Simultaneous Determination of Iron (III) and Aluminum (III) in the Presence of Titanium (IV) in Portland Cement using Derivative Spectrophotometry

K. A. Idriss, H. Sedaira , E. Y. Hashem, and A. F. Selim*

Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt.

Abstract: A spectrophotometric method relies on the use of derivative ratio-zero crossing technique has been developed for simultaneous determination of Fe (III) and Al (III) in the presence of Ti (IV). The method depends on the formation of colored complexes of metal ions with 1,2,4-trihydroxyanthraquinone (purpurin, PURP) in 50% v/v ethanol-water medium at pH 2.5 .The method was successfully applied for the determination of (1.6 – 5.58 mgL-1) iron, and (0.269 – 2.15 mgL-1) aluminum. The correlation coefficients for the obtained calibration graphs were 0.990 for iron (III), and 0.996 for aluminum (III). The sandell sensitivities of iron and aluminum were 0.24ng cm-2 and 0.20ng cm-2 respectively. The developed method was applied to the simultaneous determination of Fe2O3 and Al2O3 in Portland cement and was found to give satisfactory results.

1 Introduction

In cement industry, on-line control of cement composition is necessary to maintain the composition of the cement within strict requirements [1]. The improvement of the quality is tantamount to the improvement of the chemical composition. Several spectrophotometric methods were developed for the determination of iron and aluminum in some environmental [2]–[8], and alloy [9]–[11] samples. These methods include x-ray fluorescence XRF , atomic absorption spectroscopy AAS ,inductively coupled plasma ICP, and capillary electrophoresis. The derivatization of spectra allows to remove spectral interferences and as a consequence derivative spectrophotometry has a unique feature that it opens the possibility not only for increasing selectivity [12]–[14] but also for increasing sensitivity [15], [16]. The zero crossing method developed by O' Haver has been applied successfully for the determination of metal

ions in their binary mixtures through the formation of complexes with the same organic ligand [14].Salinas et

al.[17] developed a spectrophotometric method for resolving ternary mixtures; the method is based on the simultaneous use of the first derivative of the ratio spectra and measurements at zero-crossing wavelengths. Purpurin is known as a good analytical reagent, it was used for the determination of some metals in various samples [18]–[22]. In this work, fundamental studies of the complexation reactions of Fe (III), Al(III) and Ti(IV) with PURP were described, a rapid and sensitive first derivative ratio spectra zero-crossing method was used for simultaneous determination of Al(III) and Fe(III) in the presence of Ti(IV).The validity of the method was checked by analyzing Portland cement samples and the obtained results showed a good agreement with XRF results.

2 Experimental

2.1 Instruments

Ordinary absorption spectra and all derivative calculations were made on a T80+ (England) double beam UV/VIS

Spectrophotometer using 10-mm matched quartz cells and slit width 2 nm. The pH of solutions was measured using AD1030 pH/mV pH meter equipped with a Radiometer combined glass electrode. Normal or derivative spectra of metal-PURP systems were measured against a reagent blank, similarly prepared but containing no metal ions. The solution spectra were recorded at room temperature in water-ethanol containing 50% v/v ethanol, while keeping the ionic strength at a constant value of I= 0.1 mol L^{-1} (NaClO$_4$).

2.2 Chemicals and Solutions

All chemicals were of analytical-reagent grade and doubly distilled water or absolute ethanol was used for the preparation of solutions.

2.2.1 Purpurin (sigma reagent)

Stock solution 2×10^{-3} mol L^{-1} was prepared by dissolving an accurately weighed amount of the purified reagent in absolute ethanol.

2.2.2 Standard iron (III) Solution

A 10^{-3} mol L^{-1} stock standard solution was prepared using FeCl$_3$ AnalaR grade product in 0.1 mol L^{-1} HCl and standardized with EDTA.

2.2.3 Standard Aluminum (III) solution

A 10^{-3} mol L^{-1} stock standard solution was prepared using AnalaR grade product Al (NO$_3$)$_3$.9H$_2$O. The aluminum content of the solution was determined by conventional method [23].

2.2.4 Titanium (IV) Stock Standard Solution.

A stock standard solution (1 ml = 0.4 mg of Ti0$_2$) was prepared by dissolving 0.2 g of high-purity Ti0$_2$ in 10 ml sulfuric acid *(d* 1.84) together with *5* g of ammonium sulfate, with heating. The solution was cooled and poured into 100 ml of water while stirring, then filtered into a 500 ml calibrated flask and diluted to the mark with H$_2$S0$_4$ (1 + 19). More dilute solutions were obtained as required by accurate dilution [24] . The titanium concentration was determined spectrophotometrically using Tiron reagent.
Perchloric acid, sodium perchlorate and standard sodium hydroxide solution were all prepared from analytical grade reagents.
Solutions of diverse ions used for interference studies were prepared from AnalaR products of nitrates, acetates or chlorides of the metal ions and potassium or sodium salts of the anions to be tested.

