

The analytical techniques and the results described above lead to establish an analytical program for clinker by X-ray spectrometry. Therefore, it is important to understand that the relative intensity is directly proportional to the concentration of the element analyzed.

**Table 7** Evaluation of analytical program

Elements	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Cl <sup>-</sup>
Standard cement solution	64.57	20.98	2.97	5.27	2.51	2.28	0.73	0.09	0
Results of XRF analysis	64.57	20.95	2.97	5.27	2.51	2.29	0.73	0.09	0
Difference	0.00	0.03	0.00	0.00	0.00	0.01	0.00	0.00	0.00

Calibration curves were built using the multi-variable regression (MVR) program. Indeed, relative intensities were plotted against corresponding concentrations of oxides in the calibration solutions. In Fig. 2, it can be seen in the calibration curve for CaO. Thus, the correlation between relative intensity and concentration is high, and it was expressed by the correlation coefficient:  $R = 0.9832$ .

The calibration curve for MgO was plotted, and the regression equation was predicted with  $R = 0.9536$ . This is an erroneous value and unacceptable. So, a correction model was used to overcome this problem and to achieve better accuracy of analysis: minimizing the number of standards necessary to produce calibrations and improving the accuracy of analysis. Then, two standard solutions were removed as CK11 and CK12 and the correlation coefficient changed to 0.9850. The (Fig. 3) shows the calibration curve for MgO after correction.

Chlorine is a minor element in clinker, and it was detected in XRF analysis by goniometer, which is a universal detector. So it is not specific for chlorine. For this reason, calibration curve of chlorine shows a low correlation coefficient  $R = 0.8632$  due to the influence of interfering elements. Thus, a correction is necessary as minimizing the number of standards to eight and accepting a low value of correlation coefficient  $R$  to be 0.9627. Then, the calibration curve of chlorine after correction can be seen in (Fig. 4).

Calibration results for other element were presented in Table 6.

### Evaluation and validation

The precision and accuracy of the established analytical program were confirmed by analyzing certified reference materials (CRM) (as cement) representative of the range of analyses to be undertaken. The results of these analyses are shown in Table 7. The variations less than 0.01 confirm the validity of the program and reliability of the analytical method. Thus, Bizerte Cement uses this program for clinker and cement analysis.

### Conclusion

In the present study, an alternative method analyzing clinker and cement was presented. Indeed, calibration curves for each element were established using calibration standards. They were judged by the correlation coefficient  $R$ . The obtained

result shows that for these oxides CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and SO<sub>3</sub>  $R > 0.97$ , which can be considered an acceptable value. For MgO, Cl, and Na<sub>2</sub>O, results show a low correlation coefficient  $R < 0.97$ . Thus, a correction is necessary by minimizing the number of standards. Finally, an analytical validation was applied using certified reference materials and results of this work confirm the validity of this program and the reliability of the analytical method used.

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