2.2.5 Dissolution of Cement Samples

A 0.3 g of the sample (dried at 110°C) was weighted and dissolved in the minimum volume of hydrochloric acid. Heated to dryness, then 10 ml of HCl (6 mol L^{-1}) was added to the residue, digested and the insoluble residue was filtered into a 100 ml calibrated flask and then diluted to volume with doubly distilled water [25].

2.3 Procedure

2.3.1 Simultaneous Determination of Fe (III) and Al(III)

An aliquot of a sample solution, containing iron (III) (36-150 µg) and aluminum (III) (6 -55 µg), was transferred into a 25-ml calibrated flask. Then, 5 mL of 2×10^{-3} molL^{-1} purpurin solution was added, the pH was adjusted to 2.5 and diluted to volume, while keeping a final 50 % (v/v) ethanol content. The normal and the derivative spectra were recorded from 700 to 400 nm against a reagent blank. The absolute value of the first derivative was measured at 540 nm (zero-crossing point of Al (III) - PURP) and 580 nm (zero-crossing point of Fe (III)-PURP) for the determination of iron and aluminum respectively.

2.3.2 Simultaneous Determination of Fe (III) and Al(III) in the Presence of Ti(IV)

The obtained spectra of Fe-PURP complex, Al-PURP complex, and their ternary mixture with Ti-PURP complex were divided by a standard one of Al (III)-PURP and Fe(III)-PURP complex. The first derivative of ratio spectra were recorded. In the ternary mixture, the iron (III) concentration was proportional to the first derivative divided signal DD^1 at 638 nm and 650 nm (zero-crossing points of Ti (IV)/Al(III)). Aluminum (III) concentration could be determined by measuring the DD^1 signal at 458 nm (zero-crossing point of Ti(IV)/ Fe(III)),or by measuring the DD^1 signal at 480 nm (zero-crossing point of Fe(III)/Ti(IV)), best results were obtained by measuring the DD^1 signal at 458 nm.

2.3.3 Simultaneous Determination of Fe (III) and Al(III) in Portland Cement

Transfer a 0.2–0.5 mL aliquot of the prepared cement solution into a 25mL calibrated flask and add 5mL of PURP (2×10^{-3} M). Adjust the pH to 2.5 by the addition of 0.01 M sodium hydroxide. Dilute to volume while keeping final ethanol content of 50 % (v/v). Record the absorbance of the solution from 700 to 400 nm against a reagent blank. Divide the obtained normal spectrum by a standard one of Ti-complex, Al-complex or Fe-complex. Record the first derivative of the ratio spectrum and measure the amplitudes DD^1 at zero-crossing wavelengths as mentioned above. Iron (III) and aluminum (III) contents in Portland cement were calculated directly using proper regression equations.

3 Results and Discussion

3.1 Acid-base Properties of Purpurin

The acid -base equilibria of PURP were studied in our laboratory in 50% v/v ethanol–water medium and in the pH range 2.5–10.5, it was found that PURP exists in four different acid–base forms (LH_4^+, LH_3, LH_2^-, and LH^{2-}). The values of pKa_1 (LH_4^+: LH_3), pKa_2 (LH_3:LH_2^-), pKa_3 (LH_2^-: LH^{2-}) are 5.18 ± 0.02, 7.65 ± 0.01 and 10.27 ± 0.03, respectively [26].

3.2 Complexation Equilibria of Metal Ions with Purpurin

The complexation equilibria were studied in solution containing an excess of metal ion, equimolar concentration and an excess of the reagent over the pH range 1.5- 4. The absorbance versus pH graphs for all systems were interpreted logarithmically using the relationships given elsewhere [27],[28].The number of protons released during complexation and the equilibrium constants K_{eq} were proved graphically .

3.2.1 Complexation Equilibria Fe(III) with Purpurins

The absorption spectra of Fe(III)-PURP complex showed the formation of a complex with a maximum absorbance at 580 nm , the formation of the complex started at pH 1.0 and increased up to pH 2.7.The logarithmic analysis of absorbance-pH curves indicated the formation of $Fe(LH_3)_2^{3+}$ with the liberation of two protons according to the equilibrium (A).

$$Fe^{3+} + 2LH_4^+ \text{---} Fe (LH_3)_2^{3+} + 2H \qquad K_{eq} \qquad (A)$$
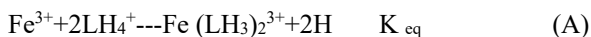
3.2.2 Complexation Equilibria Al (III) with Purpurin

The absorption spectra of Al(III)-PURP complex reflected the formation of a complex with a double headed band at 510 nm and 540 nm.

The color of the complex begins to appear at pH 2.0 and

reached its maximum intensity at pH 3.6 above which the absorbance decreased due to the hydrolysis of the complex.

The logarithmic analysis indicated liberation of two protons during the complexation according to the equilibrium (B).

$$Al^{3+} + LH_4^+ \text{----} AlLH_2^{2+} + 2H^+ \qquad K_{eq} \qquad (B)$$

3.2.3 Complexation Equilibria Ti (IV) with Purpurin

The absorption spectra of Ti(IV)-PURP complex showed the formation of complex with a band at 554 nm, the complexation begins at pH 1.5 up to pH 3.2.The logarithmic analysis of absorbance-pH curves indicated the formation of $TiLH_2^{3+}$ with the liberation of two protons according to the equilibrium (C).

$$Ti^{4+} + LH_4^+ \text{---} TiLH_2^{3+} + 2H^+ \qquad K_{eq} \qquad (C)$$
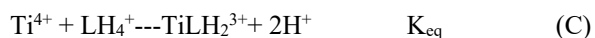
3.3 Equilibrium and Stability Constants

The equilibrium constants K_{eq} were determined by considering the equilibrium (A),(B),and (C), the stability constant of Fe(III)-PURP complex was related to equilibrium constant by the expression (I), while the stability constants of Al(III)-PURP and Ti(IV)-PURP complexes were obtained by considering expression (II)

$$\log \beta = \log K_{eq} + 2pK_{a1} \qquad (I)$$

$$\log \beta = \log K_{eq} + pK_{a1} + pK_{a2}. \qquad (II)$$

The calculated values of K_{eq} and β are shown in **Table 1**.

3.4 Stoichiometry of the Complexes

The composition of Fe-PURP complex at pH 2.5 is 1:2 (M:L) as verified by the molar ratio and the continuous variation methods, while that of Ti (IV) and Al (III) complex is 1:1 (M:L) at the same pH.

3.5 Analytical Characteristic of Ordinary Spectra

Under the optimum conditions, a linear calibration graphs for Fe-PURP and Al-PURP were obtained up to 7.8 ml L^{-1} and 2.69 mg L^{-1} respectively with a molar absorptivity 6.1967×10^3 L $mol^{-1}cm^{-1}$ for iron at 580 nm, and 9.0331×10^3 L $mol^{-1}cm^{-1}$ for aluminum at 540 nm. The reproducibility of the method was checked by analyzing a series of seven solutions containing 3.5 mg L^{-1} of iron and 1.35 mg L^{-1} of aluminum. The relative standard deviations (%RSD) were found to be 0.9% for iron and aluminum.

3.6 Simultaneous Determination of Fe(III) and Al(III) in Their Binary Mixtures

3.6.1 Absorption Spectra

Table 1: Mean values of equilibrium K_{eq} and conditional stability constants β.

	Fe (III) -PURP	Al (III) -PURP	Ti (IV) –PURP
Equilibrium constant (Log K_{eq})	(0.759)[a] (0.7805)[b]	(-1.4769)[a] (-1.266)[b]	(-0.2423)[a] (-0.2252)[b]
Conditional stability constant (log β)	11.13	11.45	12.60

[a]From the absorbance vs. pH graphs for solutions with excess ligand.
[b]From the absorbance vs. pH graphs for solutions with excess metal.

The absorption spectra of Fe-PURP, Al-PURP complexes and their binary mixture are shown in **Figure 1.** Since the absorption spectra of the two metal complexes overlap, the determination of iron and aluminum in their mixtures by ordinary spectrophotometry is frequently difficult. This problem has been overcome using zero-crossing method.

3.6.2 Zero-Crossing Method

Appropriate parameters were selected to record the first-derivative spectra using the zero-crossing method to select suitable wavelengths for obtaining linear analytical calibration graphs. The reproducibility of zero-crossing wavelengths of derivative spectra was checked by recording the first-derivative spectra of Fe–PURP and Al–PURP systems (pH 2.5) at different concentrations of the analytes **Figure 2**. The zero-crossing wavelengths of iron and aluminum in the first-derivative spectra are obtained at 580 and 540 nm respectively.
Figures 3 shows the first-derivative spectra of two series containing increment amounts of iron or aluminum ions. Iron and aluminum can be determined using the absolute value of the total derivative spectrum at a wavelength corresponding to the zero-crossing point of the other component. The first derivative values obtained at 540 nm (zero crossing point of Al(III)-PURP) and those obtained at 580 nm (zero crossing point of Fe(III)-PURP) are proportional to iron and aluminum concentrations respectively. The obtained regression equations are given in **Table 2**.

3.6.3 Effect of Diverse Ions

To assess the usefulness of the proposed method, the effects of diverse ions that are often associated with Al (III) and Fe (III) were studied. The tolerance of the method to foreign

ions was investigated with solutions containing 1.0 mgL^{-1} of Al (III), 2.5 mg L^{-1} Fe (III) and various amounts of

foreign ions. The tolerance criterion for a given ion was taken to be the deviation of the absorbance values by more than $\pm 2\%$ from the expected value. The determination of iron (III) and aluminum (III) was possible in the presence of K^+, Na^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Sr^{2+}, Mn^{2+}, Zn^{2+}, NO_3^-, SO_4^{2-}, SO_3^{2-}, Cl^-, I^-, and Br^-. Only Ti^{4+} interferes seriously and this interference was overcome by the use of derivative ratio zero crossing technique.

3.7 Simultaneous Determination of Fe(III) and Al(III) in the Presence of Ti(IV)

In order to resolve the ternary mixture, we needed carefully to select the zero-crossing wavelengths that permit an accurate determination of iron and aluminum in the presence of titanium. The zero-crossing wavelengths for Ti/Al were obtained at 638 and 650 nm, while those for Ti/Fe were obtained at 458 and 480 nm respectively.
Figure 4 illustrates the ratio spectra and the first derivative of ratio spectra of a series of ternary mixtures containing increasing concentrations of iron, using Al(III)-PURP as a divisor. while **Figure 5** shows the ratio spectra and the first derivative of ratio spectra of ternary mixtures containing increment amounts of aluminum using Fe(III)-PURP as a divisor. In order to determine the concentration of Fe(III) the absolute first derivative divided value DD^1 was taken at 638 or 650 nm (zero crossing points of Ti/Al) which are proportional to the iron concentration. For Al(III) determination the DD^1 signal at 458 (zero crossing points of Ti/Fe) was measured.

3.7.1 Effect of Divisor

A standard spectrum of Al(III) 1.35 mg L^{-1} was used as a divisor for the determination of iron(III) while a standard spectrum of Fe(III) 3.35 mg L^{-1} was used as a divisor for the determination of aluminum(III). The use of these divisors gave the best correlation between the first derivative divided values (DD^1 signals) and the concentrations of the metal ions.

Table 2: Statistical data for calibration graphs.

Metal to be determined	Regression equations	R^2	S_m	S_b
Fe (III)	**Binary mixtures** $^1D_{540} = 0.11581\ C_{Fe} + 0.0023$	0.997	0.0024	0.0123
Al (III)	$^1D_{580} = -0.0119\ C_{Al} - 0.00121$	0.999	3.37×10^{-4}	5.21×10^{-4}
Fe (III)	**Ternary mixtures** **Standard divisor 1.35 mg L^{-1} Al (III)** $DD^1_{638} = 13.251 C_{Fe} + 15.75$ $DD^1_{650} = 5.89 C_{Fe} - 0.86$	 0.98 0.99	 0.088 0.036	 0.042 0.049
Al (III)	**Standard divisor 3.35 mg L^{-1} Fe (III)** $DD^1_{458} = 0.5657 C_{Al} - 0.3971$	0.996	0.0229	0.041

^{1}DD: The first derivative divided signal
C_{Fe}: Fe(III) concentration (mg L^{-1}). C_{Al}: Al(III) concentration (mg L^{-1})
R^2: Regression coefficient
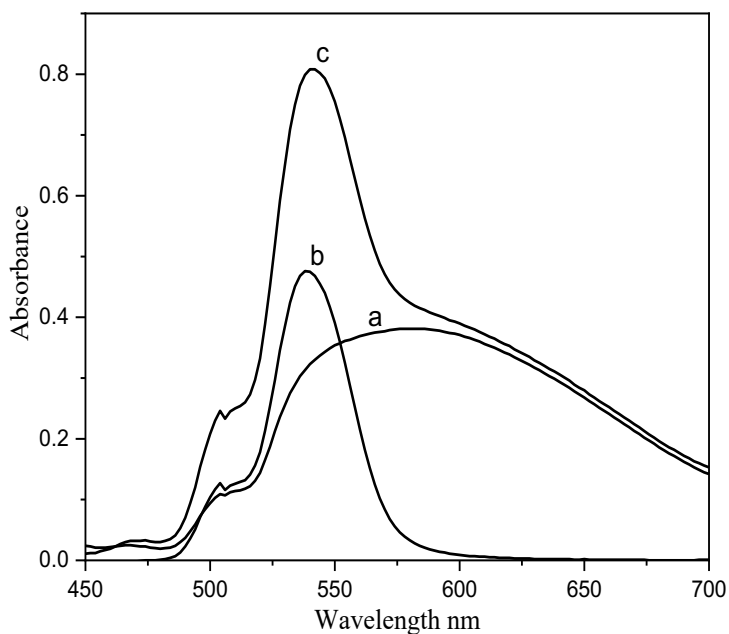S_m: Standard deviation of slope. S_b: Standard deviation of intercept

Fig. 1: Absorption spectra of (a) Fe(III)-PURP, (b) Al(III)-PURP complexes and (c) mixture of Fe(III)-and Al(III)-PURP complexes.

[Fe(III)]= 3.35 mg L^{-1} ,[Al(III)]= 1.35 mg L^{-1} , [PURP]= 4×10^{-4} M, 50% ethanol, I= 0.1 M (NaClO$_4$), and pH=2.5
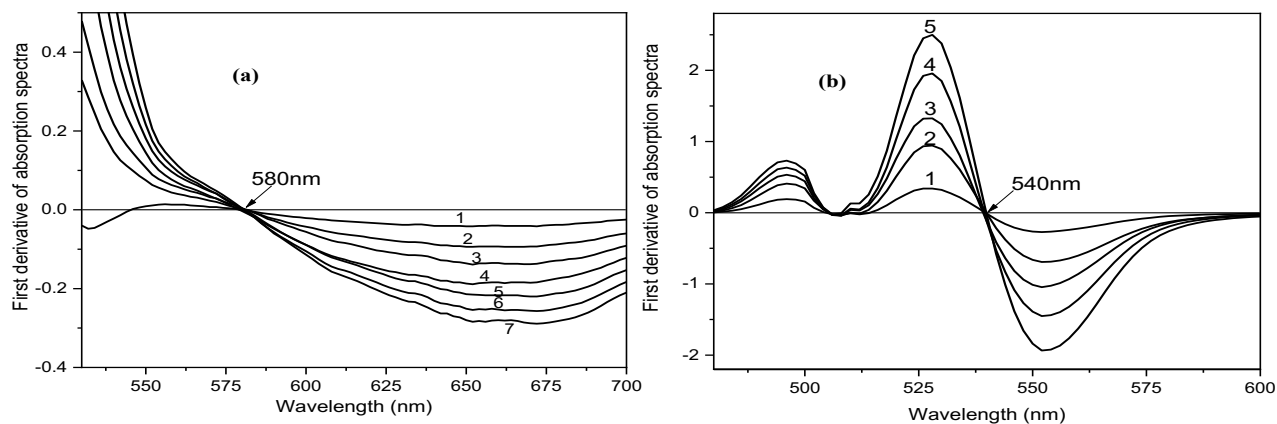
Fig. 2: First-derivative spectra of Fe(III)-PURP(a) and Al(III)-PURP (b) complexes

[Fe(III)] = 1) 1.11 ; 2) 2.23; 3) 3.35 ; 4) 4.46; 5) 5.58 ; 6) 6.70; 7) 7.81 mg L^{-1}
[Al(III)] = 1) 0.27 ; 2) 0.81; 3) 1.35 ; 4) 2.15; 5) 2.7 mg L^{-1}
[PURP]= 4×10^{-4} M, 50% ethanol, I= 0.1 M (NaClO$_4$), and pH=2.5.
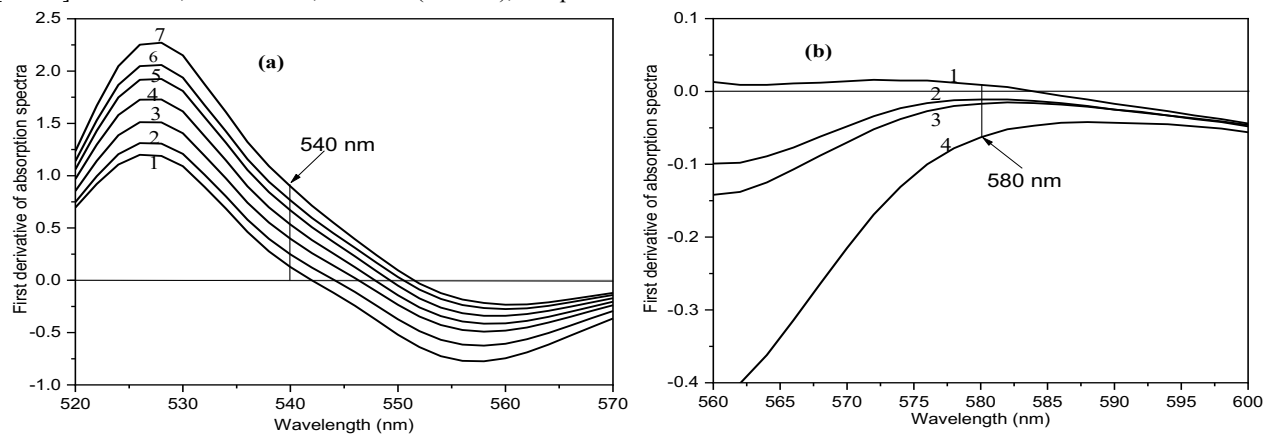

Fig. 3: First-derivative spectra of a mixture of Al(III)-PURP complex and an increasing concentrations of Fe(III)-PURP complex(a) and a mixture of Fe(III)-PURP complex and an increasing concentrations of Al(III)-PURP complex(b).
a)[Al(III)]=1.35 mg L^{-1}, [Fe(III)]= 1) 1.11; 2) 2.23 ; 3) 3.35 ; 4) 4.46; 5) 5.58 ; 6) 6.70 ; 7) 7.81 mg L^{-1}
b)[Fe(III)]=3.35 mg L^{-1} ,[Al(III)]= 1) 0.26; 2)0.81 ; 3) 1.35; 4) 2.69 mg L^{-1}
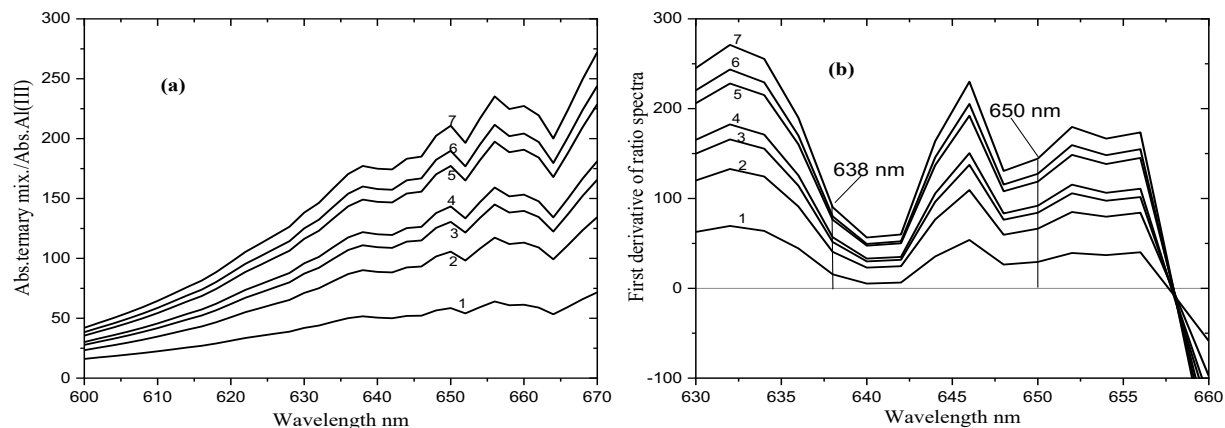[PURP]= 4×10^{-4} M, 50% ethanol, I= 0.1 M (NaClO$_4$), and pH=2.5

Fig. 4: Ratio spectra (a) and first-derivative of ratio spectra (b) of ternary mixtures of Fe(III)-, Al(III)-, and Ti(IV)-PURP complexes containing increment amounts of iron.
[Fe(III)]= 1)0.55 2)1.67 3)2.79 ; 4)3.9; 5)5.02 ; 6)5.58 ; 7) 6.14 mg L^{-1}, [Al(III)]=1.35 mg L^{-1}, and [Ti(IV)]=0.9 mg L^{-1}, [Al(III)]=1.35 mg L^{-1}as divisor, [PURP]= 4×10^{-4} M, 50% ethanol, I= 0.1 M (NaClO$_4$), and pH=2.5
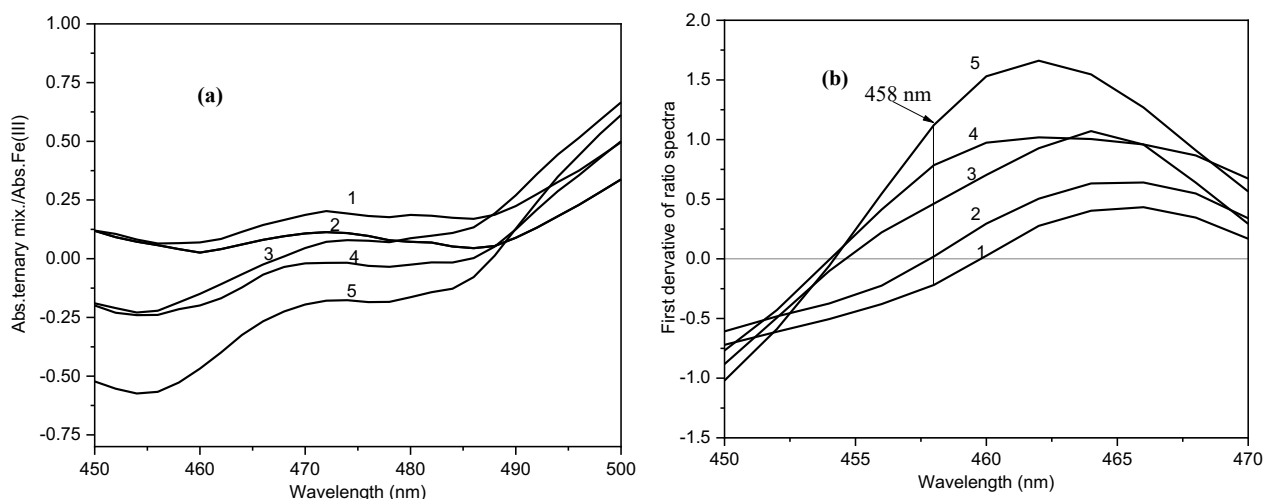
Fig. 5: Ratio spectra (a) and first-derivative of ratio spectra (b) of ternary mixtures of Al(III)-, Fe(III)-, and Ti(IV)-PURP complexes containing increment amounts of aluminum.

[Al(III)]= 1)0.26 ; 2) 0.81; 3) 1.35; 4) 2.15; 5)2.69 mg L^{-1}, [Fe(III)]= 3.35 mg L^{-1}, and [Ti(IV)]= 0.9 mg L^{-1}, [Fe(III)]=3.35 mg L^{-1} as a divisor, [PURP]= 4×10^{-4} M, 50% ethanol, I= 0.1 M (NaClO$_4$), and pH=2.5

3.7.2 Calibration Graph and Statistical Results

The calibration graphs prepared by plotting the first derivative divided signal (DD[1]) versus aluminum or iron concentrations gave a straight line over a range of 0.269-2.15 mg L^{-1} of aluminum, and 1.67-5.58 mg L^{-1} of iron. The regression equations are given in **Table 2**.

4 Applications

The proposed method was applied for the determination of iron (III) and aluminum (III) in ordinary Portland cement (OPC) **.** Fe_2O_3 and Al_2O_3 concentrations were determined by measuring [1]DD signals at appropriate wavelengths and using the regression equations indicated in **Table 2**. Fe_2O_3 concentration was determined by measuring DD[1] signals at 638 nm and at 650 nm (zero-crossing points of Ti(IV)/Al(III)) complex), while the concentration of Al_2O_3 was determined by using Fe(III)-PURP complex as a divisor, and measuring DD[1] signal at 458 nm (zero-crossing point of Ti(IV)/Fe(III) complex). The obtained results were certified using x-ray fluorescence technique **Table 3.**

Table 3: Simultaneous spectrophotometric determination of Fe_2O_3 and Al_2O_3 in Portland cement material.

Material	Proposed method		XRF method	
	% Fe_2O_3 4.95 at 638 nm 4.97 at 650 nm	%Al_2O_3 4.49	% Fe_2O_3 5.03	%Al_2O_3 4.54
Cement (OPC)				

5 Conclusions

The proposed method allows the simultaneous determination of Fe(III) (1.6-5.58 mg L^{-1}) and Al(III) (0.27-2.15 mg L^{-1}) in their solutions containing Ti(IV), using derivative ratio-zero crossing technique. This work illustrates the potential of derivative spectrophotometry as a simple, rapid and accurate tool for simultaneous determination of Fe_2O_3 and Al_2O_3 in Portland cement relative to zero order spectrophotometric technique [24],[29].

References

[1]   H. Sedaira, K. A. Idriss, M. M. Seleim, and M. S. Abdel-Aziz, "Use of quinizarin as a spectrophotometric reagent for MgO content analysis of Portland cement and cement clinker," Monatshefte fur Chemie., **129(1)**, 49–58(1998).

[2]   Sercio L C Ferreira, Neide O. Leite, Alailson F. Dantas, Jailson B. de Andrade and A. C. Spinola Costa, "spectrophotometric and derivative spectrophotometric determination of alumiium with hydroxynaphthol blue" **41 (94),** 1631–1636(1994).

[3]   K. Zarei, M. Atabati, and Z. Malekshabani, "Simultaneous spectrophotometric determination of iron , nickel and cobalt

in micellar media by using direct orthogonal signal correction-partial least squares method," Analytica Chimica Acta., **556**, 247–254(2006).

[4] K. Sözgen and E. Tütem, "Second derivative spectrophotometric method for simultaneous determination of cobalt , nickel and iron using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol," **62**, 971–976(2004).

[5] L. Zhang and K. Terada, "Spectrophotometric determination of iron (II) in sea water after preconcentration by sorption of its 3-(2-pyridyl) -5,6-bis(4-phenylsulphonic acid) -1,2,4_triazine complex complex with poly (chlorotrifluoroethylene) resin,". **2670 (94)**, 311–318(1994).

[6] A. Safavi, H. Abdollahi, and R. Mirzajani, "Simultaneous spectrophotometric determination of Fe (III), Al (III) and Cu (II) by partial least-squares calibration method," Spectrochim. Acta-Part A., **63**,196–199(2006).

[7] A. Shokrollahi, M. Ghaedi, M. S. Niband, and H. R. Rajabi, "Selective and sensitive spectrophotometric method for determination of sub-micro-molar amounts of aluminium ion," J. Hazard. Mater., **151(2–3)**, 642–648(2008).

[8] H. L. Zheng, W. Q. Xiong, Y. K. Gong, D. J. Peng, and L. C. Li, "Catalytic spectrophotometric determination of trace aluminium with indigo carmine," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., **66(4–5)**, 1243–1247(2007).

[9] P. Pohl, A. Szymczycha-madeja, and M. Welna, "Simple ICP-OES based method for determination of selected elements in brewed ground and soluble coffees prior to evaluation of their intake and chemical fractionation," Food Chem., **263**, 171–179(2018).

[10] Q. Wu, X. Wang, Y. Jiang, W. Sun, and C. Wang,M. Yang and C. Zhang "MoS2 -QD-Based Dual-Model Photoluminescence Sensing Platform for Effective Determination of Al3+ and Fe3+ Simultaneously in Various Environment," chem. select full paper., 2326–2331(2018).

[11] A. Safavi, M. Mirzaee, and H. Abdollahi, "Simultaneous Spectrophotometric Determination of Iron , Titanium , and Aluminum by Partial Least-Squares Calibration Method in Micellar Medium," Analytical Letters., **36(3)**, 699–712, 2003.

[12] K. A. Idriss, H. Sedaira, and S. S. Ahmed, "Determination of strontium and simultaneous determination of strontium oxide, magnesium oxide and calcium oxide content of Portland cement by derivative ratio spectrophotometry," Talanta., **78(1)**, 81–87(2009).

[13] M. Benamor and N. Aguerssif, "Simultaneous determination of calcium and magnesium by derivative spectrophotometry in pharmaceutical products," Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., **69(2)**, 676–681(2008).

[14] H. Sedaira, "Simultaneous determination of manganese and zinc in mixtures using first- and second-derivative spectrophotometry," Talanta., **51(1)**, 39–48(2000).

[15] T. C. O'Haver et al., "Derivative spectroscopy and its applications in analysis," Anal. Proc., **19(1)**, 22–46(1982).

[16] H. Ishii and K. Satoh, "Determination of micro amounts of samariumand europium by analogue derivative spectrophotometry," Bunseki Kagaku., **35(8)**, 704–708

(1986).

[17] J. J. B. Nevado, C. G. Cabanillas, and F. Salinas, "Spectrophotometric resolution of ternary mixtures of salicylaldehyde, 3-hydroxybenzaldehyde and 4-hydroxybenzaldehyde by the derivative ratio spectrum-zero crossing method," Talanta., **39(5)**, 547–553(1992).

[18] M. R. Ceba, A. A. Ramirez, and J. J. Burzas, "Spectrophotometric determination of trace amounts of iron(III) by extraction of the mixed-ligand iron-fluoride-purpurin complex.,"Talanta., **29(1)**, 142–144(1982).

[19] F. Capitan, A. A. Ramirez and C. J. Linares, "Spectrophotometric Determination of Trace Amounts of Iron(llI) in Oxalates by Extraction of the Mixed-ligand Iron-Oxalate -Purpurin Complex ," Analyst.,**110(JULY)**, 819–821(1985).

[20] F. Capitan, A. A. Ramirez and C. J. Linares "Spectrophotometric Determination of Trace Amounts of Iron (III) by Extraction of Mixed-Ligand Iron-Tartrate-Purpurin or Iron-NTA-Purpurin Complex ," Mikrochimica Acta, **(3)**, 197–207(1986).

[21] F. Capitan, A. A. Ramirez and C. J. Linares, "Spectrophotometric Determination of Trace Amounts of Iron(lll) in Salicylates by Extraction of the Mixed-ligand Iron - Salicylate - Purpurin Complex," Analyst., **111(JULY)**, 739–741(1986).

[22] K. A. Idriss, H. Sedaira, M. S. Abdel-aziz, and H. M. Ahmad, "Rapid test methods for minor components analysis of hydraulic cement . Spectrophotometric determination of manganese oxide content of Portland cement and cement raw meal," Talanta., **50**, 913–919(1999).

[23] A. Vogel, "Textbook of Quantitative Chemical Analysis," 5th Edition, ELBS,London, 1988.

[24] H. Sedaira, K. A. Idriss, M. S. Abdelaziz "5-Chlorosalicylic Acid Spectrophotometric Method for the Determination of Titanium and Simultaneous Determination of Titanium (IV) Oxide and Iron (III) Oxide Content of Portland Cement,"Analyst., **121(August)**, 1079–1084(1996).

[25] K. A. Idriss, H. Sedaira, and S. Dardeery, "Spectrophotometric Determination of Water-Soluble Hexavalent Chromium and Determination of Total Hexavalent Chromium Content of Portland Cement in the Presence of Iron (III) and Titanium (IV) Using Derivative Ratio Spectrophotometry," Am. J. Anal. Chem., **04(11)**, 653–660(2013).

[26] K. A. Idriss, H. Sedaira, and H. M. Ahmed, "An insight into the solution equilibria of magnesium(II) with purpurin and spectrophotometric determination of magnesium," Talanta., **54(2)**, 369–375(2001).

[27] P. Voznica, J. Havel, and L. Sommer, "The reactions of gallium, indium and thallium with 2-(2-pyridylazo)-1-naphthol-4-sulphonic acid and their spectrophotometric determination," Collect. Czechoslov. Chem. Commun., **45(1)**, 54–79(1980).

[28] K. A. Idriss, M. M. Seleim, M. S. Saleh, M. S. Abu-Bakr, and H. Sedaira, "Spectrophotometric study of the complexation equilibria of zirconium (IV) with 1-amino-4-hydroxyanthraquinone and the determination of zirconium,"

Analyst., **113(11)**, 1643–1647(1988).

[29] K. A. Idriss, E. Y. Hashem, M. S. Abdel-Aziz, and H. M. Ahmed, "Direct spectrophotometric determination of aluminium oxide in portland cement clinker. An insight into solution equilibria and analytical aspects of the aluminium-quinizarin system" Analyst., **125**, 221–225(2000).